

Document downloaded from:

<http://hdl.handle.net/10251/121854>

This paper must be cited as:

Díaz Morales, UM.; Corma Canós, A. (2018). Organic-Inorganic Hybrid Materials: Multi-Functional Solids for Multi-Step Reaction Processes. *Chemistry - A European Journal*, 24(16):3944-3958. <https://doi.org/10.1002/chem.201704185>



The final publication is available at

<http://doi.org/10.1002/chem.201704185>

Copyright John Wiley & Sons

Additional Information

This is the peer reviewed version of the following article: DÍAZ MORALES, URBANO MANUEL, Corma Canós, Avelino. (2018). Organic-Inorganic Hybrid Materials: Multi-Functional Solids for Multi-Step Reaction Processes. *Chemistry - A European Journal*, 24, 16, 3944-3958. DOI: 10.1002/chem.201704185, which has been published in final form at <http://doi.org/10.1002/chem.201704185>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Cond

Concepts

Multi-Functional Materials

Organic-Inorganic Hybrid Materials: Multi-functional Solids for Multi-step Reaction Processes

Urbano Díaz and Avelino Corma**

Dr. U. Díaz, Prof. A. Corma

Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, E-46022 Valencia, Spain

E-mail: udiaz@itq.upv.es; acorma@itq.upv.es

Abstract

The design of new hybrid materials with tailored properties at the nano-, meso- and macro-scale, with the use of structural functional nanobuilding units, is carried out to obtain specific multi-functional materials. Organization into controlled 1D, 2D and 3D architectures with selected functionalities is key for developing advanced catalysts, but this is hardly accomplished using conventional synthesis procedures. The use of pre-formed nanostructures, derived either from known materials or made with specific innovative synthetic methodologies, has enormous potential in the generation of multi-site catalytic materials for one-pot processes. The present concept article introduces a new archetype wherein self-assembled nanostructured builder units are the base for the design of multifunctional catalysts, which combine catalytic efficiency with fast reactant and product diffusion. The article addresses on a new generation of versatile hybrid organic-inorganic multi-site catalytic materials for their use in the production of (chiral) high added value products within the scope of chemicals and fine chemicals production. The use of those multi-reactive solids for more nanotechnological applications, such as sensors, due to the inclusion of electron donor-acceptor structural arrays is also considered, together with the adsorption-desorption capacities due to the combination of hydrophobic and hydrophilic sub-domains. The innovative structured hybrid materials for multipurpose processes here considered, can allow the development of multi-stage one-pot reactions with industrial applications, using the materials as one nanoreactor systems, favoring more sustainable production pathways with economic, environmental and energetic advantages.

Initial Concepts

Conceptually, hybrid materials are formed by a suitable combination of two or more components. When these structural sub-units are connected at nanometric scale, obtained solids will preserve the intrinsic characteristics of each individual component, exhibiting additional properties due to the synergetic effect between the structural builders.^[1, 2] The example of pigments used by the ancient Pre-Columbian civilizations is well-known (c. VIII-IX), such as the Blue Maya formed by the interaction between natural dyes (derived of indigo-type molecules) and lamellar clays (similar to paligorskite). Furthermore, nature offers different cases of hybrid architectures obtained after soft biomineralization synthesis routes, such as the nacre formed by hexagonal plate layers of crystallized calcium carbonate (aragonite) which are compacted through nanometric connection with elastic biopolymers (conchiolin) (Figure 1).^[3]



Figure 1. Examples of well-known hybrid materials: natural pigment as Blue Maya (left) and nacre as crystallized compacted lamellar structure present in the nature (right).

Due to the growing demand of new materials with specific physico-chemical properties, hybrid materials occupy a prominent position into the materials science. In this case, several complementary components can be integrating the structural framework of the solids, such as inorganic, organic, metallic or polymeric structural counterparts. This large variety should favor that hybrid solids can successfully be used in catalysis, adsorption or separation, sensing, microelectronic, magnetism, photochemistry, photoluminescence, semiconducting and for fuel-cell processes.^[4, 5]

Specifically, organic-inorganic hybrid materials present the main advantages of inorganic oxides, exhibiting high mechanical, thermal and structural stability, without losing the characteristics of versatile organic polymers, such as flexibility and functional variety. Different synthesis methodologies are used to prepare hybrid solids. They include from the simplest procedures, based on the physical mixtures or blends of different components, up to more attractive synthesis pathways, with the ambitious aim to obtain authentic hybrid molecular composites, based on different structural builders effectively combined at nanometric scale.^[6] On this last case, the organic and inorganic sub-domains are integrated together without phases' separation, being homogeneously distributed into the network without interfacial problems. This archetype for ideal organic-inorganic materials only can be achieved with the participation of suitable nanobuilding precursors during the synthesis process. The structural sub-units can be purely inorganic (silicospheres or individual silicoaluminate layers), purely organic (macromolecules or derived proteins) or, most interesting from our point of view, organic-inorganic precursors where stable and pre-formed connection should be established between organic and inorganic moieties, before their use during the synthesis process, such as organometallic monomers and bridged silsesquioxanes (so called disilanes) (Figure 2).^[7]

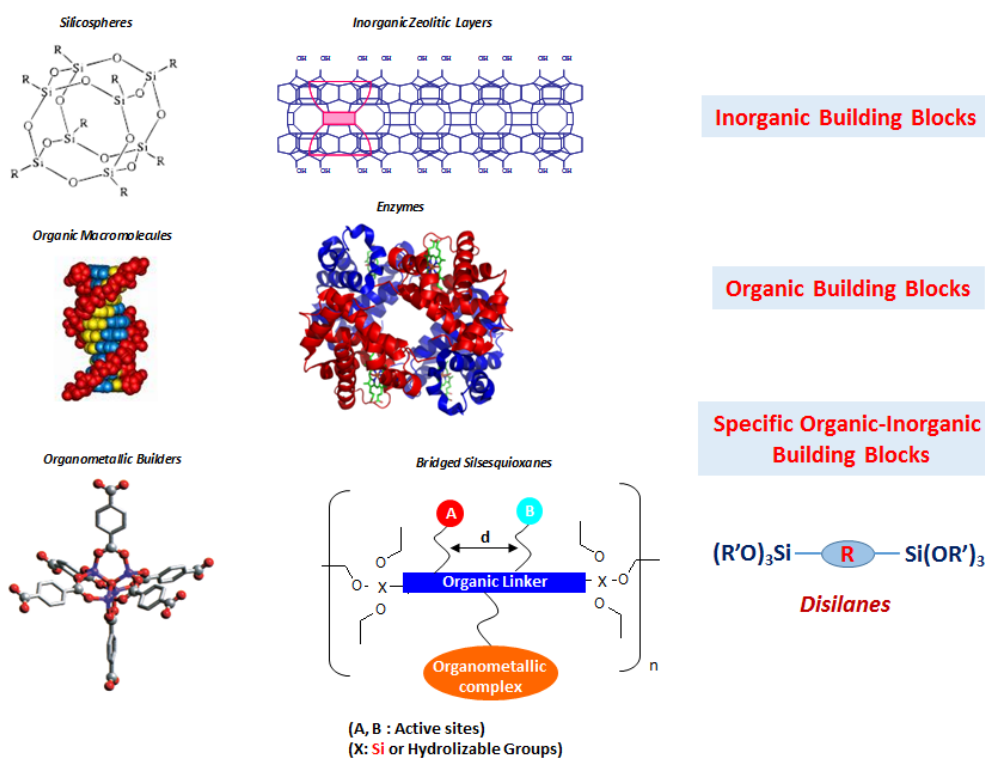


Figure 2. Main nanobuilding precursors used to synthesize organic-inorganic hybrid materials.

Hybrid Materials with Different Morphology and Nature

Bridged silsesquioxanes show important advantages compared with other monomer precursors, such as those derived of metalorganic sub-units, when they are involved in different synthesis methodologies. Disilanes are formed by organic linkers capable to be functionalized with several active sites, stabilized and separated at controlled molecular distances (see inset in [Figure 2](#)). At the end of these organic bridges, terminal reactive siloxane groups are present which allow the rapid integration, through hydrolysis and polycondensation mechanisms, of the monomer precursor into hybrid frameworks.⁸ The use of this type of disilanes facilitates the generation of practically irreversible hybrid architectures by the covalent linkages (bond strength $\sim 350 \text{ kJmol}^{-1}$) established between organic and inorganic structural builders. This can be an advantage with respect to other less robust materials based on coordination or ionic connections (bond strength of $\sim 50\text{-}250 \text{ kJmol}^{-1}$), such as metalorganic frameworks (MOFs) or porous coordination polymers.^[9]

New families of the so-called strong Class II hybrid materials are obtained with these bridged silsesquioxanes,^[10] where different organic active functions are integrated, as fixed active centers, into the network of the solids. In this case, the chemical processes, in which these materials are involved, are transferred from the internal free cavities to the walls of the solids. Novel multi-functional periodic mesoporous organosilicas (PMOs) or hydrophobic organozeolites (OZs) illustrate this synthesis approach. The high structural robustness and stability of the isolated active sites detected in these solids, largely improve the performances achieved by more traditional Class I hybrids wherein organic and inorganic counterparts are normally weakly connected by means of Van der Waals, hydrogen bonding or simple physico-chemical adsorption of soluble organocatalysts.^[11] Therefore, the use of monomer precursors derived from functionalized silanes, in suitable synthesis conditions, allows the preparation of different families of organic-inorganic hybrid materials with controllable structuration level and porous hierarchy. In this case, the induced morphology on the hybrids becomes decisive to define their physico-chemical properties and consequently their applicability.^[12] In [Figure 3](#) the main topologies which are formed starting from pre-designed siloxane precursors are schematized. In all materials, several active sites are inserted into the structural framework to generate multi-functional organic-inorganic materials capable to perform consecutive or cascade catalytic processes, using only one solid multi-site catalyst. This would allow avoiding intermediate isolation steps, use of solvents and excessive wastes generation, with the consequent development of more efficient multi-step chemical processes.^[13]

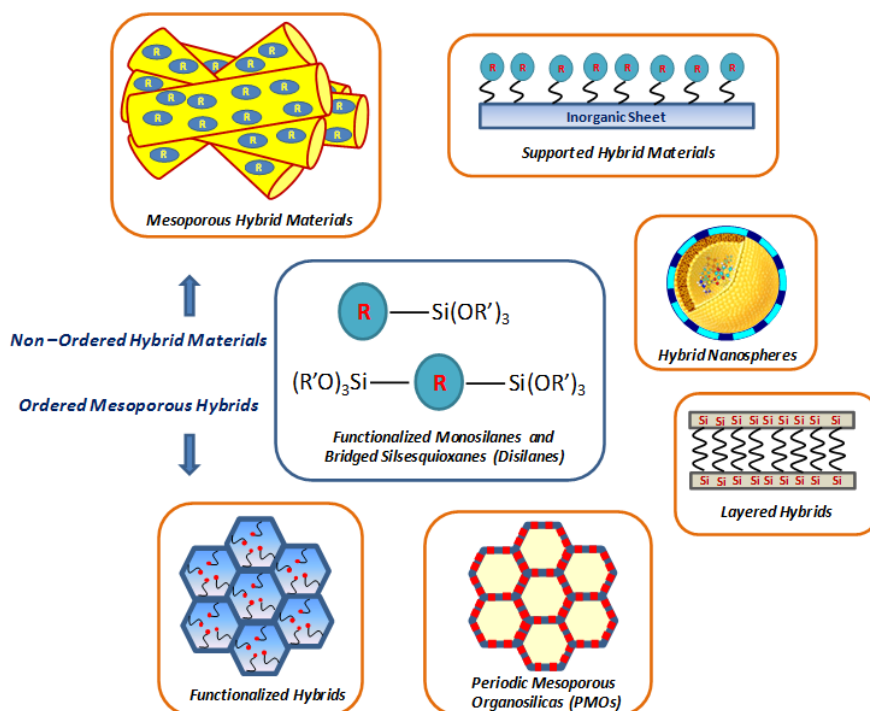


Figure 3. Hybrid materials obtained with different topologies, structural ordering and physico-chemical properties from functionalized organosilicon precursors.

Mesoporous Hybrid Materials

Considering the state-of-art, the most numerous and frequent group within the organosiliceous solids field corresponds to mesoporous hybrid materials. This is due to the capacity of bridged silsesquioxanes to be hydrolyzed and condensed around surfactant micelles, forming hexagonal long-ordered structures, such as Periodic Mesoporous Organosilicas (PMOs). Following this approach, micellar routes, in acid or base conditions, together with the presence of different types of structural directing agents (SDAs) like cationic or anionic surfactants and neutral block copolymers, allowed the synthesis of several families of PMOs. In this way, it is possible to introduce different active functions into the framework.^[14]

As alternative synthesis method, sol-gel processes in fluoride medium facilitate the preparation of accessible mesoporous organic-inorganic materials in a soft pathway synthesis. This is so because of the low temperatures (around 25°C), neutral pHs, absence of sophisticated SDAs and short aging periods required for the rapid formation of porous active hybrid solids. In this case, the generation of active pentacoordinated siloxane-fluoride intermediate facilitates the hydrolysis and condensation of bridged silsesquioxanes supported by the mineralizing effect of fluorine ions in the synthesis media (Figure 4).^[15] This synthesis route is successful to obtain non-ordered active bi-functional mesoporous hybrid materials

based on strong basic sites of protonic sponges (for instance, guanidine moieties with pK_a of ~ 25) inserted in the structural framework, together with pending sulfonic groups.^[16]

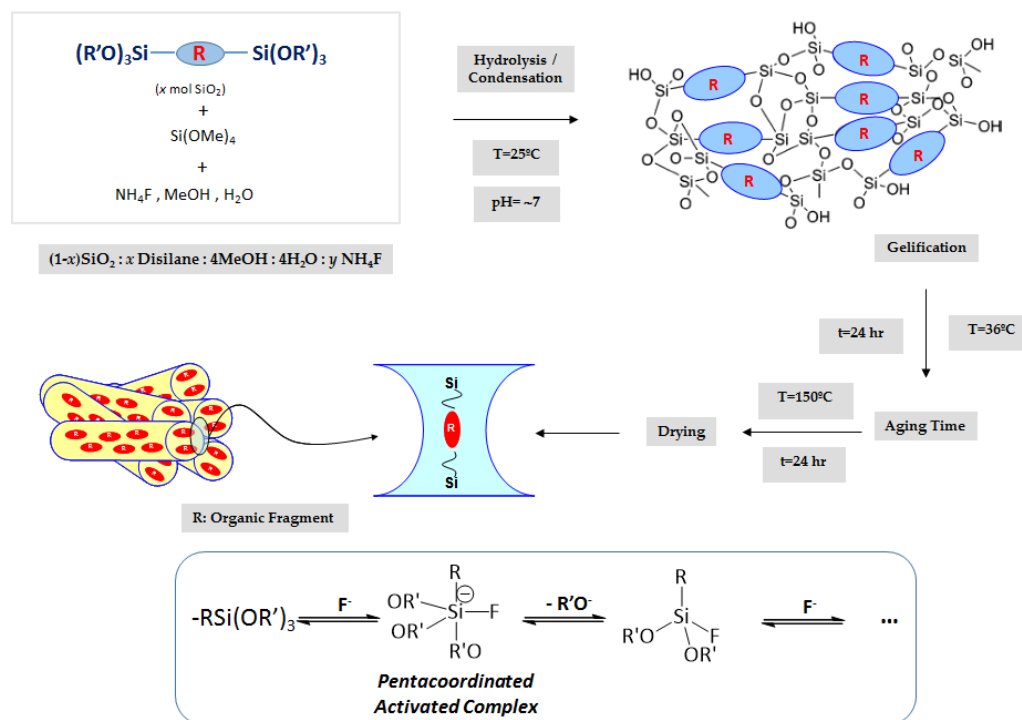


Figure 4. Synthesis route to prepare non-ordered mesoporous hybrid materials through sol-gel process in fluoride medium. In the bottom, mechanism followed during the hydrolysis and condensation of organosilicon precursors.

The synthesized mesoporous acid-base hybrid catalysts are active to perform tandem reactions, such as hemiacetal hydrolysis (catalyzed by sulfonic groups) followed by aldolic condensations (catalyzed by guanidine units) through one-pot process and using only one solid and recyclable hybrid catalyst. The validity of these multi-functional catalysts to carry out cascade or consecutive reactions was extended to different methylenic substrates with growing base demand, linked with even nitroaldol (Henry) reactions. The high stability of these catalytic materials was also confirmed because yields and selectivity were practically maintained after successive catalytic reuses.

In general, organocatalysts are stabilized into the framework of mesoporous inorganic matrixes, being their hydrothermal stability higher than in soluble form. However, the stability of the organic-inorganic solids is certainly limited by the intrinsic nature of organic moieties present in the structure. Interestingly, combination of disilanes together with cubic polyhedral oligomeric silsesquioxanes (POSS) strongly increases the robustness and structural stability of hybrid mesoporous materials. Indeed, it was possible to calcine this type of as-synthesized hybrid solids at high temperatures (around $400^\circ C$), to remove surfactant internal molecules used as structural directing agents, without destroying organic builder groups (such as derived

amino-arylic fragments) thanks to robustness supplied by D4R secondary building units from POSS monomers, used during the synthesis process.^[17, 18]

Compared with micellar routes, non-ordered mesoporous organic-inorganic materials, prepared through fluoride sol-gel processes exhibit, in many cases, higher catalytic performances than the more conventional ordered PMOs. This is because the rapid, but controllable, condensation phenomena of several bridged silsesquioxanes with different flexibility level favors the effective concomitant integration of different organic functions into the network with an elevated concentration, being them completely accessible to reactants. In opposite, micellar routes with the presence of SDAs acting as organosilicon templates, exhibit structural constraints that limit the easy integration of disilanes with longer and flexible organic functional bridges.^[19] Furthermore, the nature of bridged silsesquioxane monomers used as precursor has a strong influence on the final textural properties of the hybrid synthesized materials. Indeed, disilanes containing more flexible organic bridges (such as ethylenediamine or propyldisulfide groups), favored the formation of versatile non-ordered hybrids whose structural framework was more opened and accessible. In this case, reactive catalysts were obtained capable to perform aldolic condensations to obtain carbonyl compounds with interest as end-products and intermediates in the production of fine chemicals and commodities (perfumes, pharmaceuticals, polymers). On the contrary, the higher rigidity of bridged silsesquioxanes (such as those containing aryl units or short aliphatic chains) would explain the marked reduction in the mesoporous contribution of the hybrid mesoporous materials, the accessibility finally achieved and their associated reactivity being limited. This fact was observed with organic-inorganic materials prepared both from sol-gel routes in fluoride media and from micellar synthetic pathways.^[20]

Main Problem: Random Distribution of Active Functions

Micellar or sol-gel routes are used to obtain ordered and non-ordered mesoporous hybrid materials, as commented before.^[21] Following these methods, multi-functional hybrid materials have been prepared with the presence of different active sites cohabitating into the same network, being possible to combine acid, base and redox functions.^[22] In this sense, the effective successive post-synthesis anchoring of different organic functions onto purely siliceous porous silica structures allowed the generation of stable hybrid multi-site solids. In fact, cooperative effect due to the cohabitation of several active functions, together with the presence of free external silanol groups, improved the effectiveness of the hybrid materials used as recoverable catalysts. The supported materials obtained using this grafting mechanism

allowed the introduction of an elevated concentration of surface functional groups. Additionally, the modification of surface properties of the silica support by incorporation of hydrophobic groups increased the reactivity of the tethered active sites. However, the low structural symmetry and the inhomogeneous distribution of active centers together with the absence of shape selectivity limited their possible catalytic applications.^[23]

Frequently, random distribution of the different active sites present in the initial bridged silsesquioxanes, finally incorporated along the framework, resulted in non-homogeneous location of the structural building functions. This spatial configuration favors lower conversions and selectivity in processes wherein both sites work in a collaborative way (consecutive or cascade type reactions), due to the undesirable mutual neutralization and/or agglomeration of active centers, which result in a significant deactivation of hybrid catalysts (Figure 5, left).^[24] This fact would be avoided with the design of suitable specific organosiloxane monomer precursors where different functions would be placed in the organic bridge, being neighboring and separated at fixed molecular distances, guaranteeing the reactivity of the active centers during the catalytic process in which they are involved.^[25] This type of monomer precursors acts as authentic “platform” molecules and, when they take part as nanobuilding units in several synthesis process, it is possible to transfer the spatial arrangement of active functions from starting disilanes to the final hybrid framework where they are assembled. This working methodology should allow the generation of novel families of multi-site hybrid catalysts performing suitable one-pot multi-step catalytic routes. (Figure 5, right).

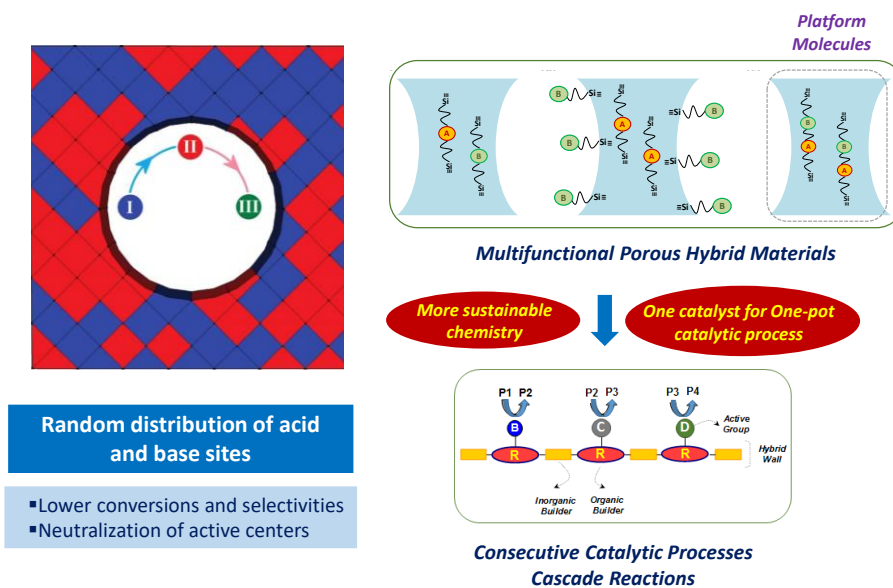


Figure 5. Representation of random distribution of active sites in the framework of hybrid materials (left), and use of platform molecules such as organosiloxane monomers as precursors of multifunctional catalysts. Figure adapted from references [2] and [24].

An illustrative example is related with the preparation of bi-functional acid-base hybrid mesoporous materials from specific bridged silsesquioxanes containing ionic imidazolium units separated by alkyl fragments. The use of these monomer precursors through micellar routes allowed the preparation of hybrid catalysts with acid and base sites separated by lineal aliphatic chains at fixed molecular distances. The catalytic results, for different Knoevenagel condensations, showed that the reactivity of catalysts with active centers distanced by only one carbon atom is higher (conversion $\sim 100\%$) than another similar catalysts with longer separation between acid and base functions (conversion $\sim 80\%$ when imidazolium units are separated by two carbon atoms). This fact effectively confirmed that the design of suitable platform molecules, as monomer precursors of multi-functional hybrid materials, is convenient to obtain highly active and efficient catalysts, which contain several functions isolated, stabilized and accessible to carry out cascade or consecutive multi-step chemical processes (Figure 6).^[26]

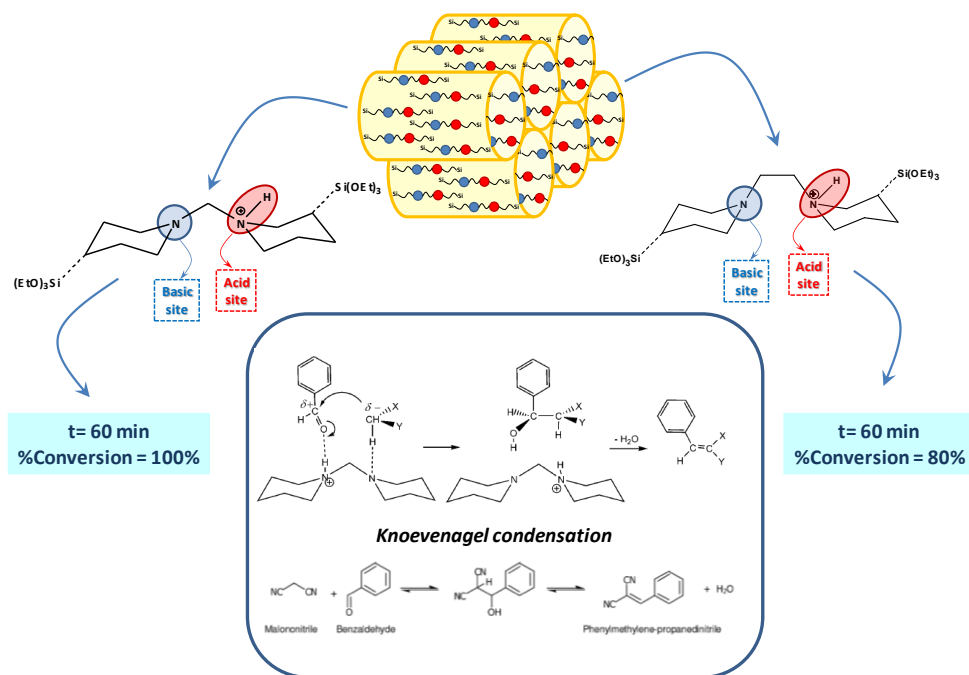


Figure 6. Acid-base bifunctional mesoporous materials based on silyl-derivative imidazolium units as active catalysts for aldolic condensations.

Chirality in Organic-Inorganic Porous Hybrid Materials

The design, specific preparation and auto-assembly of bridged silsesquioxanes, acting as platform molecules, which contain chiral groups isolated and stabilized in their organic bridges would be useful to form new families of hybrid catalysts with associated enantioselectivity.^[27] The case of chiral diphosphine ligands, similar to BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl), is well-known. This organic ligand can be anchored onto external surface of amorphous silicas or silica-aluminas through reaction with accessible silanol groups, or directly introduced into the walls of mesoporous organosilicas when it is used as monomer precursor during micellar synthesis routes.^[28] In both cases, the generated hybrid enantioselective catalysts are modified by post-synthesis treatments to deprotect the chiral phosphine ligands and successively to form organometallic complexes incorporated in the organosiliceous architectures. These chiral hybrid catalysts were active to perform asymmetric hydrogenation of different enamides, β -keto-esters and aromatic ketones. However, the family of chiral solid materials is still limited, being necessary a high number of synthesis steps to prepare active and stable hybrids, which contain into the network stabilized chiral fragments.

The use of disilanes as platform molecules would allow the generation of hybrid asymmetric catalysts with different active sites, located and stabilized into the porous architecture, being possible to combine chiral sub-units with other active centers. It is the case of chiral

mesoporous organosilicas (ChiPMOs) based on the assembly and co-condensation of disilanes that contain chiral vanadyl salen complexes^[29] or urea-cinchona derivative moieties combined with alkylamine groups.^[30] This last family of multisite catalysts^[30] was active to carry out asymmetric multicomponent reactions, such as those related to Henry condensation-Michael type addition from aldehydes, nitrocompounds and malonates. It is remarkable the high mechanical and hydrothermal resistance showed by ChiPMOs catalysts which combine different activation modes, enabling a good level of stereocontrol and reusability (Figure 7). Additionally, the combination of this chiral hybrid catalyst with palladium species facilitated the formation of heterogeneous and reusable catalytic systems optimal to perform domino sequences, toward the production of industrially relevant γ -amino butyric acid (GABA) derivatives, in racemic as well enantiomerically enriched form, through one-pot two-step reaction processes composed by seven chemical transformations, developing protocol routes with high intensification and efficiency.

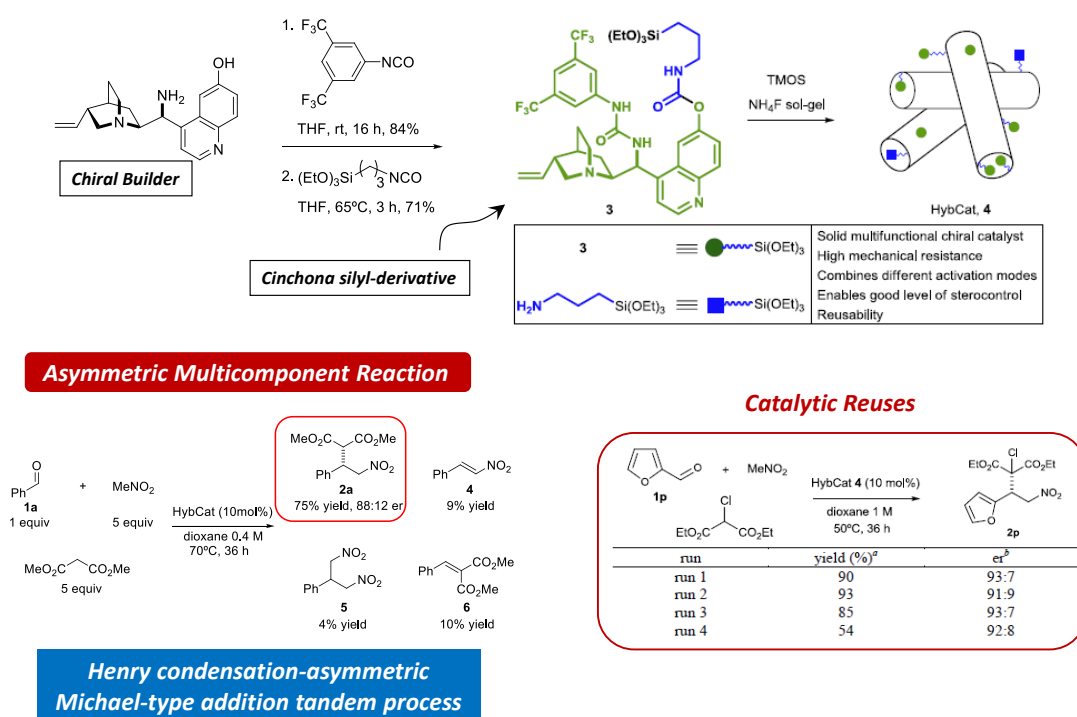


Figure 7. Chiral mesoporous hybrid catalysts containing urea-cinchona derivative moieties and alkylamine active groups for enantioselective multicomponent reactions. Figure adapted from references [25] and [30].

Taking into account these results, it is possible to see that there is still a long way to go for the preparation of more specific and reactive chiral hybrid catalysts in which the accessibility and stability of asymmetric functions are maximized and the leaching of the active sites is strongly minimized. For the design and preparation of specific disilanes as monomer precursors of

ChiPMOs-type materials would be necessary to introduce in the framework additional soluble chiral organocatalysts related with proline, quinine or pyrrolidine groups.^[31]

Hybrid Organic-Inorganic Nanospheres

Spherical hybrid architectures can be useful to generate multifunctional materials not only for catalytic application, but also as biocompatible carriers, photoluminescent materials or sensing systems. Important advances have already been achieved with purely (dense or porous) siliceous nanoparticles, normally through simple techniques based on inorganic polymerization at room temperature, using neutral silicate precursors as starting agents.^[32] However, problems associated to control release of internal active molecules or diffusional restrictions for reactants and products in catalytic processes, due to reduced and non-homogeneous porous distribution, limit the use of these nanospherical systems.^[33] On the other hand, although high porous regularity was achieved through micellar routes with the use of suitable surfactants, the mesoporous nature of these structures could exhibit reduced hydrothermal stability in aqueous media.

The incorporation of specific organic functions at the external part of the nanospheres allowed to gradually control the delivery or entrance of active principles or other substrates toward the internal part of these container-type systems. Different organosiliceous particles loaded with bioactive molecules were synthesized through different routes, such as hydrolysis and condensation, spray-drying or, mainly, sol-gel. Interestingly, the synthetic route based on consecutive micro-emulsions and controlled evaporation steps by the use of solvated phosphatidylcholine in water-chloroform mixtures was highly effective to produce regular spherical liposomal phases. The last process of hydrolysis and condensation of specific bridged silsesquioxanes around the liposomes allowed the generation of hollow core-shell nanospheres (Figure 8).^[34] These structures are formed by an internal aqueous liposomal core, where is possible to isolate and stabilize bioactive principles (for instance drugs, such as doxorubicin molecules) or reactive compounds (lipases), together with an external organosiliceous shell, where organic fragments can be used as authentic controllable molecular gates. In fact, when ester groups are present in the external shell and these hybrid nanospheres enter into the human cells, during *in vitro* tests, internal drug molecules are released due to the breaking of external ester groups by esterase enzymes present in the cells. The results confirmed the validity of these molecular nanometric containers as an effective carrier and drug-delivery system for biomedical applications.^[35]

Searching for more efficient hybrid biocatalysts which can mimic nature enzymatic processes, enzymes such as lipases were encapsulated and stabilized in the internal liposomal phase of the organic-inorganic nanospheres (see inset in Figure 8), generating active porous organosiliceous catalytic systems for biodiesel production through biomass transformation (for instance by transesterification of triolein with methanol to methyl esters).^[36]

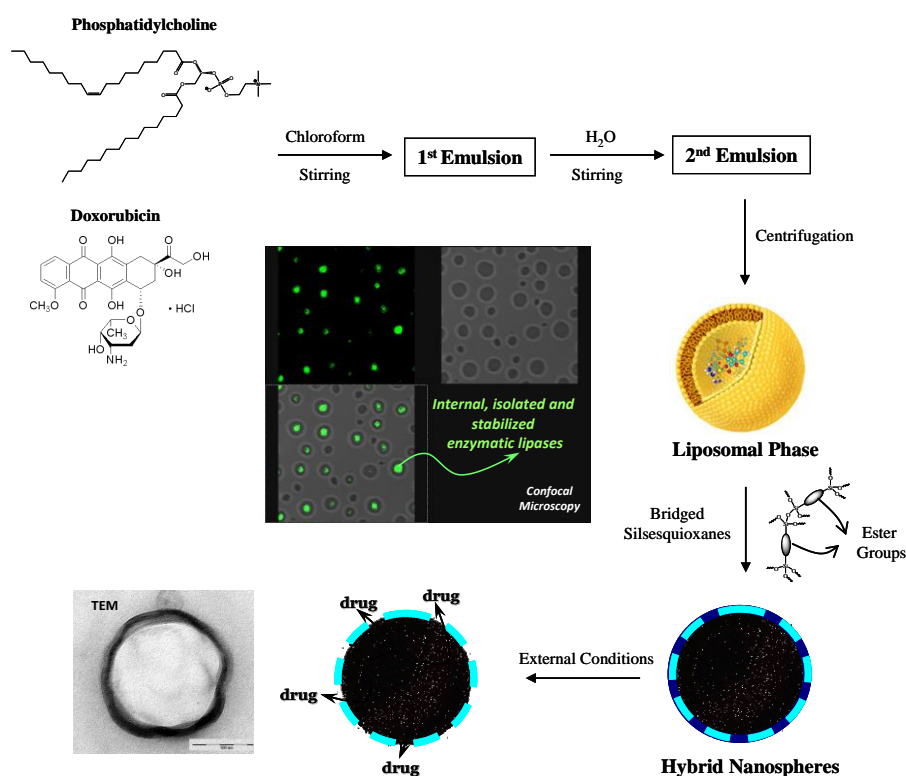


Figure 8. Synthesis route to obtain hybrid nanospheres with external molecular gates. In the inset nanospheres loaded with lipases. Figure adapted from references [35] and [36].

Considering both conceptual approaches, related with the use of these spherical materials as carriers and deliver systems of active principles, it should be possible to prepare novel hybrid nanospheres that can be used as authentic catalytic reactors at nanometric scale by the stabilization of different active sites (such as several metallic nanoparticles) in the internal part of the hollow spheres. The additional presence of organic functions homogeneously distributed along the external organosiliceous shell would facilitated the formation of multi-functional catalysts with different porous hierarchy with opening/closing of external molecular gates, maximizing the confinement effect and frequency factor during multi-step catalytic reactions. These materials would allow to carry out chemical processes with a high level of intensification (Figure 9).^[37]

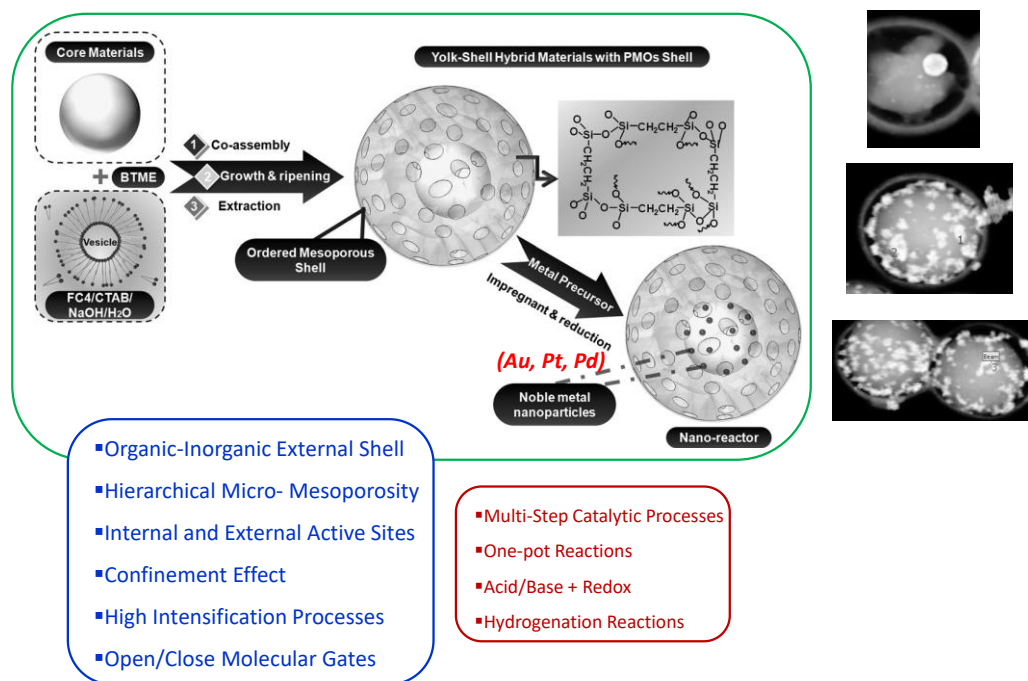


Figure 9. Schematic representation showing the potentiality of hybrid nanospheres to generate multifunctional catalysts. Figure adapted from reference [37].

Multi-functional Lamellar Hybrid Materials

The capacity of well-known versatile inorganic lamellar precursors to be morphologically modified by the introduction of organic fragments at or in between individual sheets has allowed the generation of new multi-functional structured layered materials.^[38] Illustrative is the case of MWW zeolitic lamellar precursor that is altered after successive swelling, pillarization and extraction steps with the use of aryl bridged silsesquioxanes as intercalation agents. The result was the formation of stable and robust bi-functional layered hybrid material with a hierarchical (micro and meso) porous system, cohabitating in the framework acid Brönsted sites (due to tetrahedral aluminum), placed in the inorganic counterpart (MWW individual zeolitic layers), together with base sites in the interlayer space (included in the organic aryl pillars).^[39] Additionally, the porous hierarchy is attributed to the microporous sinusoidal channels present in the MWW-type sheets and the regular mesoporous formed during the pillarization process and delimited by the organic pillars and inorganic layers (Figure 10). This bi-functional acid-base hybrid material was effective to catalyze one-pot acetal hydrolysis-Knoevenagel condensation cascade reactions, using only one solid and recyclable organic-inorganic catalyst, exploiting of inherent reactivity showed by MWW-type precursor.

The zeolitic sheets not only supplied robustness and stability to the final formed hybrid material, but also additional active sites present in the individual layers. It would be the case of

exfoliated materials based on disordered zeolitic sheets. The elevated external surface area of these delaminated zeolites combined with the high concentration of accessible and reactive silanol groups on individual layers was used to covalently incorporate other organic active groups, generating novel families of organic–inorganic hybrid materials with improved catalytic applications compared with conventional organic soluble catalysts.^[40]

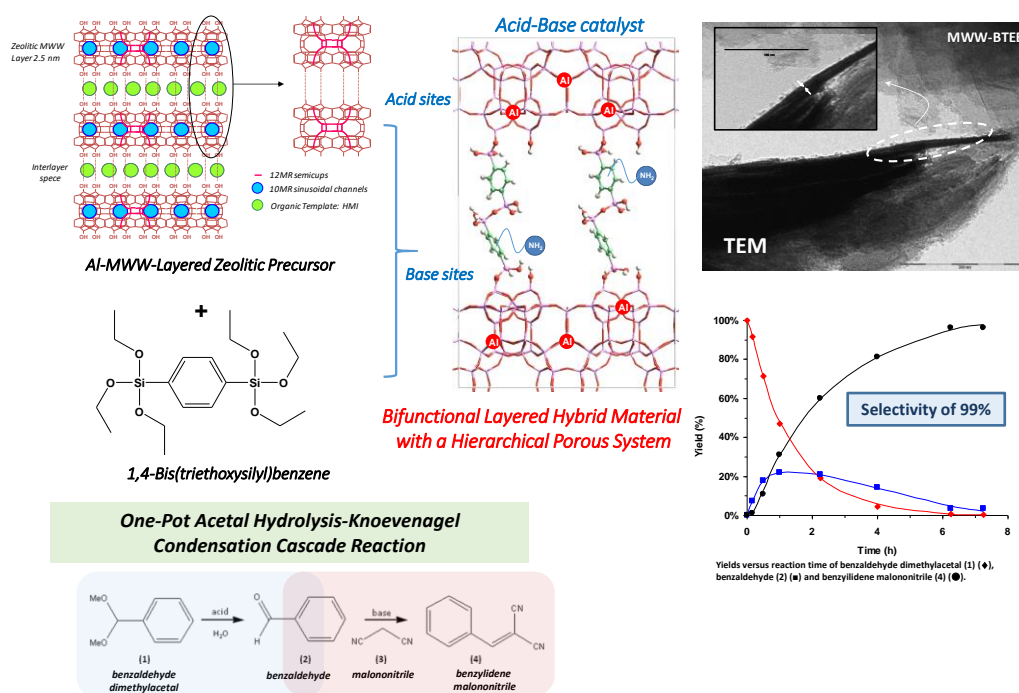


Figure 10. Representation of bi-functional acid-base hybrid catalyst based on MWW layers pillared with bridged silsesquioxanes, being active for cascade reactions. Figure adapted from reference [39].

Considering the capacity of lamellar inorganic precursors to be transformed in swelled organic-inorganic intermediate materials by the use of suitable surfactants as swelling agents, the incorporation of metallic (for instance platinum) sub-nanometric species located in the interlayer space was possible. This fact was favored by the high-achieved accessibility and the hydrophobic-hydrophilic nature of the hybrid-swelled solids. After calcination step to remove organic swelling agents, multi-functional layered material was formed, in which active metallic clusters or nanoparticles were homogeneously distributed (most with sizes below 1 nm), stabilized and isolated into the microporous cavities of the 3D zeolitic structural framework, being avoided the undesirable agglomeration and deactivation of metallic species. These synthesized catalysts were effective for redox processes at high temperatures, such as hydrogenation of light olefins, maintaining the activity after successive catalytic cycles (Figure 11).^[41]

The field related with the preparation of multi-functional lamellar hybrid materials continues to grow, due to the capacity of the inorganic precursors to be modified by exchange, swelling, pillarization or exfoliation steps. Furthermore, these lamellar hybrids should allow to combine intrinsic active sites, associated to the organic and inorganic counterparts present in the framework, and those externally incorporated onto the surface of inorganic sheets by grafting, tethering or simple deposition.^[42] Recently, direct one-step hydrothermal synthesis route have been developed to prepare pillared hybrid materials, avoiding long and expensive post-synthesis treatments, modifying conventional lamellar inorganic precursors, and without using sophisticated swelling or intercalation agents.^[43] In these type of solids, so-called LHM, the synthesis gel was formed with high aluminum content and in presence of bridged silsesquioxanes as only organosilicon source. The result is the direct synthesis of hybrid catalysts based on organized piled aluminosilicate layers covalently linked between them by specific functional organic bridges. Advances performed with these materials made possible the preparation of non-connected individual (organo)silicoaluminate layers with different spatial organization by the use of several organo(mono)siloxanes during the hydrothermal synthesis process. In this case, individual 2D hybrid nanosheets were obtained which contain two or more accessible active sites (acid, base or redox) present onto their external surface, being active to carry out consecutive or tandem reactions using only one recoverable hybrid catalyst (Figure 12).^[44]

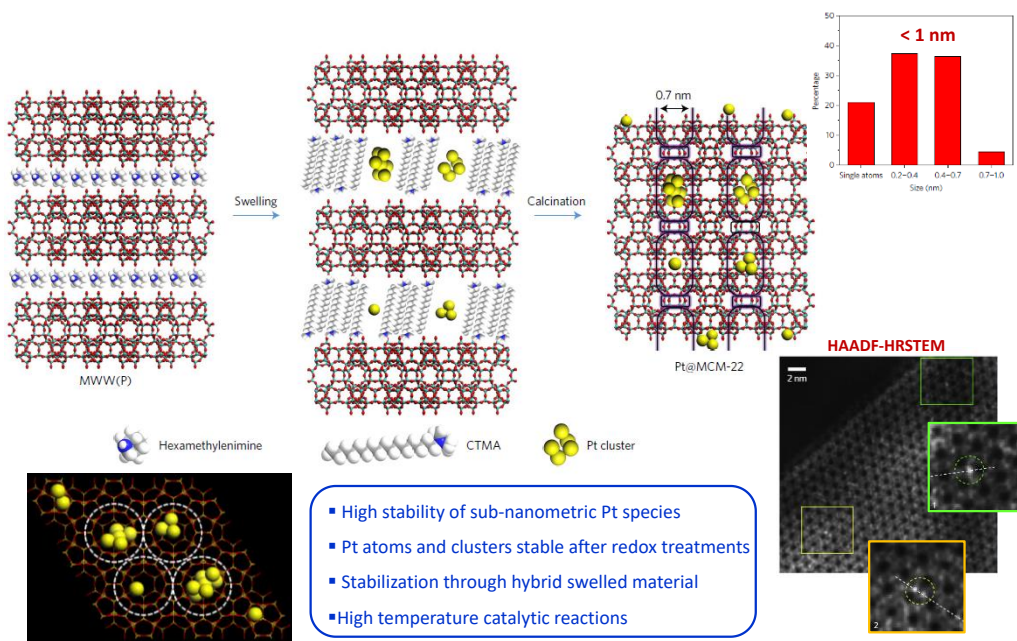


Figure 11. Preparation route to isolate and stabilize metallic nanoclusters in microporous zeolites from hybrid swelling materials. Figure adapted from reference [41].

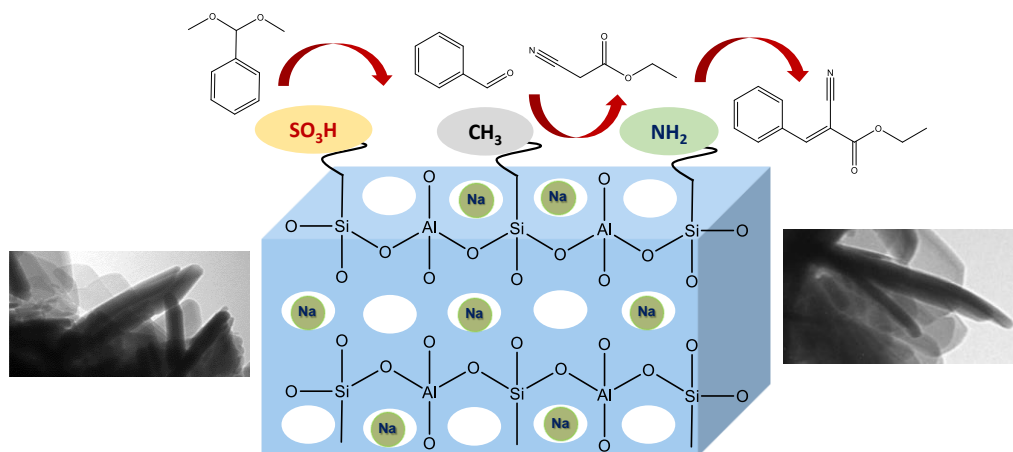


Figure 12. Lamellar hybrid material containing acid and base sites formed by the direct assembly of functionalized (organo)aluminosilicate nanosheets. Figure adapted from references [43] and [44].

Hybrid Materials based on 1D Organic-Inorganic Structural Sub-domains

It has been shown up to here that bridged silsesquioxanes or, in general, organosiloxanes can be excellent monomer precursors to generate multi-functional hybrid materials with different topologies and physico-chemical characteristics depending on the synthesis conditions. Another route to synthesize multifunctional hybrid materials would involve the previous formation of individual single organic-inorganic sub-domains, as first structuration level, which can be later assembled to form novel hybrid architectures hosting several active sites. This procedure could facilitate the formation of new hybrid structures through the suitable auto-assembly of the initial sub-domains under softer conditions.^[45] This is the case of recently prepared metalorganic derived materials based on the regular spatial assembly of 1D structural sub-domains. These last were formed by inorganic chains, structured from the coordinated association of metallic (Ni, Al or Zr) octahedra, previously isolated by the presence of long alkyl-monocarboxylate spacers located at both sides of the chains, which acted as growing modulators.

The use of the suitable solvothermal synthesis conditions should allow generating new families of metalorganic structures with controllable 1D, 2D or 3D topology and different pore hierarchy (Figure 13). The marked hydrophobic character of this type of hybrid structures, due to high organic content present in the framework (even higher than 70% in weight), facilitates the preparation of supramolecular solid catalysts where different soluble organocatalysts can be isolated and stabilized in the organic counterpart of the metalorganic structure. In this case, the hybrid materials, based on 1D structural sub-domains, act as a true micellar system, boosting organic processes in water, like enantioselective Michael reactions or multi-

component reactions from aldehydes, methylenic compounds and malonates.^[46] Additionally, these derived metalorganic materials were effective for control release of volatile organic compounds, such as insect pheromones, being useful for pest management with an innovative agrochemical application.^[47]

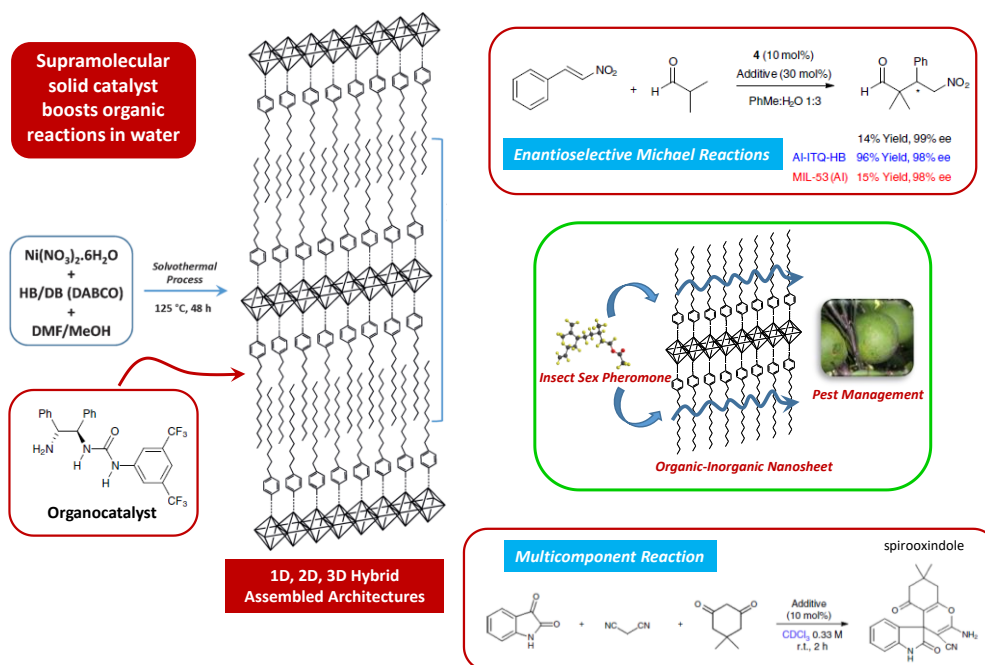


Figure 13. Metalorganic derived structures based on the assembly of 1D organic-inorganic sub-domains by the use of specific spacers as growing modulators. Different applications in catalysis or agrochemistry are shown. Figure adapted from references [46] and [47].

There results and the applicability exhibited by the hybrid materials prepared from assembly of 1D structural organic-inorganic sub-domains confirm that, the synthesis methodology based on the previous formation of well-organized building sub-structures would be a suitable synthesis pathway to obtain new hybrid materials with variable and controllable morphology, dimensionality, textural properties and adaptable reactivity.

In Table 1, a summary of the different hybrid materials above commented is shown, remarking topology, synthesis method and possible location of active sites into the framework.

Table 1. Examples of multi-site organic-inorganic hybrid materials prepared from bridged silsesquioxanes, $(R'O)_3SiRSi(OR')_3$.

Topology	Synthetic Procedure	Location Active Sites	Remarks
Ordered Mesoporous Materials	Micellar routes	Random (one-pot synthesis) Fixed (grafting methods)	Porosity control
Non-ordered Mesoporous Materials	Sol-Gel processes (acid, base or fluoride medium)	Random	Soft synthesis conditions
Hybrid Nanospheres	Consecutive micro-emulsions and evaporation steps	Fixed	Nanoreactor systems
Layered Solids	Post-modification of lamellar precursors	Fixed	Hierarchical porous materials
1D Hybrid Structures	Solvothermal processes	Fixed	Supramolecular solid catalysts

Future Perspectives: Hybrid Materials as Sensors

Different multi-site hybrid materials active to catalyze tandem or cascade catalytic reactions have illustrated the influence of the morphology and location of active centers on their reactivity. In fact, the presence of different functions along the network of the hybrids has been focused above on their role as multi-functional heterogeneous catalysts. However, the possible introduction, into the materials' architecture, of organic fragments as an ordered arrangement of electron-donor-acceptor units involved in transfer energy processes, would allow the generation of multi-functional hybrid solids capable to be used for catalytic reactions, but also as optical, electronic, magnetic devices, even combining several of those functionalities.^[48] The results would be the formation of multi-site reusable solids for selective multi-step chemical reactivity-sensing processes (see scheme in [Figure 14](#)).^[49]

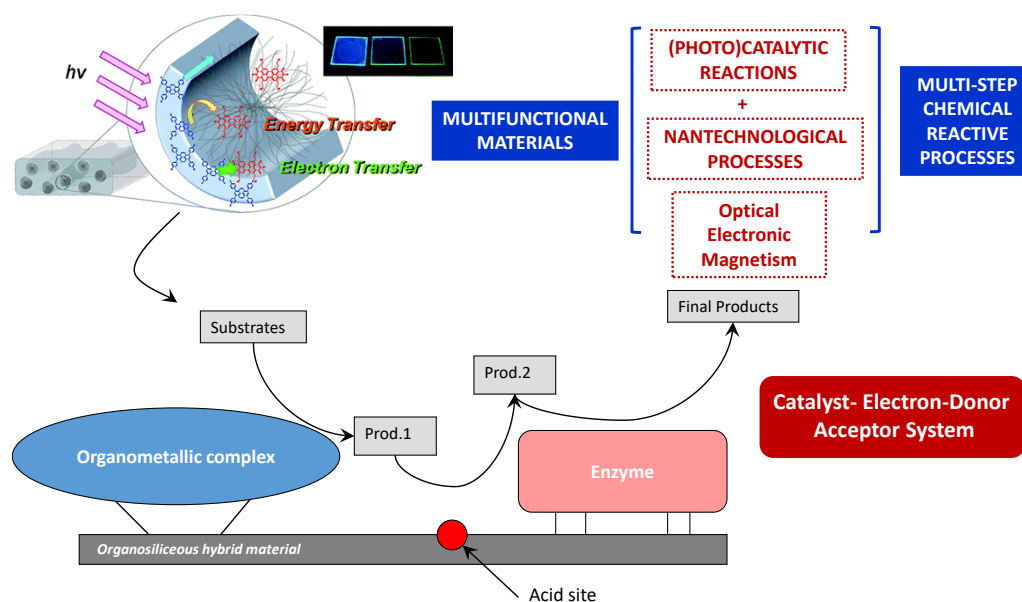


Figure 14. Schematic representation of multifunctional hybrid materials useful to perform consecutively catalytic and nanotechnological processes through multi-step chemical processes in presence of only one catalyst-electron-donor system. Part of the figure was adapted from reference [49].

Specifically, organic-inorganic materials could be used as the major component for some sensors based on conductivity, adsorptive or catalytic properties. Taking into account the topology and textural properties of the solids, one could also select a hybrid solid for specific interactions with some analytes. There are other sensing potential applications wherein the hybrids will not be the main component, but nevertheless, will play an important role. For instance, sensitive gas sensors to detect different gaseous substances such as hydrocarbons, CO, NO₂ and NH₃ can use organic-inorganic materials containing single atoms, clusters or nanoparticles of Pt, Pd, Ag, Cu, etc. within the free channels or cavities.^[50, 51] For preparing the metal nanoparticles, homogeneously distributed along the framework, different methods can be used: (i) ion exchange followed by reduction, (ii) direct synthesis wherein the metal components are in the form of metal atoms bound to organic groups pending from walls to the cavities, and (iii) by introducing the metal during the synthesis process, in the form a metal complex forming part of bridged silsesquioxanes used as organosilicon precursors.^[38, 52] Through these methods, it is possible to generate isolated metal atoms within the cavities of the hybrid materials and then to form very small clusters.^[53, 54]

Hybrid Materials in Biosensors

Hybrid architectures can also be used to immobilize enzymes,^[55] transforming them to heterogeneized enzymatic catalysts or enzyme-based sensors. By adsorbing and/or anchoring enzymes on the accessible surface of hybrid materials, long lasting micro-devices with high

sensitivity for biocatalytic functions could be prepared.^[56, 57] It would be the case of structured 2D and 3D porous materials modified with adsorbed proteins for biosensing applications.^[58] Following this approach, the protein deposition is strongly dependent on the morphology of the support. Therefore, for protein uptake, hierarchical micro-mesoporous hybrid structures with high external surface area would be convenient. Notice that for this case, the shape and textural characteristics of the organic-inorganic materials can also play an important role, since they can influence surface charge and density as well as surface curvature at the nanoscale level. In addition, hybrid structures can be deposited as a monolayer or thin film and used as a biocompatible surface model to study the cell-adhesion behavior.^[59] In fact, cells can grow on asymmetrically functionalized supports in defined patterns. Then, the combination of living cells and non-leaving (hybrid films) components is expected to find application as biosensors.

Optical Sensors

Other type of hybrid multi-functional materials corresponds to optical sensors based on dye-induced excitation energy-transfer phenomena, being possible to develop photonic devices due to the presence of suitable organic and inorganic builders in the network.^[60] It is the case of lamellar modified organozeolites with high accessibility in which efficiency and stability of the emitting dyes is increased.^[61] The external surface of the dye loaded support has also been modified with organic molecules, the hybrid material being compatible with additional polymers. Thus, the dispersion of modified support in the polymer would improve the luminescence of the material, opening new perspectives to engineer nanodevices.^[62]

Energy transfer phenomena could be increased when the hybrid materials are prepared in the form of thin films through different techniques such as screen-printing, sol-gel methods, dip and spin coating or direct growth with and without substrate pre-seeding treatments.^[63] In these cases, the solids could act as a key functional element in the sensor based on their adsorption properties, hydrophobic-hydrophilic nature, concentration effect and interaction with the analytes. On the other hand, an acceptor or donor stopcock fluorophore can also be placed in the pores to trap or inject electronic excitation energy from or to the nanodevice system-type film. The host-guest formed material could be tested for the collection, trapping and energy transport.^[64]

Optical sensors based on hybrid mesoporous materials doped with metallic nanoparticles, as we said before, would be developed to analyze chemicals and biologic products among others. In the case of Hg(II) sensing, a silver-embedded organosiliceous thin film based fiber optic sensor, could be used for *in situ* real time monitoring Hg(II) in aqueous solution. An important issue is

the high sensitivity and selectivity over competing analytes.^[65] Even, the incorporation of fluorescent rhodamine units in the framework of the films would facilitate the generation of off-on systems owing to structural transformation from a non-emissive to highly emissive device, giving a fast response towards Hg(II) detection.

Alternatively, the presence of different metals into the network of hybrid materials combined with high adsorption capacity, make these solids attractive for sensing chemical gases and vapors.^[66] Moreover, the incorporation of lanthanides would increase the potentiality of these hybrid solids as luminescent sensing materials. For instance, hybrid core-shell materials prepared by coating with polyelectrolytes are excellent sensor systems for dipicolinic acid that is related with the presence of many pathogenic spore-forming bacteria.^[67] Also, relevant is the formation of hybrid materials by the combination of photopolymers with modified microporous structures for the design of holographic sensors.^[68]

Electrochemical Sensors

In the case of organic-inorganic materials with pores within molecular dimensions, it is possible to introduce some molecular shape selectivity by size, but also because of the charges as part of the hybrid structure that can also act as an ionic filter. So, these solids can allow further discrimination by acting as passive molecular discriminators, as for instance pre-concentrating a given analyte or reactant. Furthermore, by introducing additional units with catalytic properties on the electrodes of different electronic devices, one could combine heterogeneous catalysis in an electrochemical interphase, achieving synergetic effects. This is the case of systems based on 2D graphene nanolayers combined with MoS₂ sub-domains, generating heterogeneous interfaces that can modify chemical and physical material properties with a wide range of applications in electrochemical energy storage, catalysis and sensing. The vertical assembly of 2D C-MoS₂ nanosheets with Li metal electrodes, and a lithium hexafluorophosphate solution in ethylene carbonate and diethyl carbonate electrolyte, significantly increase the electrochemical activity and chemical conversion.^[69]

In this way, organic moieties, organometallic monomolecular compounds or organic-inorganic nanosheets could be adsorbed, covalently bonded to, deposited on, or self-assembled on an electrode surface to improve electrochemical characteristics of the electrodes combined with catalytic properties.^[70] The modified electrodes could perform multiple tasks, including also heterogeneous electron transfers. These modified electrodes would improve their durability by increasing long-term stability, during the reaction conditions. Hybrid modifiers could overcome drawbacks of more conventional polymeric electrodes related with their duration,

possible dissolution, decomposition or chemical degradation phenomena, being the base for the design of integrated systems with complex molecularity.^[71] For instance, modified electrodes would be active to sequester Hg^{2+} and Ag^+ from aqueous solutions at open circuit and when required under potential control, reveal the amount of metal species retained.^[72] Finally, there is also the possibility of using electrodes containing hybrid modifiers together with metal nanoparticles or organometallic complexes as novel electrode materials without a direct electrical contact.^[73]

In conclusion, the use of organic-inorganic components for electrode modification would allow improving selectivity and detection limit of sensing nanodevices. However, we believe there are still open opportunities on using new families of hybrid materials with different assembled organic and inorganic counterparts with controllable electron transfer phenomena, to generate optical or electrochemical sensor systems combined with catalytic properties.

Definitively, multi-site organic-inorganic materials offer the possibility, which is singular in the materials science, to combine heterogeneous (photo)catalytic reactivity together with electronic or optical properties, using only one stable and reusable material which would act as authentic catalyst-electron donor–acceptor nanoreactor capable to carry out, in one-pot, multi-step chemical reactive processes.

We have attempted to show a number of functional possibilities that solid hybrid organic-inorganic materials can offer in the fields of catalysis, sensing and, more generally, for materials science. We have seen that regardless of following a soft sol-gel or a templated synthesis procedure, the use of structural functional nanobuilding units allow to prepare organized specific multi-functional materials. Therefore, the use of self-assembled functionalized nanostructured builder units is still an open field for preparing multi-functional materials in the fields of catalysis, sensor, etc.

Acknowledgements

The authors are grateful for financial support from the Spanish Government by MAT2014-52085-C2-1-P and Severo Ochoa Excellence Program SEV-2016-0683. The European Union is also acknowledged by ERC-AdG-2014-671093-SynCatMatch.

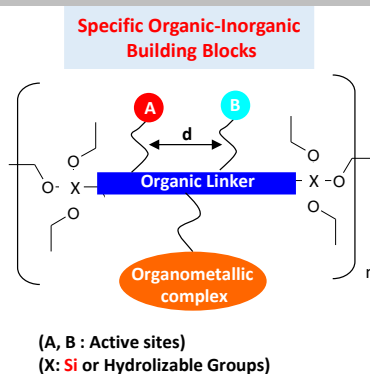
Conflict of interest

The authors declare no conflict of interest.

Keywords: *Hybrid materials; Nanobuilder units; Multi-functional materials; Cascade reactions; Nanotechnology; Sensor*

CONCEPT

The use of pre-formed nanobuilding units with associated functionalities are necessary to prepare hybrid multi-functional materials to perform multipurpose processes in the fields of catalysis, sensing and for materials science.



Multi-functional Materials

U. Díaz, A. Corma**

Page No. – Page No.

**Organic-Inorganic Hybrid Materials:
Multi-functional Solids for Multi-step
Reaction Processes**

References

- [1] D. A. Loy, K. J. Shea, *Chem. Rev.* **1995**, *95*, 1431–1442.
- [2] U. Díaz, D. Brunel, A. Corma, *Chem. Soc. Rev.* **2013**, *42*, 4083–4097.
- [3] F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem., Int. Ed.* **2006**, *45*, 3216–3251 and references therein.
- [4] U. Díaz, A. Corma, *Coord. Chem. Rev.* **2016**, *311*, 85–124.
- [5] C. Sánchez, F. Ribot, *New J. Chem.* **1994**, *18*, 1007–1047.
- [6] G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191–214.
- [7] A. P. Wight, M. E. Davis, *Chem. Rev.* **2002**, *102*, 3589–3614.
- [8] S. Fujita, S. Inagaki, *Chem. Mater.* **2008**, *20*, 891–908 and references therein.
- [9] N. R. Shiju, A. H. Alberts, S. Khalid, D. R. Brown, G. Rothenberg, *Angew. Chem. Int. Ed.* **2011**, *50*, 9615–9619.
- [10] C. Sánchez, B. Julián, P. Belleville, M. Popall, *J. Mater. Chem.* **2005**, *15*, 3559–3592.
- [11] D. Ajami, L. Liu, J. Rebek, *Chem. Soc. Rev.* **2015**, *44*, 490–499.
- [12] J. L. C. Rowsell, O. M. Yaghi, *Micropor. Mesopor. Mat.* **2004**, *73*, 3–14.
- [13] J. M. Notestein, A. Katz, *Chem.–Eur. J.* **2006**, *12*, 3954–3965.
- [14] M. P. Kapoor, S. Inagaki, S. Ikeda, K. Kakiuchi, M. Suda, T. Shimada, *J. Am. Chem. Soc.* **2005**, *127*, 8174–8178.
- [15] E. Reale, A. Leyva, A. Corma, C. Martínez, H. García, F. Rey, *J. Mater. Chem.* **2005**, *15*, 1742–1754.
- [16] E. Gianotti, U. Díaz, A. Velty, A. Corma, *Eur. J. Inorg. Chem.* **2012**, *32*, 5175–5185.
- [17] U. Díaz, T. García, A. Velty, A. Corma, *Chem.–Eur. J.* **2012**, *18*, 8659–8672.
- [18] H. C. L. Abbenhuis, *Angew. Chem. Int. Ed.* **1999**, *38*, 1058–1060.
- [19] T. Asefa, M. J. MacLachlan, N. Coombs, G. A. Ozin, *Nature* **1999**, *402*, 867–871.
- [20] U. Díaz, T. García, A. Velty, A. Corma, *J. Mater. Chem.* **2009**, *19*, 5970–5979.
- [21] R. Mouawia, A. Mehdi, C. Reye and R. J. P. Corriu, *J. Mater. Chem.* **2008**, *18*, 4193–4203.
- [22] S. Shylesh, A. Wagener, A. Seifert, S. Ernst, W. R. Thiel, *Angew. Chem. Int. Ed.* **2010**, *49*, 184–187.
- [23] E. L. Margelefsky, R. K. Zeidan, M. E. Davis, *Chem. Soc. Rev.*, **2008**, *37*, 1118–1126.
- [24] A. Kuschel, M. Drescher, T. Kuschel, S. Polarz, *Chem. Mater.* **2010**, *22*, 1472–1482.
- [25] P. García-García, A. Zagdoun, C. Coperet, A. Lesage, U. Díaz, A. Corma, *Chem. Sci.* **2013**, *4*, 2006–2012.
- [26] M. Boronat, M. J. Climent, A. Corma, S. Iborra, R. Montón, M. J. Sabater, *Chem.–Eur. J.* **2010**, *16*, 1221–1231.
- [27] R. Noyori, H. Takaya, *Acc. Chem. Res.* **1990**, *23*, 345–350.
- [28] A. R. McDonald, C. Müller, D. Vogt, G. P. M. van Klink, G. van Koten, *Green Chem.* **2008**, *10*, 424–432.
- [29] C. Baleizao, B. Gigante, D. Das, M. Álvaro, H. García, A. Corma, *Chem. Commun.* **2003**, *15*, 1860–1861.
- [30] A. Leyva-Pérez, P. García-García, A. Corma, *Angew. Chem. Int. Ed.* **2014**, *53*, 8687–8690.
- [31] C. Baleizao, B. Gigante, D. Das, M. Álvaro, H. García, A. Corma, *J. Catal.* **2004**, *223*, 106–113.
- [32] V. P. Torchilin, *Nanoparticulates as Drug Carriers*, Imperial College Press, London, **2006**.
- [33] H. González, S. J. Hwang, M. E. Davis, *Bioconjugate Chem.* **1999**, *10*, 1068 – 1074.
- [34] S. Bégu, S. Girod, D. A. Lerner, N. Jardiller, C. Tourné-Péteilh, J. M. Devoisselle, *J. Mater. Chem.* **2004**, *14*, 1316 – 1320.
- [35] U. Díaz, A. Corma, M. Arrica, E. Fernández, I. Ortega, *Angew. Chem. Int. Ed.* **2009**, *48*, 6247–6250.
- [36] F. Verri, U. Díaz, A. Macario, A. Corma, G. Giordano, *Process Biochem.* **2016**, *51*, 240–248.
- [37] J. Liu, H. Q. Yang, F. Kleitz, Z. G. Chen, T. Yang, E. Strounina, G. Q. Lu, S. Z. Qiao, *Adv. Funct. Mater.* **2012**, *22*, 591–599.

- [38] H. Van Olphen, *An Introduction to Clay Colloid Chemistry*, John Wiley & Sons, New York, **1963**.
- [39] A. Corma, U. Díaz, T. García, G. Sastre, A. Velty, *J. Am. Chem. Soc.*, **2010**, *132*, 15011–15021.
- [40] A. Fuerte, A. Corma, M. Iglesias, E. Morales, F. Sánchez, *J. Mol. Catal. A: Chem.*, **2006**, *246*, 109–117.
- [41] L. Liu, U. Díaz, R. Arenal, G. Agostini, P. Concepcion, A. Corma, *Nature Mater.* **2017**, *16*, 132-138.
- [42] G. Bellussi, E. Montanari, E. Di Paola, R. Millini, A. Carati, C. Rizzo, W. O. N. Parker Jr., M. Gemmi, E. Mugnaioli, S. Zanardi, *Angew. Chem., Int. Ed.* **2012**, *51*, 666–669.
- [43] A. Gaona, J. M. Moreno, A. Velty, U. Díaz, A. Corma, *J. Mater. Chem. A* **2014**, *2*, 19360–19375.
- [44] A. Gaona, U. Díaz, A. Corma, *Chem. Mater.* **2017**, DOI: 10.1021/acs.chemmater.6b04563.
- [45] R. Tanoue, R. Higuchi, N. Enoki, Y. Miyasato, S. Uemura, N. Kimizuka, A.Z. Stieg, J.K. Gimzewski, M. Kunitake, *ACS Nano* **2011**, *5*, 3923–3929.
- [46] J. M. Moreno, I. Navarro, U. Díaz, J. Primo, A. Corma, *Angew. Chem. Int. Ed.* **2016**, *55*, 11026 – 11030.
- [47] P. García-García, J. M. Moreno, U. Díaz, M. Bruix, A. Corma, *Nature Commun.* **2016**, *7*:10835, doi:10.1038/ncomms10835.
- [48] I.-H. Park, R. Medishetty, J.-Y. Kim, S.S. Lee, J.J. Vittal, *Angew. Chem. Int. Ed.* **2014**, *53*, 5591–5595.
- [49] N. Mizoshita, K-I. Yamanaka, S. Hiroto, H. Shinokubo, T. Tani, S. Inagaki, *Langmuir* **2012**, *28*, 3987–3994.
- [50] S. Thomas, P. Bazin, L. Lakiss, V. de Waele, S. Mintova, *Langmuir* **2011**, *27*, 14689-14695.
- [51] X. W. Xu, J. Wang, Y. C. Long, *Sensors* **2006**, *6*, 1751-1764.
- [52] M. Moliner, J. E. Gabay, C. E. Kliewer, R. T. Carr, J. Guzman, G. L. Casty, P. Serna, A. Corma, *J. Am. Chem. Soc.* **2016**, *138*, 15743–15750.
- [53] R. Martínez-Franco, M. Moliner, J. R. Thogersen, A. Corma, *ChemCatChem.* **2013**, *5*, 3316-3323.
- [54] G. Budroni, A. Corma, *Angew. Chem. Int. Ed.* **2006**, *118*, 3406-3409.
- [55] A. Corma, V. Fornés, J.L. Jordá, F. Rey, R. Fernández-Lafuente, J.M. Guisán, C. Mateo, *Chem. Commun.* **2001**, *5*, 419-420.
- [56] T. Yu, Y. H. Zhang, C. P. You, J. H. Zhuang, B. Wang, B. H. Liu, Y. J. Kang, Y. Tang., *Chem. -Eur. J.* **2006**, *12*, 1137-1143.
- [57] J. Ji, Y. H. Zhang, N. Ren, Y. Tang, *Anal. Chem.* **2008**, *80*, 2457-2463.
- [58] Y. Hu, Y.H. Zhang, N. Ren, Y. Tang, *J. Phys. Chem.C.* **2009**, *113*, 18040-18046.
- [59] N. S. Kehr, K. Riehemann, J. El-Gindi, A. Schäfer, H. Fuchs, H. J. Gala, *Adv. Funct. Mater.* **2010**, *20*, 2248-2254.
- [60] C. Minkowski, R. Pansu, M. Takano, G. Calzaferry, *Adv. Funct. Mater.* **2006**, *16*, 273-285.
- [61] A. Corma, U. Díaz, B. Ferrer, V. Fornés, M. S. Galletero, H. García, *Chem. Mater.* **2004**, *16*, 1170-1176.
- [62] V. Vohra, G. Calzaferry, S. Detri, M. Pasini, W. Porzio and C. Botta, *ACS Nano* **2010**, *4*, 1409-1416.
- [63] X. G. Li, P.K. Dutta, *J. Phys. Chem. C.* **2010**, *114*, 7986-7994.
- [64] V. Vohra, A. Bolognesi, G. Calzaferry, C. Botta, *Langmuir* **2009**, *25*, 12019-12023.
- [65] N. Liu, L. Liangxiong, G. Cao, R. Lee, *J. Mater. Chem.* **2010**, *20*, 9029-9031.
- [66] M. Aziz, A. J. Orr-Ewing, *J. Environmental Monitoring* **2012**, *14*, 3094-3100.
- [67] H. Li, W. Cheng, Y. Wang, B. Liu, W. Zhang, H. Zhang, *Chem. -Eur. J.* **2010**, *16*, 2125-2130.
- [68] E. Leite, I. Naydenova, S. Mintova, L. Leclercq, V. Toal, *Appl. Opt.* **2010**, *49*, 3652-3660.
- [69] L. Oakes, R. Carter, T. Hanken, A. P. Cohn, K. Share, B. Schmidt, C. L. Pint, *Nature Commun.*, **2016**, *7*:11796, DOI: 10.1038/ncomms11796.
- [70] D. R. Rolison, *Chem. Rev.* **1990**, *90*, 867-878.
- [71] Z. Li, C. M. Wang, L. Persand, T. E. Mallouk, *J. Phys. Chem.* **1988**, *92*, 2592-2597.
- [72] L. Zhuang, J. Jin, H. D. Abbruña, *J. Am. Chem. Soc.* **2007**, *129*, 11033-11035.
- [73] D. R. Rolison, E. A. Hayes, W. E. Rudzinski, *J. Phys. Chem.* **1989**, *93*, 5524-5531.