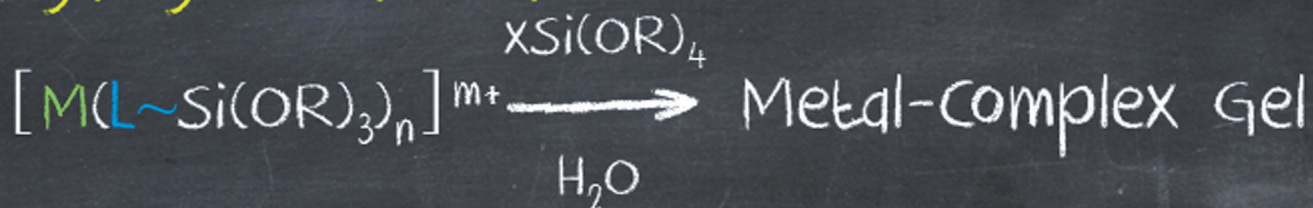
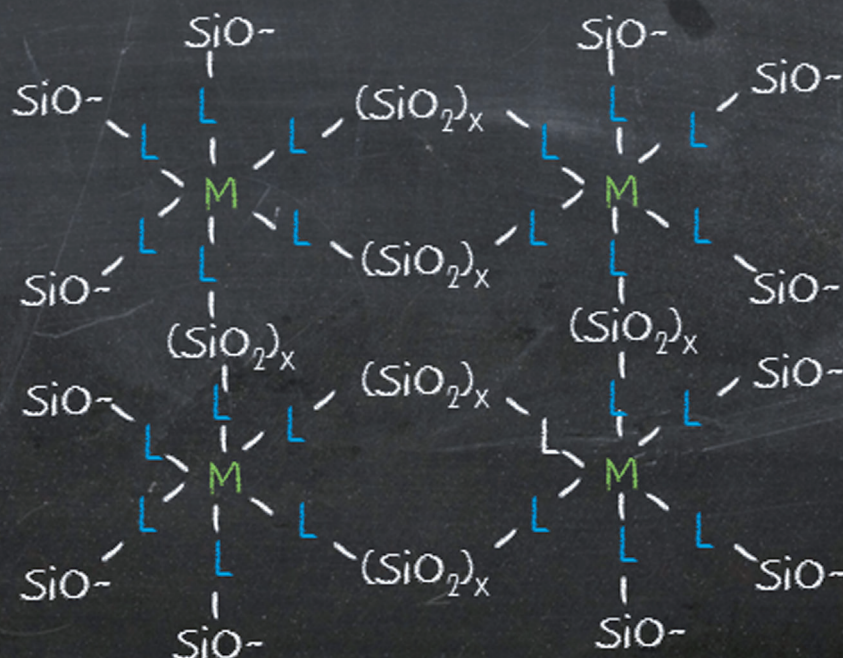


DOI: 10.1002/cctc.201200938

 **Sol-Gel Coordination Chemistry: Building Catalysts from the Bottom-Up**Elena Serrano,^[a] Noemi Linares,^[a] Javier Garcia-Martinez,^{*,[a]} and Jesús. R. Berenguer^{*,[b]}**Sol-Gel Coordination Chemistry****Complex Formation****Hydrolysis and Condensation****Gel
Structure**

The development of synthetic routes for the tailoring of efficient silica-based heterogeneous catalysts functionalized with coordination complexes or metallic nanoparticles has become an important goal in chemistry. Most of these techniques have been based on postsynthetic treatments of preformed silicas. Nevertheless, there is an emerging approach, so-called sol-gel coordination chemistry, based on co-condensation during the sol-gel preparation of the hybrid material of the corresponding complex or nanoparticle modified with terminal trialkoxysilane groups with a silica source (such as tetraethoxysilane) and

in the presence of an adequate surfactant. This method leads to the production of new mesoporous metal complex-silica materials, with the metallic functionality incorporated homogeneously into the structure of the hybrid material, improving the stability of the coordination complex (which is protected by the silica network) and reducing the leaching of the active phase. This technique also offers the actual possibility of functionalizing silica or other metal oxides for a wider range of applications, such as photonics, sensing, and biochemical functions.

1. Introduction

Catalysts play a vital role in improving the quality of life and economic progress of human beings, as more than 90% of the industrial processes, such as petrochemical fertilizers and food industries, are induced catalytically. More than 90% of these catalysts correspond to heterogeneous catalysis,^[1] which are preferred industrially. Nevertheless, most of the catalytic processes engaged in the preparation of bulk and fine chemicals are homogeneous in nature; the major drawback of these homogeneous processes are the difficulty in separating the relatively expensive catalyst from the reaction mixture, its recycling and reuse, and avoiding the possible contamination of the final product. These processes produce a large amount of byproduct waste materials, which are hazardous to the environment.

A general strategy for converting a homogeneous process to a heterogeneous one is to support the soluble catalyst onto large-surface area inorganic carriers.^[2] In this context, conventional sol-gel processes have been used extensively in the preparation of nanostructured porous oxide materials, which serve either as catalysts or as supports for the catalytically active species (nanoparticles, organometallic compounds, enzymes, etc.).^[1b,3a,b]

The *IUPAC Gold Book* defines the sol-gel process as "the process through which a network is formed from solution by a progressive change of liquid precursor(s) into a sol, to a gel, and in most cases finally to a dry network".^[4] Sols are disper-

sions of colloidal particles, that is, solid particles with diameters ranging from 1 to 100 nm. A gel is a rigid, interconnected network with pores of submicrometer dimensions or a polymer network with polymeric chains having average lengths greater than a micrometer.^[5] Thus, a versatile strategy for the synthesis of materials consists in the formation of a solid network starting from a liquid phase, usually a metal alkoxide precursor $M(OR)_n$ ($M = Si, Al, Ti, \text{etc.}$, and $R = (C_xH_{2x+1})$). Once the hydrolysis of the alkoxide starts in the aqueous phase, subsequent polycondensation reactions occur, which increases the viscosity of the solution from a sol to a rigid gel.

However, in the preparation of mixed oxides, the control of composition, homogeneity, and texture is not straightforward. The main problem is found in the disparity of reaction rates of different sol-gel precursors because their reactivity has to be matched to obtain a homogeneous material. In addition, to improve the control of the properties of final materials in conventional sol-gel procedures, several techniques such as spray processing^[3c] or nonhydrolytic sol-gel methods^[3b] have been implemented.

In the case of silica materials, the application of the sol-gel method to grow inorganic solids around supramolecular structures, obtained through the molecular self-assembly of surfactants, led to a new concept in the synthesis of materials and the creation of a new family of mesostructured materials, such as M41S, MSU, and SBA families.^[6]

Several strategies have been developed to incorporate functionality into silica materials for various applications.^[7-10] The chemical functionality has typically been incorporated into these solids through postsynthetic techniques, such as ion exchange, impregnation, precipitation, vapor deposition, and grafting, depending on the functionality to be incorporated.^[11]

The immobilization of homogeneous catalysts through chemical grafting consists in the covalent bonding of the chemical functionality with the silanol groups of the silica surface. Although widely used, this technique has two main drawbacks: a poor control over the geometry and location of the active phase, which is difficult to characterize, and a partial pore blocking.^[8,12] A great effort has been made to improve this technique through the previous chemical modification of the silica surface before the grafting step.^[13,14] Finally, postsynthetic techniques imply more synthetic steps, longer preparation time, higher quantity of reagents, and, subsequently, a higher cost of the final catalyst.

[a] Dr. E. Serrano, Dr. N. Linares,* Dr. J. Garcia-Martinez
Molecular Nanotechnology Lab
Department of Inorganic Chemistry
University of Alicante
Carretera San Vicente s/n, E-03690 Alicante (Spain)
Fax: (+34)965903454
E-mail: j.garcia@ua.es
Homepage: www.ua.es/grupo/nanolab

[b] Dr. J. R. Berenguer
Departamento de Química-Centro de Investigación en Síntesis Química
Universidad de La Rioja
E-26006, Logroño (Spain)
Fax: (+34)941299621
E-mail: jesus.berenguer@unirioja.es

[*] Current address:
Istituto di Chimica dei Composti Organico Metallici
Consiglio Nazionale delle Ricerche
50019 Sesto Fiorentino (Italy)

An emerging approach to the incorporation of chemical functionalities into porous silica materials is based on the in situ incorporation of the functionality during the sol-gel preparation of the material. This approach leads to mesoporous solids with a more homogeneous distribution of the active phase. In addition, embedding functional groups into the silica walls is a new strategy for avoiding agglomeration or leaching and even increasing its stability.^[11] This goal has been partially achieved—not only in silicas but also in other metal oxide materials—through the entrapment of several coordination metal complexes by using sol-gel methods.^[3b, 15]

At present, the most extended applications of the in situ incorporation is the synthesis of periodic mesoporous organosilica (PMO) materials.^[7, 16–17] The co-condensation of organoalkoxysilanes ($R-Si(OR')_3$) with the silica precursor, typically tetrae-

thoxysilane (TEOS), in the presence of surfactants yields porous hybrid organic-inorganic silica materials. In these materials, organic moieties are located preferentially on the surface of the mesoporous support, possibly owing to their occlusion caused in the hydrophobic interior of surfactant micelles.^[17] Recent reviews on amino-functionalized mesoporous silicas pointed out that the direct co-condensation results in a more homogeneous distribution of amino-organic moieties on the silica wall than the postsynthetic grafting approach, in which most amino-organic moieties concentrate near the openings of channels and/or on the external surface.^[7] These organofunctionalized silica materials have been widely used as adsorbents, drug delivery systems, and solid organocatalysts in recent years.

However, although the in situ incorporation methodology on mesoporous materials has been thoroughly studied in the past years, the incorporation of more complex functions, as metal complexes or nanoparticles, during the preparation of the silica material is a less explored field and these methods can be of great benefit to the scientific and industrial community. This contribution aims to provide a critical overview of the various strategies based on these in situ methods to incorporate these kind of metallic functionalities into mesoporous silicas, which leads to the synthesis of the new materials called mesoporous metal complex-silica. This review provides the most relevant contributions by our research group to this field.

Javier Garcia-Martinez is Director of the Molecular Nanotechnology Lab at the University of Alicante, Spain. He has published extensively in the areas of nanomaterials and energy and is the author of more than 25 patents. His latest books are *Nanotechnology for the Energy Challenge* (Wiley, 2010) and *The Chemical Element* (Wiley, 2011). He is a cofounder of Rive Technology, Inc. (Boston, MA), a venture capital-funded Massachusetts Institute of Technology (MIT) spin-off commercializing advanced nanomaterials for energy applications. He has received the Europe Medal in 2005, the Silver Medal of the European Young Chemist Award in 2006, and the TR 35 Award from MIT's *Technology Review* magazine; in 2009, he was selected as a Young Global Leader. Since 2010, he is member of the World Economic Forum Council on Emerging Technologies. He is Fellow of the Royal Society of Chemistry, member of the Global Young Academy and Bureau member of the IUPAC.



Jesús R. Berenguer received his PhD in chemistry from the University of Zaragoza, Spain, in 1994. In 1995, he performed postdoctoral research with Prof. G. Erker's group at the Organic Chemistry Institute of the Westfälische Wilhelms-Universität Münster. Since 2001, he has been Associate Professor of Inorganic Chemistry at the University of La Rioja, Spain, in which he is also responsible for the X-ray diffraction laboratory. He has codirected five doctoral theses and co-authored more than 50 scientific publications. His research interests include the syntheses and study of the reactivity of transition-metal complexes bearing unsaturated groups acting as bridging ligands, the design of molecular and supramolecular systems, their optoelectric properties, and, more recently, the preparation of functionalized mesoporous materials.



2. Sol-Gel Coordination Chemistry: Fundamentals

Sol-gel coordination chemistry is based on the use of a coordination complex with ligands containing terminal trialkoxysilane groups, which can be hydrolyzed with or without the presence of other silica sources, to produce a coordination complex-silica network.^[11]

Using sol-gel coordination chemistry, a wide range of functional materials can be obtained. The hydrolysis and co-condensation of both precursors—the metal complex with terminal trialkoxysilane groups and $Si(OR)_4$ —in the presence of a structure-directing agent lead to a surfactant-templated gel, which enables us to obtain a hybrid mesoporous material after the calcination/extraction of the surfactant (Figure 1 a–c). This methodology enables us to incorporate not only coordination complexes but also a wide range of chemical functionalities such as Pd^0 nanoparticles,^[18] Pd^{2+} complexes in both mesoporous silica^[19] and organosilica materials,^[20] as well as cationic Cu^{2+} and Ni^{2+} metal complexes.^[21] Moreover, we have extended our approach to the incorporation of inorganic clusters^[22] and luminescent metal complexes^[23] into mesoporous MCM-41 and MSU-X silicas. The versatility of the proposed methodology thus enables the synthesis of mesoporous materials by using cationic, neutral, or anionic surfactants. These materials have unique properties because, in addition to cationic or neutral metal complexes, almost any chemical moiety functionalized with terminal alkoxy silanes can be incorporated, as described in the following sections.

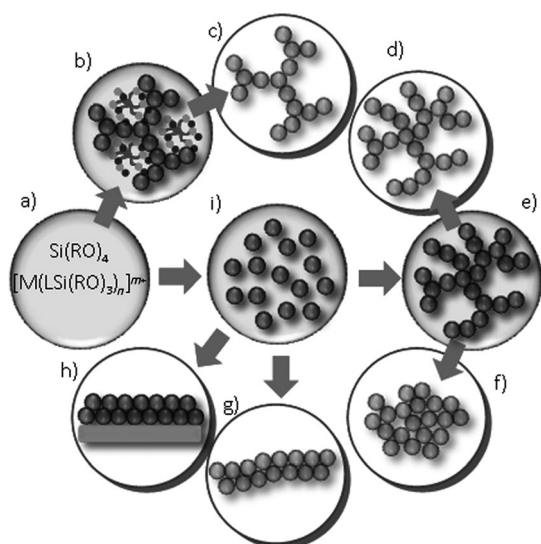


Figure 1. Sol-gel coordination chemistry approach developed for the in situ incorporation of chemical functionalities into the framework of silica and organosilica porous materials.

As illustrated in Figure 1, the sol resulting from the hydrolysis and condensation of precursors (Figure 1 a) without the use of surfactants (Figure 1 i) can be used to obtain films by coating (Figure 1 h), for the synthesis of fibers, spinning (Figure 1 g), or gelification (Figure 1 e). This gel could be dried afterward to obtain a xerogel (Figure 1 f) or an aerogel (Figure 1 d). Xerogels are obtained through evaporation at room temperature, and thus the pore structure and translucency of the sol precursor are lost (Figure 1 f). However, aerogels are usually obtained by using a supercritical fluid extraction process, which enables them to preserve their pore structure and optical translucency (Figure 1 d). These properties make them ideal candidates not only for catalysts but also for the design of chemical sensors and in energy applications, such as solar cells or hydrogen extraction from water.

Following this approach, several silica gels have been obtained. Schubert et al. described the synthesis of two distinct xerogels containing Co^0 and Rh^+ derivatives and the use of these as catalysts in several organic processes,^[24a, b] whereas Baiker's group prepared both xerogels^[24c] and aerogels^[24d] containing phosphine-Ru²⁺ complexes, which were used in the synthesis of *N,N*-diethylformamide from CO_2 , H_2 , and diethylamine. We have also prepared a series of aerogels with TEOS and an Fe^{3+} complex with (3-aminopropyltriethoxysilane) (APTS) as

a ligand. After gelification catalyzed with sodium fluoride at room temperature, samples were dried by using the critical point method and a translucent gel was obtained. The preservation of porosity was confirmed by nitrogen adsorption-desorption isotherms and TEM analysis (Figure 2). Samples showed excellent textural properties, with BET surface areas of approximately $650 \text{ m}^2 \text{ g}^{-1}$ and pore volumes of approximately $1.4\text{--}1.5 \text{ cm}^3 \text{ g}^{-1}$.

3. Coordination Complexes Incorporated into Mesoporous Silica

Coordination complexes, and mainly organometallic derivatives, have been widely used in homogeneous catalysis because of their incomparable catalytic activity and selectivity.^[25] Nevertheless, their use presents severe limitations in practical applications because of their complicated separation procedures from the reaction mixtures as well as difficulties in their recycling, all of which leads to high cost and high metal pollution.^[25] To minimize these problems, the organometallic homogeneous catalysts have also been explored in water medium reactions, which are more environmentally friendly systems.^[26] This is an emerging subject of study that still presents limited efficiencies and difficulties in recycling and reuse.

As mentioned in the Introduction, a widely used approach includes the heterogenization of the homogeneous catalysts. One of the most used strategies is the functionalization of mesoporous silicas by covalent anchoring of organic ligands to a silica preformed support and a subsequent reaction of these fixed species with a metal salt (or an appropriate metallic fragment) to finally obtain the desired metal complex (postsynthetic grafting methods).^[27] This synthetic method presents some disadvantages such as poor dispersion of complexes on the support or difficulty in preparing, controlling, and characterizing certain structures. Moreover, the coordination com-

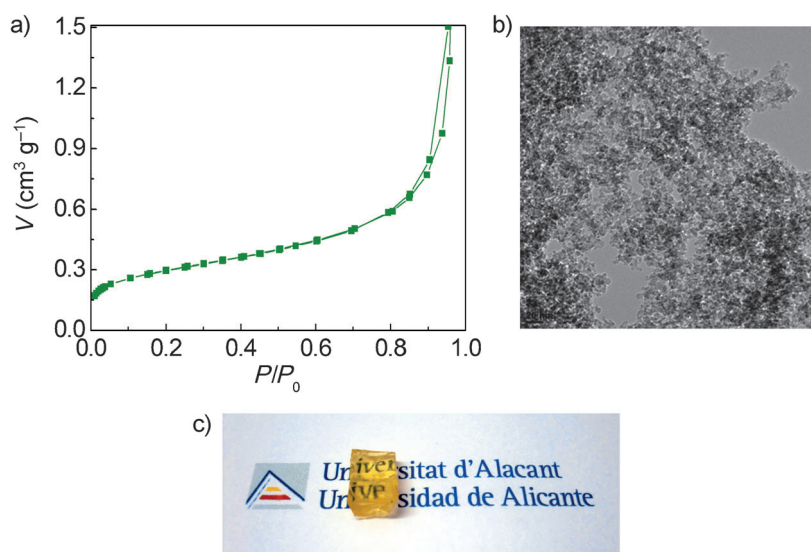


Figure 2. a) Nitrogen adsorption-desorption isotherm and b) TEM image of an aerogel obtained from an Fe^{3+} -APTS complex and TEOS as silica precursors. Scale bar = 20 nm. c) A photograph of the obtained gel showing optical translucency.

pounds are located mainly on the pore surface of the support, which usually results in a decrease in the surface area and accessible pore volume with the consequent decrease in the catalytic properties and the concurrence of agglomeration or leaching of the active sites if the catalyst is used in liquid phase reactions.

An alternative approach to chemical grafting is the formation of PMOs, in which ligands with organic species containing alkoxy-silyl groups react the metallic centers to give the corresponding organometallic species.^[28] This method also solves the low-dispersion problem of the active sites and thus produces more homogeneous materials by avoiding the use of large amounts of organic solvents used typically in the conventional grafting methods. Nevertheless, this synthetic methodology does not solve other problems such as the control of the final structure of the coordination complexes formed or the decrease in the surface area and pore volume.

Most of these problems have recently been overcome with the incorporation of the catalytic metal-coordinated functionalities into the walls of mesoporous silica materials instead of grafting them onto the pore walls. The first step in achieving this goal is the synthesis of the desired organometallic catalyst bearing multiple polycondensable organosiloxane-functionalized ligands, which can be fully structurally characterized at the molecular level. In situ co-condensation of these organosilica complexes with the appropriate source of silicon (such as TEOS, sodium silicate solutions, or other organic species bearing terminal alkoxy-silyl groups) and in the presence of a structure-directing agent yields, as in the case of PMOs, mesoporous metal complex-silica materials. This incorporation of the catalytic sites into the walls of the nanostructured silicas not only produces most homogeneously functionalized materials but also shows improvements in activity and durability owing to the diminished pore blockage and the intensified stability (hydrothermal stability and the stability of the active sites against leaching in catalysis).

Following this synthetic procedure, several hybrid silicas have been obtained with TEOS as a silica source. Most of these materials present similar or better catalytic properties than those of the corresponding homogeneous catalysts, as well as an improved activity compared to the related mesoporous silicas functionalized by using classical postsynthetic grafting methods. Corriu et al. reported a series of SBA-15 silicas con-

taining cyclam complexes with Cu^{2+} and Co^{2+} (Figure 3a), which were obtained through a neutral templating route by use of the structure-directing agent Pluronic F127.^[29] Corma et al. synthesized MCM-41 materials containing vanadyl Schiff base complexes (Figure 3b) or a carbapalladacycle derivative (Figure 3c) through a basic route by use of the surfactant cetyltrimethylammonium bromide (CTAB).^[30] The latter materials showed the catalytic activity toward the cyanosilylation of aldehydes and Suzuki–Miyaura cross-coupling reactions, respectively. In addition, following an acidic route (CTAB as surfactant), Bonneviot's group has described the incorporation of a phosphinorhodium(I) complex (Figure 3d) into SBA-3 and its use in the hydrogenation of alkenes.^[31]

By using a neutral route, Li and co-workers described the synthesis of some mesoporous silica and organosilica materials functionalized with chloride–phosphine coordination complexes of Ru^{2+} , Rh^+ , Pd^{2+} , and Au^+ , which resulted in efficient catalysts via several water medium organic reactions.^[32] This group has also reported the preparation of a bifunctional catalyst for a one-pot two-step cascade reaction, which contains two kinds of phosphine organometallic complexes: Rh^+ and Pd^{2+} derivatives, which are uniformly incorporated into the walls of a PMO.^[33]

Nevertheless, a key aspect of any catalyst is the accessibility of its active sites. It is not clear yet which parameters control metal accessibility required for eventual adsorption or catalytic properties; however, several efforts have already been made in showing, both through the theoretical prediction and experimental evidence,^[34] that the microenvironment of the active sites (thus including electronic state, dispersion, or coordination geometry) plays a key role in their catalytic efficiency and durability.

To date, the syntheses of all these discussed examples of preparation of mesoporous metal complex-silica materials involve thermal steps, which also need the presence of certain amounts of organic cosolvents, such as ethanol or tetrahydrofuran, for the addition of the metal complex. Moreover, most of them are performed in acidic or basic media, and in all cases, the extraction of the surfactant has been performed in refluxing ethanol or ethanolic solutions of HCl. However, all this can present a problem, because a good number of catalytically interesting transition-metal complexes are unstable under these reaction or extraction conditions.

To overcome these difficulties, we have recently reported a new versatile method based on the use of a neutral surfactant (N^{0} route) at room temperature and neutral pH for the incorporation of several neutral Pd^{2+} complexes into the mesoporous MSU-X-type silica framework^[19] and also into organosilicas.^[20] This is an environmentally friendly one-pot method that works under aerobic conditions, in which the use of organic cosolvents is avoided by using the silica source [TEOS or bis-(triethoxysilyl)ethane (BTEE)] as a solvent (Scheme 1).

Thus, [*trans*- PdCl_2L_2] ($\text{L} = \text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OEt})_3$, APTS, 4- $\text{C}_5\text{H}_4\text{N}(\text{CH}_2)_2\text{Si}(\text{OEt})_3$, PETS, $\text{PPh}_2(\text{CH}_2)_2\text{Si}(\text{OEt})_3$, PPETS) complexes were obtained in high yields by reacting [$\text{PdCl}_2(\text{PhCN})_2$] with the corresponding triethoxysilane ligands directly in TEOS, which is fully characterized by elemental and spectroscopic analyses. In

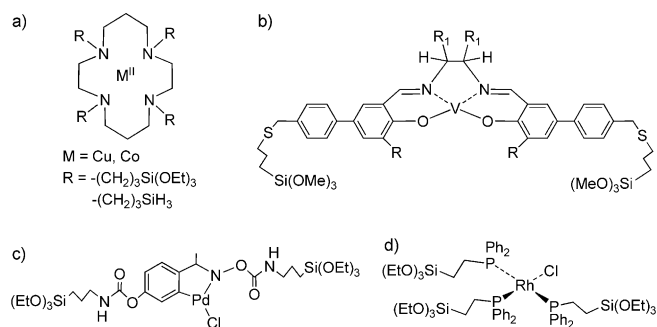
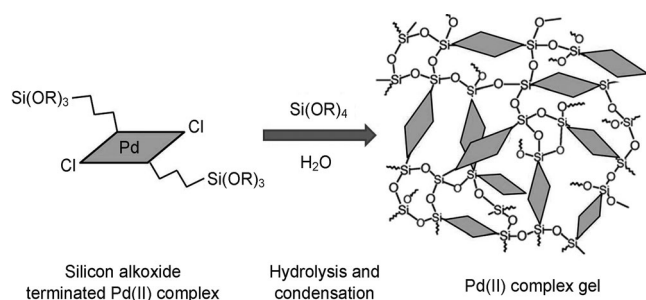


Figure 3. Some of the trialkoxysilane-coordination complexes used in sol-gel processes together with TEOS as a silica source.



Scheme 1. Representation of a Pd complex containing ligands with trialkoxysilane terminal groups (left) and its incorporation into the mesoporous silica framework via the covalent bonding of these terminal trialkoxysilane groups with the silica precursor (right).

addition, monocrystal X-ray diffraction studies were performed for two of them, which confirmed their *trans* configurations (Figure 4).

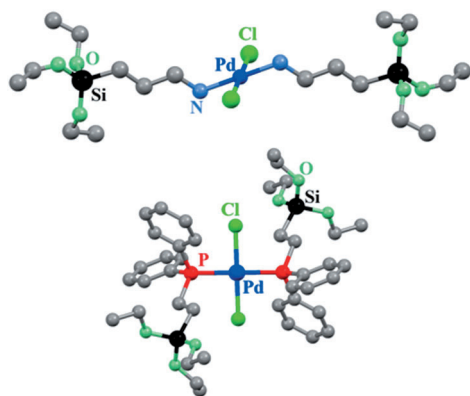


Figure 4. X-ray molecular structure of $[trans-PdCl_2L_2]$ (L = APTS, up; PPETS, down) complexes.

Different functionalized mesoporous silica materials were obtained through in situ co-condensation of these three complexes and TEOS in the presence of a neutral surfactant (Triton X-100) and ammonium fluoride as a condensation inductor after 12 h of stirring at room temperature. Finally, the surfactant was completely removed through ethanol extraction at room temperature for 12 h.^[19] The materials thus obtained had a Pd content up to 0.7 wt% (determined by using inductively coupled plasma optical emission spectrometry). The preservation of Pd^{2+} coordination complexes once in the structure of silica materials was confirmed by using FTIR, Raman, and diffuse reflectance UV/Vis (DRUV) spectroscopies (Figure 5) even in the case of the primary amine,

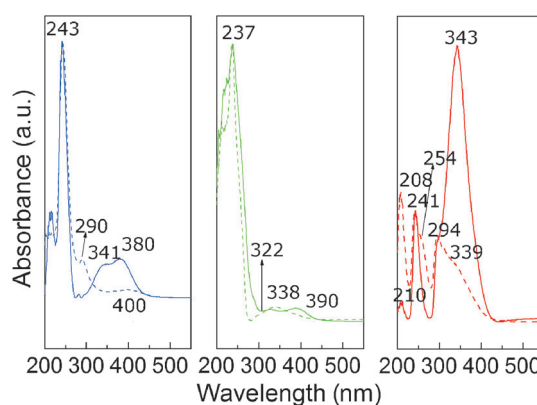


Figure 5. DRUV spectra of the hybrid Pd complex mesoporous silicas (solid lines) in comparison with those of $[trans-PdCl_2L_2]$ (dotted lines: L = APTS in blue, PETS in green, PPETS in red) complexes.

which was the weaker ligand chosen to coordinate to Pd^{2+} centers, mainly owing to the mild conditions used in this synthetic method.

All hybrid Pd–silica materials show bimodal porosity with small (3.5 nm) mesopores and large interparticle mesopores/macropores. This feature was observed by using nitrogen adsorption–desorption isotherm and TEM (Figure 6). Compared to the complex-free materials, the BET surface area is not affected ($\approx 700 \text{ m}^2 \text{ g}^{-1}$) by the incorporation of these complexes. Pd^0 nanoparticles were not observed by using TEM, which indicates that Pd^{2+} is atomically dispersed and no agglomeration occurs during the synthesis and extraction steps.

The materials containing the pyridine and phosphine complexes are efficient catalysts in the Suzuki–Miyaura coupling reaction of solid phenylboronic acid with liquid or solid aryl bromides in solvent-free conditions and at room temperature (Table 1). The reaction with solid 4'-bromoacetophenone under mechanochemical conditions (ball milling) gives conversion values up to 78% for the mesoporous Pd^{2+} pyridine silica material and 65% for the phosphine ligand, with a high reproducibility in both cases, which is always an important goal in solid-state reactions.^[19]

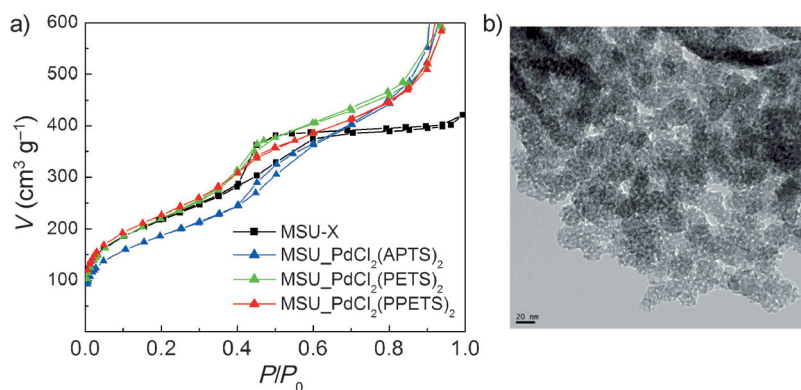


Figure 6. a) Selected nitrogen adsorption–desorption isotherms of hybrid Pd^{2+} complex-mesoporous silica materials. b) TEM image of $MSU_PdCl_2(APTS)_2$. Scale bar = 20.

Table 1. Suzuki–Miyaura coupling reaction of phenylboronic acid with 4'-bromoacetophenone at room temperature by using Pd²⁺ complexes containing MSU material catalysts.^[a]

Complex incorporated	Pd [mol %]	PhB(OH) ₂ [equiv.]	K ₂ CO ₃ [equiv.]	Stirring ^[a]	t [h]	Conversion [%]
Pd ²⁺ –pyridine complex	0.1	1.5	2	mag.	16	8
	0.5	1.5	2	mech.	1.5	50
	0.5	2.0	3	mech.	4.5	75
Pd ²⁺ –phosphine complex	0.1	1.5	2	mag.	16	–
	0.25	2.0	3	mech.	1.5	42
	0.25	1.3	2	mech.	7.0	65

[a] mag. = Magnetic agitation; mech. = mechanochemical agitation.

The excellent catalytic activity, even under challenging diffusion conditions, confirms the excellent accessibility of metal complexes in the walls of mesoporous materials.

Despite the difficulty inherent in the synthesis of PMOs through the neutral route at room temperature^[35] and because Pd²⁺ pyridine and Pd²⁺ phosphine complexes [*trans*-PdCl₂L₂] (L = 4-C₅H₄N-(CH₂)₂Si(OEt)₃ PETS, PPh₂(CH₂)₂Si(OEt)₃ PPETS) can also be synthesized with the organosilica source BTEE as a solvent, we decided to extend this procedure to the synthesis of hybrid organosilica materials.^[20]

In a way similar to that described previously for the MSU-X materials, the in situ co-condensation of solutions of both the Pd²⁺ complexes in BTEE in the presence of a neutral surfactant and NH₄F produced several hybrid Pd²⁺ complexes-organosilica materials. In addition, the surfactant extraction was performed in ethanol at room temperature. A systematic study of the effect of several reaction parameters on the formation of these materials was also conducted. The reaction parameters were the neutral surfactant (Triton X-100 or Brij-56) and reaction temperature (25 or 45 °C; higher temperatures were not studied because of the observation of Pd⁰ agglomeration in the reaction media), different molar ratio of reagents, or the prehydrolysis of inorganic precursors (12 h) before the addition of the fluoride. This study showed that tuning the synthetic conditions induced dramatic changes in the textural properties of the obtained materials. For instance, reactions at higher temperatures yielded larger mesopore sizes, and a poorer porogene has been observed for Brij-56 at room temperature, but not at 45 °C.

Pd contents of 0.75–0.85 or 0.50–0.60 wt% determined by using inductively coupled plasma optical emission spectrometry were observed for the materials containing pyridine or phosphine complexes, respectively. All materials show type IV isotherms and, except prehydrolyzed materials, also present bimodal porosity with a continuous organization built from irregular mesoporous nanoparticles of smaller size compared to those observed for the related complex-free organosilica (≈200 nm). The average size of the nanoparticles ranges from

30 to 100 nm depending on the reaction conditions; the interparticle volume of the material is higher if the nanoparticles are smaller and more irregular.

On the contrary, the prehydrolyzed materials have monomodal mesoporosity with a narrow mesoporous size distribution (Figure 7).

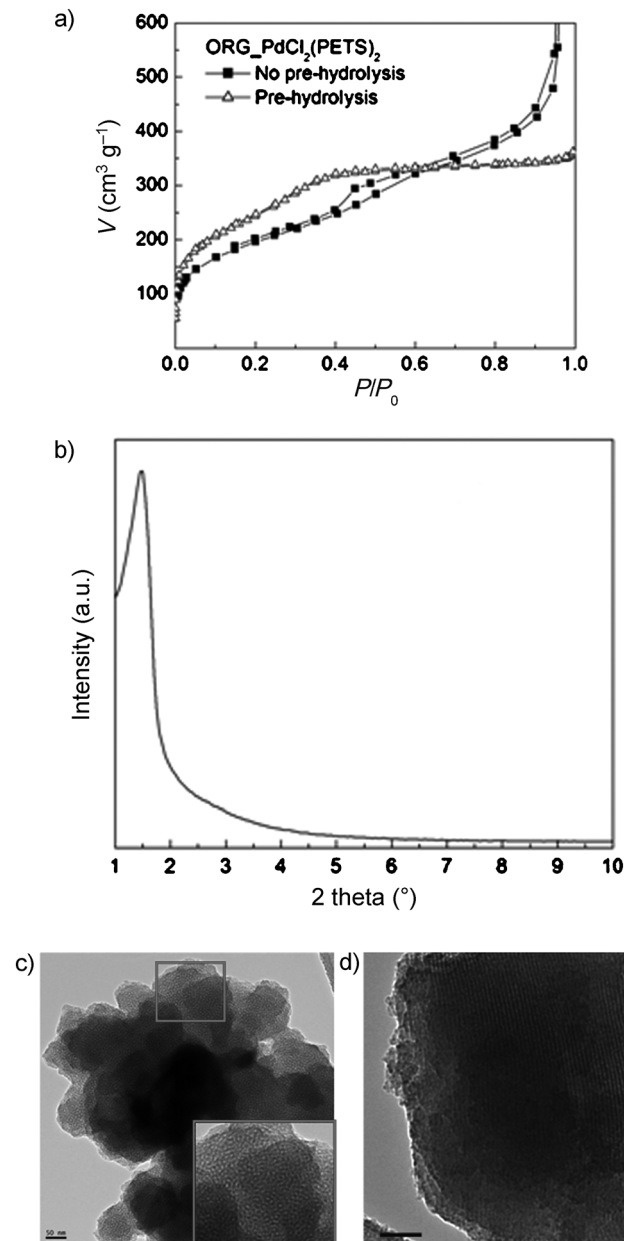


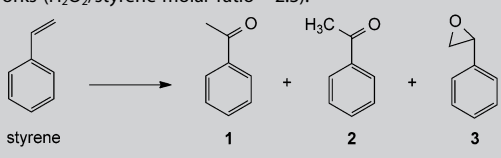
Figure 7. a) Nitrogen adsorption–desorption isotherms of the hybrid organosilica sample containing Pd²⁺–pyridine complex prepared with and without the prehydrolysis treatment. b) XRD spectra for the prehydrolyzed sample containing Pd²⁺–pyridine complex. TEM images for c) the complex-free organosilica (scale bar = 20 nm) and d) the prehydrolyzed sample containing Pd²⁺–pyridine complex (scale bar = 20 nm).

As expected, the mesoporous materials prepared through the prehydrolysis route do not present XRD spectra of ordered hexagonal mesoporous materials (Figure 7), but TEM studies

showed the presence of hexagonally ordered particles in these materials (Figure 7c). Thus, higher mixing and reaction times improve the interaction between BTEE and the nonionic surfactant (N^{0} assembly) to give a better structuration, narrower pore distribution, and higher BET surface areas.

These hybrid organosilica materials were tested in the catalytic oxidation of styrene with H_2O_2 (Table 2). The studies show the accessibility of the substrate to Pd^{2+} active sites and high activity (71% for the pyridine complex and 89% for the phos-

Table 2. Catalytic oxidation of styrene with H_2O_2 in the presence of hybrid silica and organosilica materials with Pd^{2+} complexes in their frameworks (H_2O_2 /styrene molar ratio = 2.3).^[a]



Catalyst	Pd ^[a] [mol%]	Solvent	T [°C]	t [h]	TOF [h ⁻¹]	Selectivity [%]			
						1	2	3	Other
org_Pd ²⁺ pyridine	0.1	–	80	6	118	8	20	–	72
	0.4	MeCN	80	6	4.4	84	4	12	–
MSU_Pd ²⁺ pyridine	0.2	–	80	4	68	24	66	–	32
	0.5	MeCN	80	10	3	89	1	10	–
org_Pd ²⁺ phosphine	0.1	–	65	6	148	5	24	–	71
	0.25	MeCN	65	6	11	65	28	7	–
MSU_Pd ²⁺ phosphine	0.5	MeCN	80	10	4	65	30	5	–

[a] Oxidation reaction of styrene with H_2O_2 and the possible products.

phine complex); however, low selectivity was observed under solvent-free conditions (>70% of byproducts). Comparatively, under similar reaction conditions, the use of acetonitrile as solvent affords low activity ($\approx 20\%$) but high selectivity toward the formation of the benzaldehyde product (>80% for the pyridine ligand and 65% for the phosphine ligand).

The incorporation of the organic moiety into the Pd^{2+} -containing mesoporous silica increases its hydrophobic character, which enhances the diffusivity of the reactants and therefore the catalytic activity. For example, with the Pd^{2+} -pyridine-containing catalyst, under solvent-free conditions the activity increases from a turnover frequency (TOF) of 68 to 118 h^{-1} if the organic moiety is incorporated, whereas if the solvent (acetonitrile) is used, conversion increases from 3 to 4.4 h^{-1} even with lower Pd contents. If the Pd^{2+} -phosphine-containing catalyst is used, a similar trend is observed.

Incorporation of cationic complexes through the anionic surfactant templating route

The proposed method of incorporation of metal complexes into the mesoporous silica framework through the co-condensation of ligands with the silica precursor is not limited to the neutral or cationic surfactant templating route.

In 2003, Tatsumi et al. reported the synthesis of unique anionic surfactant templated mesoporous silicas by use of anionic surfactants.^[36] El Hankari et al. synthesized hybrid silica materials containing ionic groups by use of an anionic surfactant via the ionic interaction of the surfactant and the hybrid silica precursor.^[38] Many metal complexes are cationic, and thus, the incorporation of these complexes through this $S^-N^+I^-$ route (S^- : anionic surfactant; N^+ : cationic amino group; I^- : inorganic precursor), in which the ligands of the complexes contain the amino groups, seems plausible.

Inspired by these studies, we have recently reported the synthesis of metal-complex ionosilicas with cationic complexes incorporated into the mesoporous silica framework, which were prepared by use of anionic surfactants [sodium dodecyl sulfate (SDS) and sodium dodecanoate (SD)].^[21] In our case, however, the N^+I^- interaction is not an electrostatic interaction but a covalent linkage, because the amino ligands contain trialkoxysilanes as terminal groups for the co-condensation with the TEOS precursor, which thus ensures effective metal complex interaction (see Scheme 1). In this synthetic procedure, the metal precursor, the amino ligands (APTS), the TEOS, and the surfactant (SDS or SD) are added together to a mixture of water and ethanol and reacted at 60°C for 24 h, which makes this procedure a simple and environmentally friendly one-pot method. Finally, the surfactant was removed by using the ion-exchange process, which preserves its complex structure.

This anionic synthetic route leads to disordered hybrid mesoporous materials with homogeneous complex incorporation and very high metal contents (up to 4.8 wt% Ni^{2+} and 8.6 wt% Cu^{2+}) and the metal complex incorporation yield is approximately 90%. The DRUV and FTIR spectra of hybrid materials compared with those of metal complexes confirmed that the surfactant extraction method preserves the complex structure during the whole process. The Cu^{2+} complex incorporated into the silica material maintained the square planar structure, with no apparent substitution of the APTS ligand by water molecules (Figure 8a). In the hybrid materials with Ni^{2+} complexes, the hexagonal structure is retained; however, the substitution of a portion of amine ligands by water molecules yields $[Ni(H_2O)_{6-x}(APTS)_x]^{2+}$ (Figure 8b). All hybrid materials showed type IV isotherms, typical of mesoporous solids, with good textural properties (BET area values of $300\text{--}400\text{ m}^2\text{g}^{-1}$) and a narrow pore size distribution (Figure 8c).^[21]

Another interesting step of this strategy is the synthesis of a new family of hybrid mesoporous materials through the self-condensation of amino groups of the ligands in the metal complexes and then precipitation without using a silica precursor, that is, solids from only metal complexes. Following this approach, we synthesized mesoporous complex materials of $[M(NH_2(CH_2)_3SiO_{3/2})_n]_{mA}$ stoichiometry ($M=Ni^{2+}$ and $A=\text{counteranion surfactant}$).^[21] In those materials, the flexible and large length of the aliphatic chain in the APTS ligand led to a collapse of the structure during the surfactant extraction and, thus, other ligands should be tested for this purpose.

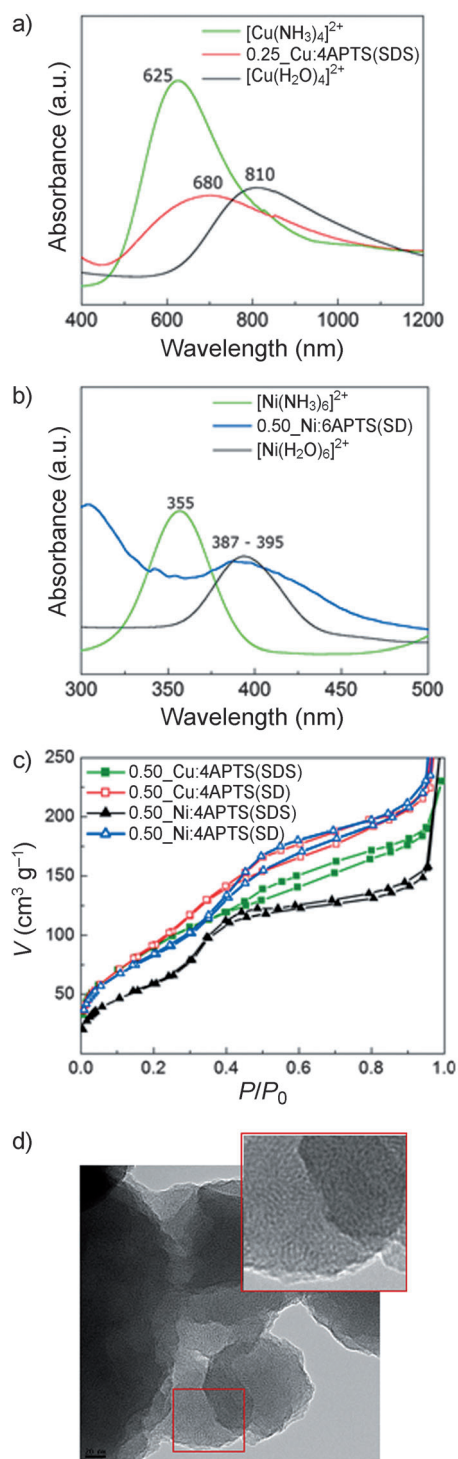


Figure 8. a, b) DRUV spectra and c) nitrogen adsorption-desorption isotherms at 77 K of hybrid materials prepared with APTS/TEOS molar ratios of 0.25 and 0.5 and with both SDS and SD surfactants. DRUV spectra for neat $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{M}(\text{NH}_3)_6]^{2+}$ complexes have been included for comparison. d) Representative TEM image of the 0.50_Ni:4APTS(SDS) sample. Scale bar = 20 nm.

4. Metal Clusters Incorporated into Mesoporous Silica

This synthetic in situ approach can be extended effectively to larger and more complicated structures, and thus we have recently reported the incorporation of an incomplete cubane-type Mo_3S_4 molybdenum cluster into the mesoporous silica framework.^[22]

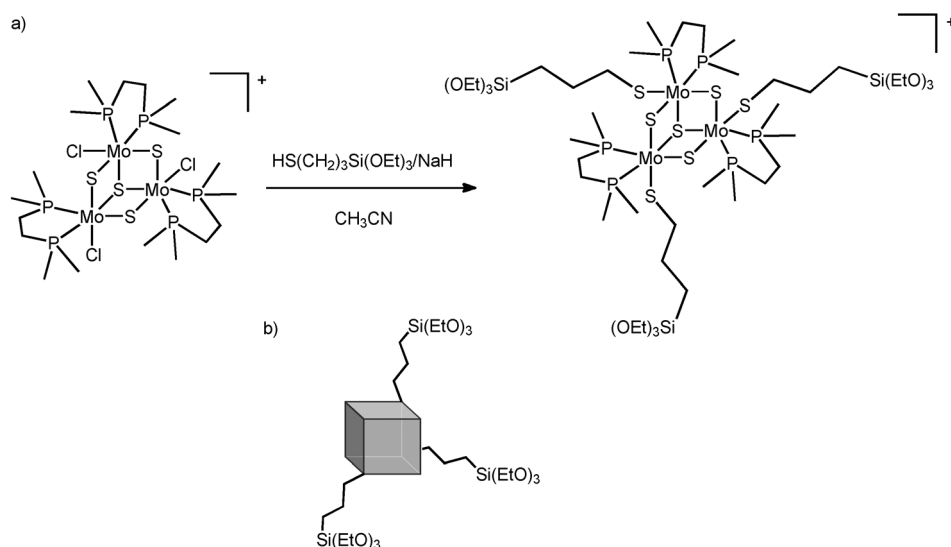
Mononuclear molybdenum complexes are typically immobilized onto mesoporous MCM-41-type silica by using grafting methods to be used as heterogeneous catalysts in organic reactions, such as hydrogenation of aromatic compounds, dehydrogenation of methanol, and epoxidation of olefins.^[38]

The immobilization of polymolybdenum complexes containing metal-metal bonds onto mesoporous silica structures increases the efficiency of these transformations considerably; however, it is limited to a few references.^[39,40] For example, dimolybdenum(II,II) complexes have been grafted to MCM-41- and FSM-16-type silica materials. These materials resulted in active catalysts for the polymerization of cyclopentadiene and propene metathesis, respectively.^[39,40] Trinuclear molybdenum cluster chalcogenides have also been incorporated into porous supports. Weber et al. supported $[\text{Mo}_3\text{S}_{13}]^{2-}$ cluster anions on γ -alumina and amorphous silica for hydrodesulfurization reactions.^[41a] Herbst et al. prepared alumina-supported bimetallic catalysts through the impregnation of γ -alumina with bimetallic $\text{Mo}_3\text{S}_4\text{M}'$ cluster cores ($\text{M}' = \text{Ru}, \text{Rh}, \text{Ir}, \text{Pd}, \text{Pt}$).^[41b] In both the cases, the cube-type clusters have been used as precursors of amorphous or microcrystalline MoS_2 after thermal decomposition, which thus lose their identity.^[41]

Our group has obtained a new molybdenum siloxo cluster of $[\text{Mo}_3\text{S}_4(\text{dmpe})_3(\text{MPTES})_3]\text{PF}_6$ ($\text{dmpe} = 1,2$ -bis(dimethylphosphino)ethane; $\text{MPTES} = (3\text{-mercaptopropyl})\text{triethoxysilane}$) that has been used as a building block for the bottom-up synthesis of a cubane-mesoporous silica hybrid (Scheme 2).^[22] The MPTES group enables the co-condensation of the metal cluster with the silica precursor (TEOS) in the presence of CTAB, which leads to the in situ incorporation of this functionality into the mesoporous silica framework (Figure 9, right). As far as we know, it has been the first time that this approach was used for the incorporation of a metal cluster into a mesoporous silica framework. For comparison, the molybdenum siloxo cluster was also immobilized via covalent attachment on the surface of a previously synthesized mesoporous silica MCM-41 (Figure 9, left).

The covalent linkage of the terminal trialkoxysilane groups of the cluster with the MCM-41 surface, in the case of grafting materials, or with TEOS, in the incorporation approach, was corroborated by using ²⁹Si NMR spectroscopy (Figure 10, up left), whereas the integrity of the cluster after its incorporation was confirmed by ³¹P NMR and DRUV analysis.^[22]

This synthetic strategy led to disordered mesoporous materials owing to the use of methanol as a cosolvent during the co-condensation procedure (Figure 10d), whereas the grafted materials maintained the hexagonal order of the MCM-41 mesoporous material as confirmed by using TEM (Figure 10c) and XRD analysis. Both materials showed nitrogen adsorption-de-



Scheme 2. a) The synthesis of molybdenum siloxo cluster of formula $[\text{Mo}_3\text{S}_4(\text{dmpe})_3(\text{MPTES})_3]\text{PF}_6$ ($\text{dmpe} = 1,2$ -bis-dimethylphosphinoethane; $\text{MPTES} = (3\text{-mercaptopropyl})\text{triethoxysilane}$). b) Representation of the molybdenum siloxo cluster product.

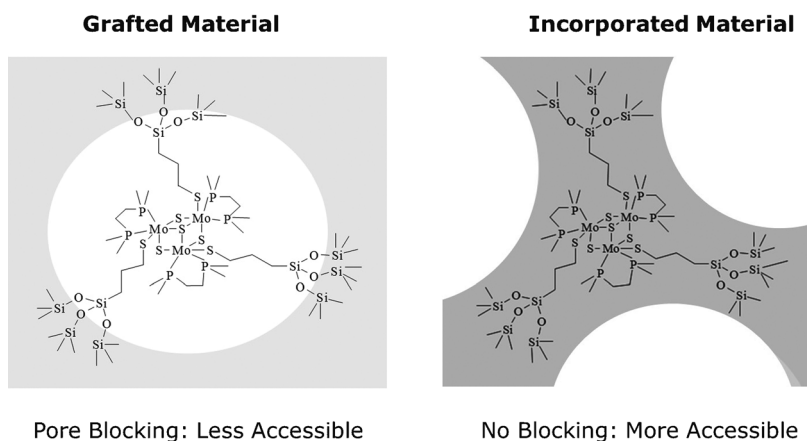


Figure 9. Representation of the molybdenum siloxo cluster grafted to the preexisting support in comparison to the in situ incorporation approach during the mesoporous silica synthesis.

sorption isotherms typical of mesoporous silica materials with a narrow pore size distribution (Figure 10b). The values of textural properties of the grafted materials decrease as the cluster content increases; that is, the BET surface area values decrease from $940 \text{ m}^2 \text{ g}^{-1}$ for neat MCM-41 to $650 \text{ m}^2 \text{ g}^{-1}$ for the hybrid sample with 1.5 wt% Mo/SiO_2 and the pore volume decreases from 0.9 to $0.5 \text{ cm}^3 \text{ g}^{-1}$. Interestingly, the in situ approach yielded hybrid materials, with the textural properties of the matrix remaining unaltered: typically the BET surface area was $750 \text{ m}^2 \text{ g}^{-1}$ and pore volume $0.65 \text{ cm}^3 \text{ g}^{-1}$.

Cubane-type Mo_3CuS_4 clusters are active in cyclopropanation reactions. Thus, preliminary studies of the reactivity of our hybrid materials synthesized by the in situ approach to capture copper(I) as the second metal were performed. DRUV analysis revealed the copper coordination to the metalloligand that produces the Mo_3CuS_4 species, which is reflected by the color change from pink (Mo_3S_4) to purple (Mo_3CuS_4).^[22] The ability of

the trinuclear cluster to incorporate a second metal opens a new way to the synthesis of heterogeneous catalysts.

5. Metal Nanoparticles Incorporated into Mesoporous Silica

We have extended our synthetic sol-gel approach to the incorporation of metal nanoparticles (MNPs) into mesoporous silica. The immobilization of MNPs onto porous materials is a widely used technique to prepare heterogeneous catalysts^[42–47] because it enables us to overcome the main drawbacks associated with the use of the catalysts, such as agglomeration and difficulty in handling, recovering, and recycling.^[42]

The immobilization of MNPs has been performed classically with preexisting supports by using a postsynthetic method. A large number of mesoporous inorganic oxides have been used for this purpose, mainly with uniform and controlled porosity and different porous arrays (hexagonal,^[43] cubic,^[44,45] wormhole,^[46] bimodal,^[47] etc.). Various MNPs have been immobilized onto these supports by using conventional postsynthetic methods, such as impregnation/reduction, ion exchange, grafting, and chemical vapor deposition.^[43–47] These methods often lead to materials with a weak interaction between MNPs and the support, which results in poor dispersion in the material, especially if the MNP size is similar to or larger than the pore size of the support. Moreover, even if such MNPs are homogeneously loaded onto the pores, the weak interaction with the support can cause their agglomeration and leaching under reaction conditions.

In recent times, a new trend for the immobilization of nanoparticles has emerged as a superior way to incorporate nanoparticles during the synthesis of the mesoporous material. For this purpose, two approaches can be used: 1) the in situ incorporation of the metal precursor during the synthesis of the mesoporous material and 2) the preparation of MNPs in a colloidal suspension and their subsequent addition during the synthesis of the mesoporous material, usually as functionalized nanoparticles.

For this purpose, two approaches can be used: 1) the in situ incorporation of the metal precursor during the synthesis of the mesoporous material and 2) the preparation of MNPs in a colloidal suspension and their subsequent addition during the synthesis of the mesoporous material, usually as functionalized nanoparticles.

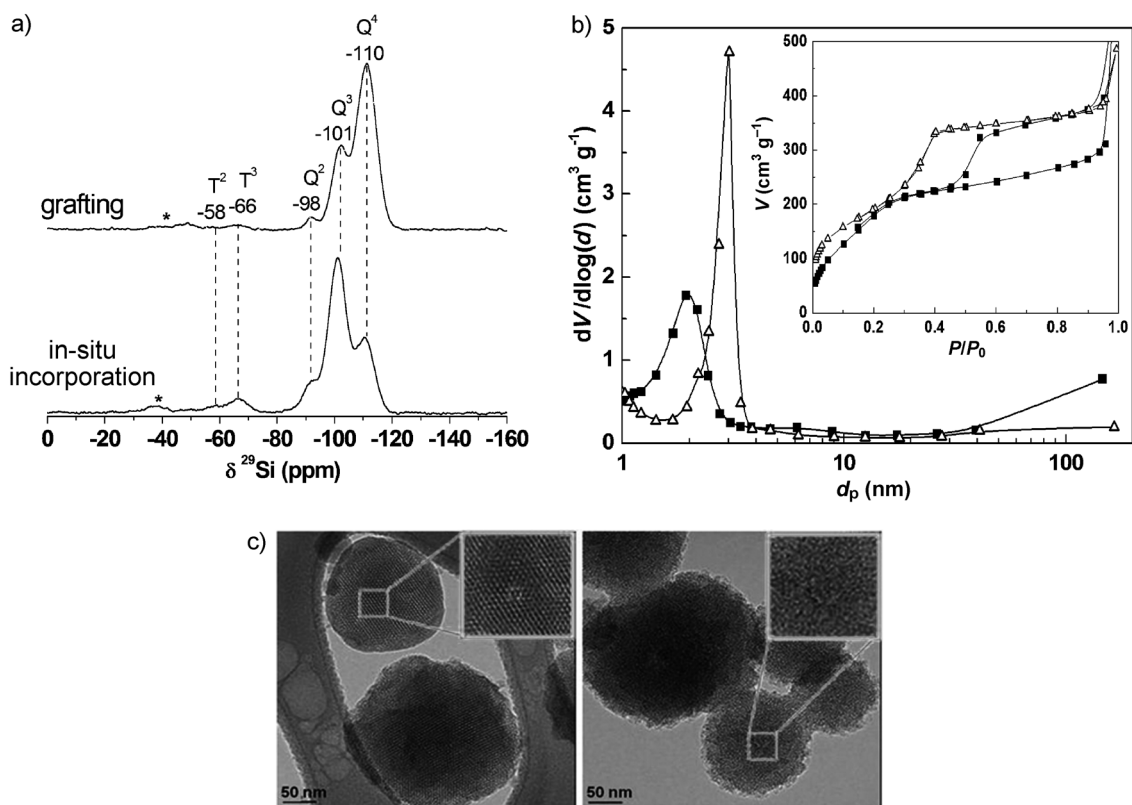
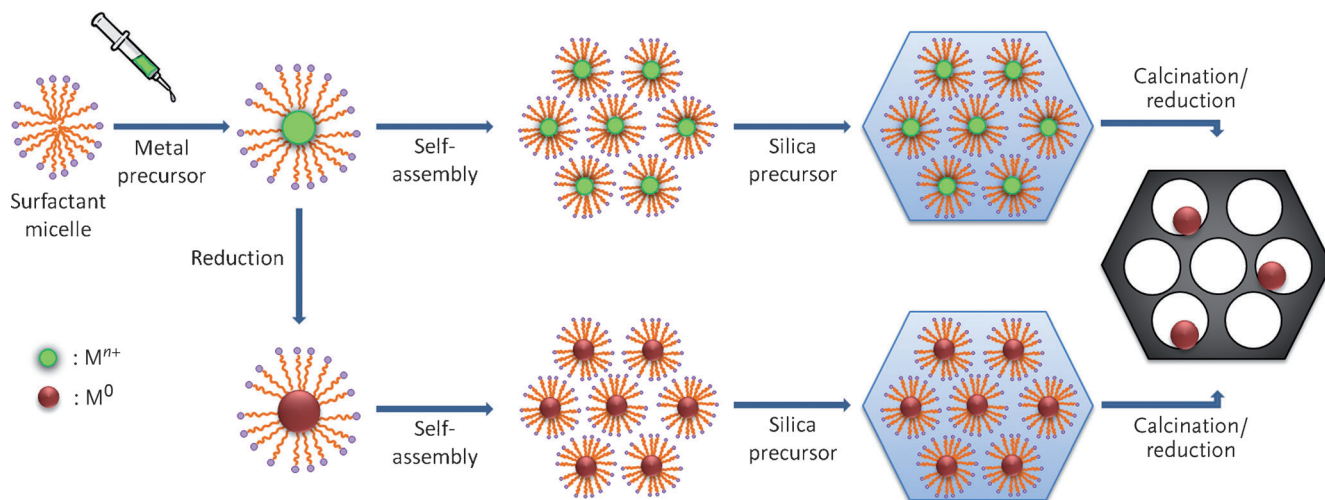


Figure 10. a) ^{29}Si cross-polarization magic angle spinning NMR spectra and b) pore size distribution calculated from the adsorption branch of nitrogen adsorption–desorption isotherms at 77 K by using the BJH method of the hybrid cubane–mesoporous silica samples prepared through grafting (Δ) and in situ approach (\blacksquare) with 1 wt% Mo/SiO $_2$ (d_0 = pore diameter). The inset shows corresponding nitrogen adsorption–desorption isotherms at 77 K. c) TEM images correspond to samples prepared through grafting (left) and in situ approach (right) with 1 wt% Mo/SiO $_2$.

In the past years, one of the most used in situ approaches is the one that incorporates the metal precursor during the synthesis of the material (Scheme 3). MNPs are located in the mesopores of the material, and they are formed during the calcination of the material (Scheme 3, top)^[48–61] or before the addition of the silica precursor (Scheme 3, bottom).^[62,63] In the latter

case, the surfactant acts both as a capping agent of the nanoparticles and as a template for the mesoporous material.

In this context, Kibombo and Koodali recently published a study in which Pt nanoparticles were immobilized onto mesoporous TiO $_2$ –SiO $_2$ mixed oxide materials by using three methods:^[63] the above-mentioned in situ approaches—reducing the



Scheme 3. Simultaneous immobilization of the mesoporous nanoparticles during the synthesis of mesoporous silica by using the self-assembly approach.

Pt precursor before the formation of the mesoporous material or after the calcination step—and a typical impregnation/reduction method. These three methods were used for the photocatalytic degradation of phenol under solar simulated conditions. Despite the best textural properties showed for the in situ prepared catalysts, the photocatalytic degradation of phenol was found to be independent of the crystallite size of Pt regardless of the synthesis method used. This result owes to the deposition of MNPs onto the external material surface.

The new strategy proposed by our group (among others) is the incorporation of the nanoparticles into the internal structure of the support, which are totally or partially trapped in the walls of nanostructured materials^[64–69]; this can, in theory, reduce the agglomeration and leaching of nanoparticles while maintaining the accessibility of reactants. This alternative strategy is based on the synthesis of colloidal nanoparticles and their subsequent functionalization, which enables the appropriate interaction between the functional groups of MNPs and the silica precursor (typically TEOS) during the formation of the mesoporous silica^[65–70]; in this way, MNPs are incorporated into the silica framework. Moreover, this method has other advantages, such as the use of colloidal dispersions with excellent size and shape control.^[64] Numerous methods have been described for the synthesis of colloidal nanoparticles that lead, in some cases, to monodispersed solutions, in which the average particle size can be controlled easily.^[18] Once incorporated into the mesoporous material, the final catalyst retains the monodispersity and the controlled size of the initial colloidal nanoparticles.

By using this approach, in 2005, Corma and co-workers reported the synthesis and use of *N*-[3-(triethoxysilyl)propyl]O-2-(dicetylmethylammonium)ethyl urethane as a ligand stabilizer for MNPs.^[65,66] This molecule was used as a functionalizing agent; the Au NPs interact with the quaternary ammonium ions; and the triethoxysilyl group co-condensates with the silica precursor during the formation of the material. The formed solid demonstrated a high catalytic activity for the solvent-free aerobic oxidation of alcohols to carbonyl compounds in the absence of a base, which are unstable in aqueous media.^[65]

These preliminary results led the same group to publish two subsequent reports based on a similar approach.^[67] A mixture of 1-dodecanethiol and (3-mercaptopropyl)trimethoxysilane was used in both the cases to stabilize Au^[67a] and Pd nanoparticles.^[67b] The co-condensation of silanols present in the MPTS ligands with TEOS enabled the preparation of an “open” sponge-like silica material with accessible MNP embedded into it, as confirmed by the catalytic performance of these materials. The Au-based catalyst was used for the catalytic oxidation of CO, whereas the Pd catalyst performed the Suzuki–Miyaura coupling of electron-rich aryl bromides; both the cases demonstrate a very high reaction rate. In the case of the Au–silica material, the activity was superior to that of similar silica catalysts prepared by using traditional methods and was comparable to that obtained for Au–TiO₂ catalysts.^[67a] However, despite the high turnover numbers showed for the Pd catalyst, which were comparable to the reported values for the most active homo-

geneous phosphine–Pd catalysts, leaching tests performed during this work revealed that the activity could be partially attributed to the leaching of Pd species from the solid catalyst.^[67b]

Following a similar in situ approach, our group incorporated Pd nanoparticles into the framework of well-ordered MCM-41-type silica materials.^[18b] The synthesis of Pd colloids was performed by using a modified Brust method.^[18a,68] By tuning the synthetic conditions, monodispersed Pd MNPs with a narrow particle size distribution and particle sizes between 1 and 3.5 nm were obtained (Figure 11). In this case, the preparation

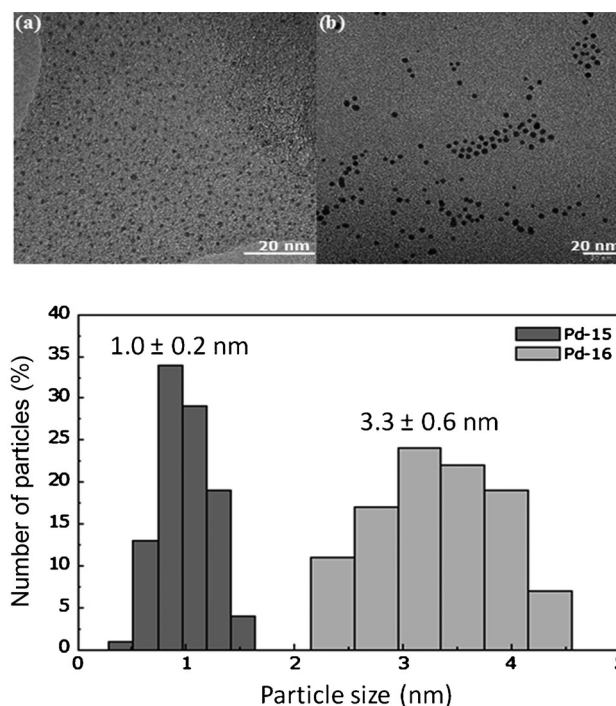


Figure 11. TEM images of colloidal solutions of Pd nanoparticles with different average sizes and their corresponding size distribution.

was performed in toluene, but the colloids can be easily transferred to water without any significant change in particle size, distribution, or stability.

The aqueous suspension of Pd nanoparticles was then functionalized by following two pathways (see Figure 12):

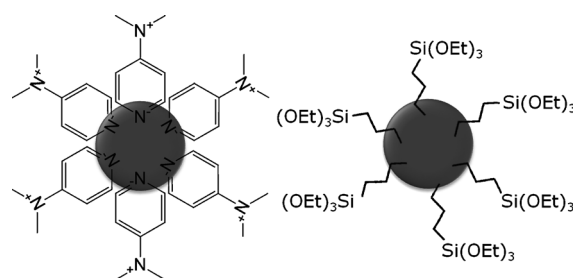


Figure 12. Functionalized nanoparticles with DMAP (left) and MPTES (right).

1) With cationic groups that induce the formation of silica around them by using an $M^{+}I^{-}$ mechanism, which is similar to that proposed for the synthesis of mesostructured materials with cationic surfactants ($S^{+}I^{-}$). In this case, 4-dimethylamino-pyridine (DMAP; used as a transfer agent during the MNP synthesis) provides the Pd nanoparticle with a cationic shell composed of quaternary amines, which is similar to that of the cationic surfactant CTAB used as a template in the synthesis of MCM-41 silica materials.

2) By covalent binding of Pd nanoparticles with the thiol-terminal triethoxysilane (MPTES), which permits the subsequent co-condensation of nanoparticles with the silica precursor during the support formation.

The combined use of these functionalized nanoparticles with the CTAB surfactant thus produced ordered materials with a typical MCM-41-type silica structure, high surface areas ($\approx 1000 \text{ m}^2 \text{ g}^{-1}$), and highly dispersed MNPs into their structure (Figure 13). After the calcination of these materials at 550°C , a slight particle growth was observed, which was clearly dependent on the quantity of Pd in the final material and the temperature during the synthesis. Despite this, small nanoparticles (an average size of ≈ 3.0 and 3.8 nm for MPTES and DMAP, respectively) could be observed for the 1 wt% Pd on MCM-41 after calcination at 550°C .

The catalytic performance of these materials was tested in cyclooctene hydrogenation and Heck C–C coupling reactions. For comparison purposes, catalysts with similar textural and structural properties were prepared through incipient wetness impregnation and subsequent reduction. Regarding the hydrogenation reaction, our in situ prepared materials showed TOFs 7 times greater than those of the more conventionally prepared catalysts. Owing to the difficulty in controlling the particle growth in the impregnation/reduction method, it was impossible to prepare catalysts with the same particle size than our embedded materials. As the hydrogenation of cycloalkenes is a structure-sensitive reaction,^[70] the different particle sizes and distributions of the catalysts account for their different behavior. For this reason, we decided to perform a non-structure-sensitive reaction and chose the Heck coupling between iodobenzene and styrene. In this case, our catalyst showed 4 times greater TOF values than those of materials prepared by using the impregnation/reduction method. Moreover, leaching Pd tests for both catalysts (embedded vs. impregnated) during the Heck reaction resulted in 3 times less Pd in the solution for the Pd-embedded materials than for the Pd-impregnated materials.

6. Beyond Catalysis: Luminescent Hybrid Mesoporous Materials

As discussed before, functionalized mesoporous silica materials have been studied extensively because of their interesting physicochemical properties for catalytic applications. Nevertheless, these are not the only opportunities that these materials present. In the past few years, they have also been used in applications such as nanocomposite design, recognition and selection, sensing, or biochemical functions.^[11,71] In this sense, lu-

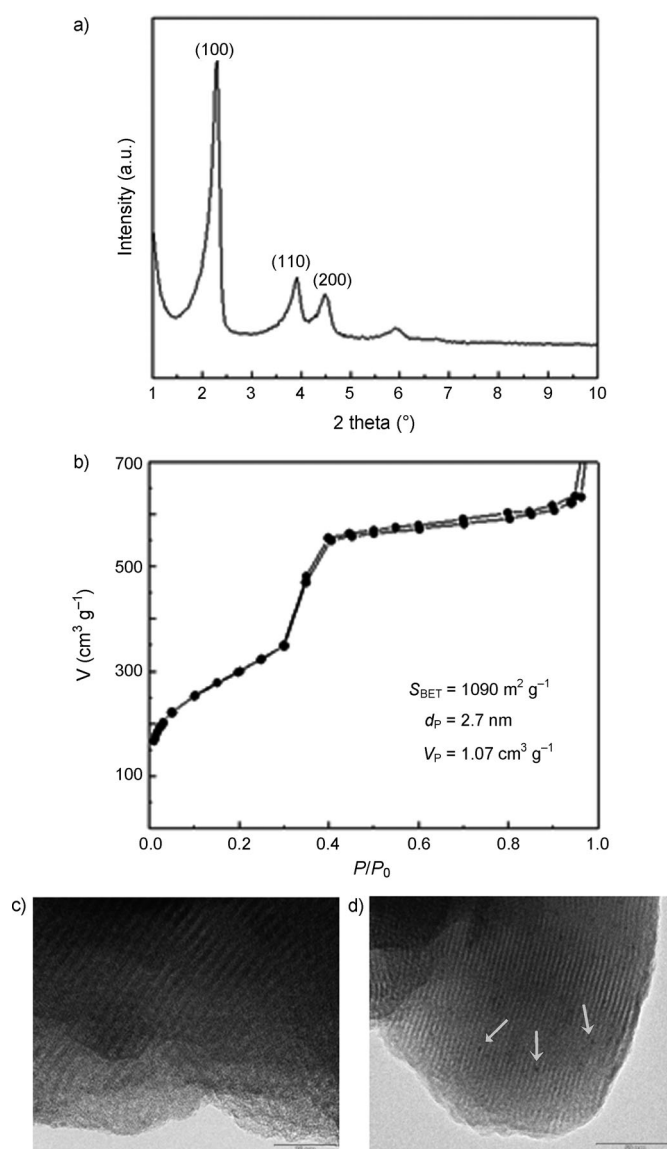


Figure 13. a) XRD pattern and b) nitrogen adsorption–desorption isotherm of 1 wt% Pd/MCM-41 synthesized with DMAP-functionalized Pd nanoparticles after calcination at 550°C . TEM images of that sample c) before and d) after calcination. Scale bars = 50 nm.

minescent mesoporous silicas have attracted a great deal of attention for potential biomedical or photonic applications or their photocatalytic activity.^[72] These luminescent materials have been synthesized mostly through incorporation into the solution of organic or inorganic chromophores as a host by impregnation^[73] or covalent postsynthetic grafting^[72,74] of a previously prepared mesoporous material. Nevertheless, and as discussed before, these two methods often present leaching problems and poor textural properties.

A good number of luminescent PMOs, prepared through the total or partial co-condensation of organic chromophores bearing alkoxy-silyl groups, have also been described.^[75] The materials thus obtained present better textural properties and absence of leaching, but lack the tunability that coordination complexes possess.

A more judicious method has recently been reported, which consists in the synthesis of a PMO that contains 2-phenylpyridine moieties in its framework and the posterior thermal treatment with Rh^{2+} or Ir^{3+} coordination moieties to form organometallic complexes through efficient cyclometalation reactions. Although this method assures a better thermal stability and a high density distribution of the chromophores, the emitters are still grafted onto the walls of the mesopores.^[28]

With the aim of extending the proposed sol-gel chemistry approach to the synthesis of this kind of functionalized materials, we recently reported the synthesis of luminescent hydrothermally stable hybrid materials with a neutral surfactant ($\text{N}^{0/0}$ route) at room temperature and neutral pH for the incorporation of a tetrametallic acetylide Cu^+ complex into the mesoporous MSU-X-type silica framework. The surfactant was also completely removed through ethanol extraction at room temperature.^[23]

For that purpose, the highly emissive step-like organometallic tecton $[\text{Cu}(\text{C}\equiv\text{CTol})(\text{PPETS})]_4$ has been synthesized. This green emitter tetracopper complex, the emission of which is likely due to the excited state of the $\text{Cu}_4(\text{C}\equiv\text{CTol})_4$ core, holds four triethoxysilyl phosphine PPETS ligands, which enable the co-condensation with the silica precursor (TEOS) for the in situ incorporation (sample denoted as *IS-MSU*₄ in which $[\text{Cu}]_4$ refers to the tetranuclear copper complex; Scheme 4).

This new hybrid mesoporous material prepared by the in situ approach (*IS-MSU*₄) showed homogeneous metal complex distribution and good textural properties, with a BET surface area of $600 \text{ m}^2 \text{ g}^{-1}$ (the BET surface area for complex-free MSU-X was $1000 \text{ m}^2 \text{ g}^{-1}$), type IV isotherms, and a narrow pore size distribution, with an average pore diameter of 3.8 nm, which are similar to the neat MSU-X sample (Figure 14b). The sample prepared through chemical grafting, however, showed poor textural properties, probably owing to the use of ammonium fluoride for the precipitation of the complex on the silica surface (Figure 14b). TEM analyses cor-

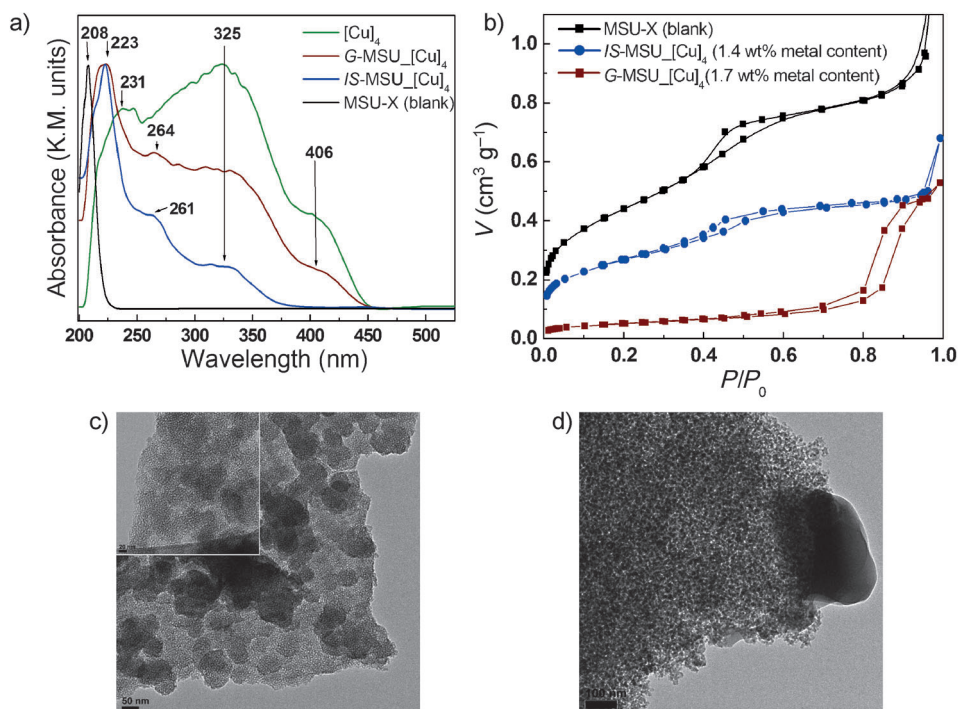
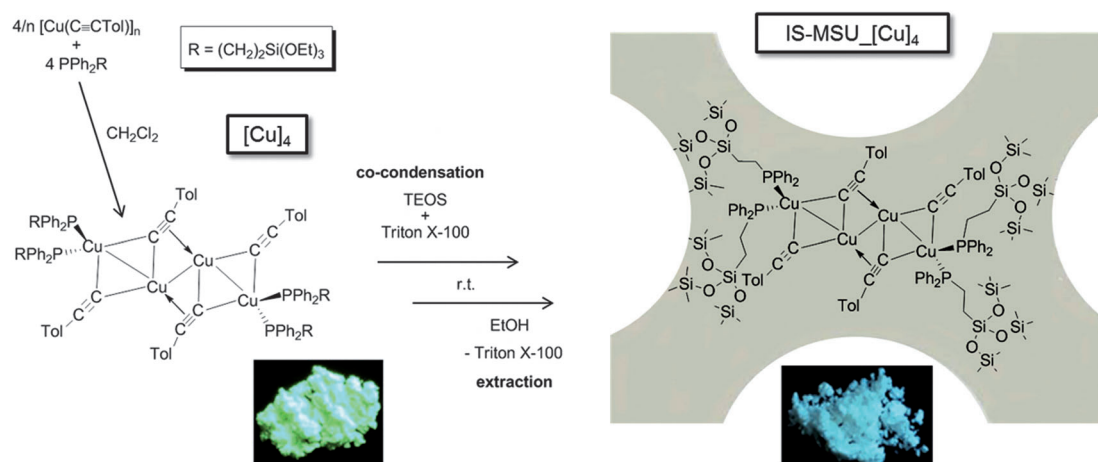


Figure 14. a) DRUV spectra (K.M. = Kubelka–Munk) and b) nitrogen adsorption–desorption isotherm of the luminescent hybrid mesoporous materials prepared through in situ (*IS-MSU*₄) and deposition (*G-MSU*₄) approaches, as compared to the neat silica and complex samples. Representative TEM images of c) *IS-MSU*₄ (scale bar = 50 nm) and d) *G-MSU*₄ hybrids (scale bar = 100 nm). The inset in part c shows a TEM image of neat MSU-X silica (scale bar = 20 nm).



Scheme 4. Representation of the synthesis of *IS-MSU*₄ in which $[\text{Cu}]_4$ refers to the tetranuclear copper complex.

borated the mesoporous nature of the $IS_MSU_Cu_4$ material, as well as the mesoporous blocking in the $G_MSU_Cu_4$ sample (Figure 14c,d).

The luminescent properties of the synthesized samples were analyzed, which indicated that the grafted materials $G_MSU_Cu_4$ present a similar emissive behavior to the Cu_4 complex (green emission). Notwithstanding, the in situ materials $IS_MSU_Cu_4$ demonstrated a dual blueshift emission, which could be due to some degree of distortion on the $Cu_4(C\equiv CtO)_4$ core associated with the immobilization of the copper complex onto the mesoporous silica framework (Figure 15). That immobilization also served as a protection for Cu^+ cen-

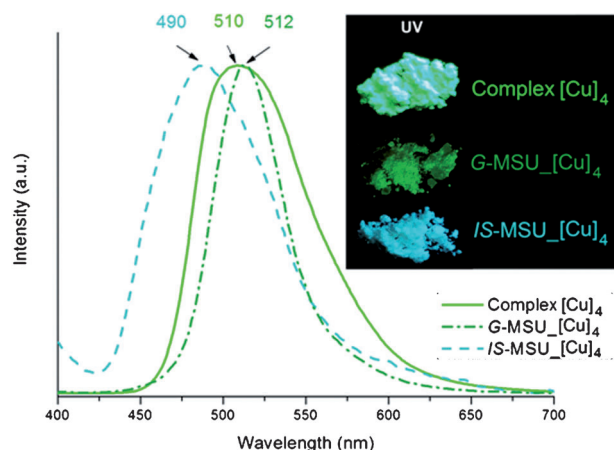


Figure 15. Emission spectra of the tetrametallic complex $[Cu(C\equiv CtO)]_4$ (PPETS) $_4$ (complex $[Cu]_4$) and the hybrid copper-silica materials $IS_MSU_Cu_4$ and $G_MSU_Cu_4$ in solid state at room temperature.

ters, as confirmed by the really high hydrothermal stability of the $IS_MSU_Cu_4$ sample in comparison with both the grafting sample and the copper complex alone.

Under the same in situ conditions but without using a surfactant, we have also prepared a hybrid copper-silica gel, with a BET surface area of only $380\text{ m}^2\text{ g}^{-1}$ and an average pore size corresponding to interparticle porosity (17 nm). Compared with $IS_MSU_Cu_4$, this material presents a similar emissive profile but lower efficiency of the emission.^[23] Also recently, and following a similar sol-gel approach, it has been described as a thermochromic luminescent silica gel on the basis of the immobilization of a tetracopper heterocubane complex $[Cu(PPETS)]_4$.^[76]

7. Summary and Outlook

The incorporation of different chemical functionalities into the structure of mesoporous materials by using sol-gel coordination chemistry has been described for various systems, which shows the versatility and potential of this technique. This method has significant advantages over more conventional postsynthetic techniques such as chemical grafting: for example, better control over the geometry, location, and dispersion of the active phase, enhanced stability, and superior catalytic

performance for some relevant chemical processes. This method is based on the hydrolysis of metal complexes with ligands bearing alkoxy silane terminal groups and its co-condensation with a silica source. Herein, specific examples of the use of this technique are described to incorporate not only metal complexes but also MNPs and clusters with catalytic and luminescent properties into mesoporous silica materials.

This bottom-up approach, based on the use of the active site as a building block, has clear advantages over more classical postsynthetic techniques that are commonly used to prepare catalysts. A better control on the active site is possible because the support is built around it instead of just loading the active phase over a preformed material. In addition, a better dispersion of the active phase is obtained because not only the external area but all the material is used to disperse it. Pore blocking, a classical limitation of postsynthetic techniques caused by loading the active phase on a porous support, is greatly overcome as shown here with many specific examples. The active phase incorporated into the structure of mesoporous materials by using the method described herein is easily accessible to the reactants, as evidenced by different catalytic tests described in this and previous articles. The use of bottom-up techniques, some of them frequently used in molecular nanotechnology, has been adapted, including sol-gel chemistry and the presence of surfactants to control the generation of mesoporosity, to have a better control over the location, dispersion, and accessibility of the active sites. All these parameters are of great importance to many chemical processes.

The proposed methodology enables the incorporation of various industrial or technologically interesting chemical functionalities that are susceptible to modification with terminal trialkoxy silane groups. We envision the possibility of incorporating metal complexes with biological activity and biomolecules, such as enzymes, into nanoparticles for biomedical applications. This synthetic technique also has great potential in the energy sector, an area we are working on with the aim to incorporate homogeneously semiconductor nanoparticles into the structure of various mesoporous metal oxides.

Acknowledgements

We thank the Spanish MINECO (Projects CTQ2011-28954-C02-01 and CTQ2008-06669-C02-02/BQU) and the CAR (COLABORA project 2009/05) for financial support. E.S. acknowledges financial support from JCI 2008-2165 and BEST2011/223 projects. We are grateful to Prof. R. Llúsar and Ivan Sorribes (Universitat Jaume I, Spain), Prof. Carmen Nájera (UA, Spain), Prof. Elena Lalinde (Universidad de La Rioja, Spain), and Dr. R. Luque (UCO, Spain) for their support and collaboration. We also thank Dr. A.I. Carrillo (Canada), Marisa Rico and Aida Grau (University of Alicante, Spain), and A.E. Sepulveda (Universidad de La Rioja, Spain) for their excellent work. Technical services of the University of Alicante are also gratefully acknowledged.

Keywords: coordination chemistry · mesoporous silica · metal complexes · nanoparticles · synthetic methods

- [1] a) J. A. Dumesic, G. W. Hubert, M. Boudart in *Principles of Heterogeneous Catalysis*, Wiley-VCH, Weinheim, Germany, **2008**; b) J. R. H. Ross, *Heterogeneous Catalysis. Fundamentals and Applications*, Elsevier, Amsterdam, The Netherlands, **2012**.
- [2] S. L. Wegener, T. J. Marks, P. C. Stair, *Acc. Chem. Res.* **2012**, *45*, 206–214.
- [3] a) I. E. Wasch, C. A. Roberts, *Chem. Soc. Rev.* **2010**, *39*, 5002–5017; b) D. P. Debecker, P. H. Mutin, *Chem. Soc. Rev.* **2012**, *41*, 3624–3650; c) C. Boissiere, D. Grosso, A. Chaumonnot, L. Nicole, C. Sánchez, *Adv. Mater.* **2011**, *23*, 599–623.
- [4] IUPAC. Compendium of Chemical Terminology, 2nd ed. (the “Gold Book”). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: <http://goldbook.iupac.org> (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0–9678550–9–8. DOI:10.1351/goldbook. Accessed on September 2012.
- [5] L. L. Hench, J. K. West, *Chem. Rev.* **1990**, *90*, 33–72.
- [6] a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710A; b) P. T. Tanev, T. J. Pinnavaia, *Science* **1995**, *267*, 865–867; c) S. A. Bagshaw, E. Prouzet, T. J. Pinnavaia, *Science* **1995**, *269*, 1242–1244; d) Q. Huo, D. I. Margolese, G. D. Stucky, *Chem. Mater.* **1996**, *8*, 1147–1160.
- [7] a) S. Meth, A. Goeppert, G. K. S. Prakash, G. A. Olah, *Energy Fuels* **2012**, *26*, 3082–3090; b) J. A. Melero, J. Iglesias, J. Moreno in *Mesoporous Materials: Properties, preparation and applications* (Ed.: L. T. Burness), Nova-pubishers, San Diego, **2009**, pp. 239–280; c) T. Yokota, Y. Kubotab, T. Tatsumi, *Appl. Catal. A* **2012**, *421–422*, 14–27.
- [8] a) J. Garcia-Martinez in *Tomorrow's Chemistry Today* (Ed.: B. Pignataro), Wiley-VCH, Weinheim, **2007**, pp. 47–51; b) H. Yoshitake, *J. Mater. Chem.* **2010**, *20*, 4537–4550; c) A. Walcarius, L. Mercier, *J. Mater. Chem.* **2010**, *20*, 4478–4511.
- [9] a) B. J. Melde, B. J. Johnson, *Anal. Bioanal. Chem.* **2010**, *398*, 1565–1573; b) M. E. Davis, *Nature* **2002**, *417*, 813–821.
- [10] a) Q. He, J. Shi, *J. Mater. Chem.* **2011**, *21*, 5845–5855; b) Y. Zhao, B. G. Trewyn, I. I. Slowing, V. S.-Y. Lin, *J. Am. Chem. Soc.* **2009**, *131*, 8398–8400; c) B. G. Trewyn, S. Giri, I. I. Slowing, V. S.-Y. Lin, *Chem. Commun.* **2007**, 3236–3245.
- [11] N. Linares, E. Serrano, M. Rico, A. M. Balu, E. Losada, R. Luque, J. Garcia-Martinez, *Chem. Commun.* **2011**, *47*, 9024–9035.
- [12] a) A. Taguchi, F. Schüth, *Microporous Mesoporous Mater.* **2005**, *77*, 1–9; b) F. Hoffman, M. Fröba in *Supramolecular chemistry of organic–inorganic hybrid materials* (Eds.: K. Rurack, R. Martinez-Manez), Wiley, Hoboken, **2010**, pp. 39–45; c) D. Brühwiler, *Nanoscale* **2010**, *2*, 887–892; d) P. Kumar, V. V. Gulians, *Microporous Mesoporous Mater.* **2010**, *132*, 1–14.
- [13] a) B. W. Glasspoole, J. D. Webb, C. M. Crudden, *J. Catal.* **2009**, *265*, 148–154; b) D. J. Webb, S. Macquarrie, K. McEleney, C. M. Crudden, *J. Catal.* **2007**, *252*, 97–109; c) A. Corma, A. Fuentes, M. Iglesias, E. Morales, F. Sánchez, *J. Mol. Catal. A-Chem.* **2006**, *246*, 109–117.
- [14] a) D. S. Shepard, W. Zhou, T. Maschmeyer, J. M. Matters, C. L. Roper, S. Parsons, B. F. G. Johnson, M. J. Duer, *Angew. Chem.* **1998**, *110*, 2881–2883; *Angew. Chem. Int. Ed.* **1998**, *37*, 2717–2719; b) Y. Xie, S. Quinlivan, T. Asefa, *J. Phys. Chem. C* **2008**, *112*, 9996–10003; c) J. Sun, D. Ma, H. Zhang, X. Liu, X. Han, X. Bao, G. Weinberg, N. Pfaender, D. Su, *J. Am. Chem. Soc.* **2006**, *128*, 15756–15764; d) T. Asefa, B. Lennox, *Chem. Mater.* **2005**, *17*, 2481–2483; e) N. Gartmann, D. Bruehwiler, *Angew. Chem.* **2009**, *121*, 6472–6475; *Angew. Chem. Int. Ed.* **2009**, *48*, 6354–6356.
- [15] R. Abu-Reziq, D. Avnir, I. Miloslavski, H. Schumann, J. Blum, *J. Mol. Catal. A-Chem.* **2002**, *185*, 179–185.
- [16] a) C.-C. Chen, S. Cheng, L.-Y. Jang, *Microporous Mesoporous Mater.* **2008**, *109*, 258–270; b) T. M. Suzuki, T. Nakamura, K. Fukumoto, M. Yamamoto, Y. Akimoto, K. Yano, *J. Mol. Catal. A-Chem.* **2008**, *280*, 224–232; c) S. L. Hruby, B. H. Shanks, *J. Catal.* **2009**, *263*, 181–188; d) J. Mondal, M. Nandi, A. Modak, A. Bhaumik, *J. Mol. Catal. A-Chem.* **2012**, *363–364*, 254–264.
- [17] L. Mercier, T. J. Pinnavaia, *Chem. Mater.* **2000**, *12*, 188–196.
- [18] a) E. Coronado, A. Ribera, J. Garcia-Martinez, N. Linares, L. M. Liz-Marzán, *J. Mater. Chem.* **2008**, *18*, 5682–5688; b) J. Garcia-Martinez, N. Linares, S. Sinibaldi, E. Coronado, A. Ribera, *Microporous Mesoporous Mater.* **2009**, *117*, 170–177.
- [19] N. Linares, A. E. Sepúlveda, M. C. Pacheco, J. Berenguer, E. Lalinde, C. Nájera, J. García-Martínez, *New J. Chem.* **2011**, *35*, 225–234.
- [20] N. Linares, A. E. Sepúlveda, J. Berenguer, E. Lalinde, J. García-Martínez, *Microporous Mesoporous Mater.* **2012**, *158*, 300–308.
- [21] N. Linares, E. Serrano, A. Carrillo, J. Garcia-Martinez, *Mater. Lett.* **2013**, *95*, 93–96.
- [22] A. I. Carrillo, J. Garcia-Martinez, R. Llusar, E. Serrano, I. Sorribes, C. Vicente, J. A. Vidal-Moya, *Microporous Mesoporous Mater.* **2012**, *151*, 380–389.
- [23] M. Rico, A. E. Sepúlveda, E. Serrano, S. Ruiz, J. Garcia-Martinez, J. R. Berenguer, E. Lalinde, *Chem. Commun.* **2012**, *48*, 8883–8885.
- [24] a) U. Schubert, K. Rose, H. Schmidt, *J. Non-Cryst. Solids* **1988**, *105*, 165–168; b) U. Schubert, C. Egger, K. Rose, C. Alt, *J. Mol. Catal.* **1989**, *55*, 330–339; c) L. Schmid, O. Kröcher, R. A. Köppel, A. Baiker, *Microporous Mesoporous Mater.* **2000**, *181*, 35–38; d) L. Schmid, M. Rohr, A. Baiker, *Chem. Commun.* **1999**, 2303–2304.
- [25] a) *The Organometallic Chemistry of the Transition Metals* (Ed.: R. H. Crabtree), Wiley, New York, **2009**; b) D. Astruc, *Organometallic Chemistry and Catalysis*, Springer, Berlin, **2007**; c) E. N. Jacobsen, A. Pfaltz, *Comprehensive Asymmetric Catalysis I–III*, Springer, New York, **1999**; d) W. A. Herrmann, B. Cornils, *Angew. Chem.* **1997**, *109*, 1074–1095; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1048–1067; e) R. A. Sheldon, *Green Chem.* **2005**, *7*, 267–278; f) R. Sheldon, H. van Bekkum in *Fine Chemicals through Heterogeneous Catalysis*, Wiley, Weinheim, **2001**, pp. 1–11.
- [26] a) L. Bellarosa, J. Díez, J. Gimeno, A. Lledós, F. J. Suárez, G. Ujaque, C. Vicent, *Chem. Eur. J.* **2012**, *18*, 7749–7765; b) M. Ferreira, H. Bricout, A. Sayede, A. Ponchel, S. Fourmentin, S. Tilloy, E. Monflier, *Adv. Synth. Catal.* **2008**, *350*, 609–618; c) C. J. Li, *Chem. Rev.* **2005**, *105*, 3095–3165.
- [27] a) S. L. Wegener, T. J. Marks, P. C. Stair, *Acc. Chem. Res.* **2012**, *45*, 206–214; b) M. R. Maurya, A. Kumar, J. C. Pessoa, *Coord. Chem. Rev.* **2011**, *255*, 2315–2344; c) S. Minakata, M. Komatsu, *Chem. Rev.* **2009**, *109*, 711–724; d) K. Sarkar, M. Nandi, M. Islam, M. Mubarak, A. Bhaumik, *Appl. Catal. A* **2009**, *352*, 81–86; e) J. M. Richardson, C. W. Jones, *J. Mol. Catal. A-Chem.* **2009**, *297*, 125–134; f) C. Li, H. Zhang, D. Jiang, Q. Yang, *Chem. Commun.* **2007**, 547–558; g) P. McMorn, G. J. Hutchings, *Chem. Soc. Rev.* **2004**, *33*, 108–122.
- [28] a) M. Waki, N. Mizoshita, T. Tani, S. Inagaki, *Angew. Chem.* **2011**, *123*, 11871–11875; *Angew. Chem. Int. Ed.* **2011**, *50*, 11667–11671; b) A. Kuschel, M. Luka, M. Wessig, M. Drescher, M. Fonin, G. Kiliani, S. Polzar, *Adv. Funct. Mater.* **2010**, *20*, 1133–1143; c) P. Wang, X. Liu, J. Yang, L. Zhang, Q. Yang, C. Li, *J. Mater. Chem.* **2009**, *19*, 8009–8014; d) S. Fujita, S. Inagaki, *Chem. Mater.* **2008**, *20*, 891–908; e) J. Alauzun, A. Mehdi, C. Reyé, R. J. P. Corriu, *J. Mater. Chem.* **2007**, *17*, 349–356; f) T. Kamegawa, T. Sakai, M. Matsuoka, M. Anpo, *J. Am. Chem. Soc.* **2005**, *127*, 16784–16785.
- [29] R. P. J. Corriu, A. Mehdi, C. Reyé, C. Thienleux, *Chem. Commun.* **2003**, 1564–1567.
- [30] a) B. Baleizão, B. Gigante, D. Das, M. Álvaro, H. García, A. Corma, *J. Catal.* **2004**, *223*, 106–113; b) A. Corma, D. Das, H. García, A. Leyva, *J. Catal.* **2005**, *229*, 322–331.
- [31] V. Dufaud, F. Beauchesne, L. Bonneviot, *Angew. Chem.* **2005**, *117*, 3541–3543; *Angew. Chem. Int. Ed.* **2005**, *44*, 3475–3477.
- [32] a) X. Yang, F. Zhu, J. Huang, F. Zhang, H. Li, *Chem. Mater.* **2009**, *21*, 4925–4933; b) J. Huang, F. Zhu, W. He, F. Zhang, W. Wang, H. Li, *J. Am. Chem. Soc.* **2010**, *132*, 1492–1493.
- [33] J. Huang, F. Zhang, H. Li, *Appl. Catal. A* **2012**, *431–432*, 95–103.
- [34] a) J. Huang, M. Wang, S. Zhang, B. Hu, H. Li, *J. Phys. Chem. C* **2011**, *115*, 22514–22522; b) W. J. Zhou, B. Albel, P. Perriat, M. Y. He, L. Bonneviot, *Langmuir* **2010**, *26*, 13493–13501.
- [35] a) M. D. McInall, J. Scott, L. Mercier, P. J. Kooyman, *Chem. Commun.* **2001**, 2282–2284; b) W. J. Hunks, G. A. Ozin, *J. Mater. Chem.* **2005**, *15*, 3716–3724; c) L. Zhang, Q. Yang, W.-H. Zhang, Y. Li, J. Yang, G. Zhu, C. Li, *J. Mater. Chem.* **2005**, *15*, 2562–2568.
- [36] a) S. Che, A. E. Garcia-Bennett, T. Yokoi, K. Sakamoto, H. Kuneda, O. Terasaki, T. Tatsumi, *Nat. Mater.* **2003**, *2*, 801–805; b) T. Yokoi, H. Yoshitake, T. Tatsumi, *Chem. Mater.* **2003**, *15*, 4536–4538.

- [37] a) S. El Hankari, B. Motos-Pérez, P. Hesemann, A. Bouhaouss, J. J. E. Moreau, *Chem. Commun.* **2011**, 47, 6704–6706; b) S. El Hankari, P. Hesemann, *Eur. J. Inorg. Chem.* **2012**, DOI: 10.1002/ejic.201200419.
- [38] a) M. Vasconcellos-Dias, C. D. Nunes, P. D. Vaz, P. Ferreira, P. Brandão, V. Félix, M. J. Calhorda, *J. Catal.* **2008**, 256, 301–305; b) M. Masteri-Farahnani, *J. Mol. Catal. A-Chem.* **2010**, 316, 45–51; c) M. S. Saraiva, C. D. Nunes, T. G. Nunes, M. J. Calhorda, *J. Mol. Catal. A-Chem.* **2010**, 321, 92–98.
- [39] H. Seino, M. Hidai, *Chem. Sci.* **2011**, 2, 847–857.
- [40] a) M. Pillinger, I. S. Goncalves, A. D. Lopes, P. Ferreira, J. Rocha, G. Zhang, M. Schafer, O. Nuyken, F. E. Kuhn, *Phys. Chem. Chem. Phys.* **2002**, 4, 696–702; b) K. Zama, Y. Imada, A. Fukuoka, M. Ichikawa, *Appl. Catal. A* **2000**, 285, 194–195.
- [41] a) V. P. Fedin, J. Czyniewska, R. Prins, T. Weber, *Appl. Catal. A* **2001**, 213, 123–132; b) K. Herbst, M. Brorson, A. Carlsson, *J. Mol. Catal. A-Chem.* **2010**, 325, 1–7.
- [42] a) E. Roduner in *Nanoscale Materials. Size-dependent Phenomena*, RSC Publishing, Cambridge, **2006**, pp. 239; b) R. J. White, R. Luque, V. Budarin, J. H. Clark, D. J. Macquarrie, *Chem. Soc. Rev.* **2009**, 38, 481–494; c) R. Luque in *Supported metal nanoparticles in catalysis, Progress in Heterogeneous Catalysis* (Ed.: D. Marmaduke), Novapublishers, San Diego, **2008**, pp. 74–91.
- [43] a) R. Long, R. T. Yang, *Ind. Eng. Chem. Res.* **1999**, 38, 873–885; b) L. Barrio, J. M. Campos-Martín, M. P. Frutos-Escrig, J. L. G. Fierro, *Microporous Mesoporous Mater.* **2008**, 113, 542–553; c) H.-Y. Chen, W. M. H. Sachtler, *Catal. Today* **1998**, 42, 73–83; d) Y. Wu, L. Zhang, G. Li, C. Liang, X. Huang, Y. Zhang, G. Song, J. Jia, C. Z. Hixiang, *Mater. Res. Bull.* **2001**, 36, 253–257.
- [44] a) R. Köhn, M. Fröba, *Catal. Today* **2001**, 68, 227–236; b) R. Köhn, D. Paneva, M. Dimitrov, T. Tsoncheva, I. Mitov, C. Minchev, M. Fröba, *Microporous Mesoporous Mater.* **2003**, 63, 125–137.
- [45] a) J. M. Campelo, A. F. Lee, R. Luque, D. Luna, J. M. Marinas, A. A. Romero, *Chem. Eur. J.* **2008**, 14, 5988–5995; b) H. Gies, S. Grabowski, M. Bandyopadhyay, W. Grünert, O. P. Tkachenko, K. V. Klementiev, A. Birkner, *Microporous Mesoporous Mater.* **2003**, 60, 31–42.
- [46] L. M. Bronstein, S. Polarz, B. Smarsly, M. Antonietti, *Adv. Mater.* **2001**, 13, 1333–1336.
- [47] N. Linares, S. Hartmann, A. Galarneau, P. Barbaro, *ACS Catal.* **2012**, 2, 2194–2198.
- [48] Y. Zhou, S.-H. Yu, A. Thomas, B.-H. Han, *Chem. Commun.* **2003**, 262–263.
- [49] N. Kim, M. Serk Kwon, C. Min Park, J. Park, *Tetrahedron Lett.* **2004**, 45, 7057–7059.
- [50] A. Papp, G. Galbács, A. Molnár, *Tetrahedron Lett.* **2005**, 46, 7725–7728.
- [51] A. Papp, A. Molnár, A. Mastalir, *Appl. Catal. A* **2005**, 289, 256–266.
- [52] P. Krawiec, E. Kockrick, P. Simon, G. Auffermann, S. Kaskel, *Chem. Mater.* **2006**, 18, 2663–2669.
- [53] L.-C. Wang, C.-Y. Huang, C.-Y. Chang, W.-C. Lin, K.-J. Chao, *Microporous Mesoporous Mater.* **2008**, 110, 451–460.
- [54] S. Jana, B. Dutta, R. Bera, S. Koner, *Inorg. Chem.* **2008**, 47, 5512–5520.
- [55] A. K. Prashar, R. P. Hodgkins, R. Kumara, R. N. Devi, *J. Mater. Chem.* **2008**, 18, 1765–1770.
- [56] P. Wang, Q. Lu, J. Li, *Catal. Lett.* **2009**, 131, 444–450.
- [57] I. Alonso-Lemus, Y. Verde-Gomez, A. Aguilar-Elguézabal, L. Álvarez-Contreras, *J. Nanomater.* **2010**, 302898.
- [58] A. K. Prashar, S. Mayadevi, P. R. Rajamohan, R. Nandini Devi, *Appl. Catal. A* **2011**, 403, 91–97.
- [59] A. Samadi-Maybodhi, M. Teymour, A. Vahid, A. Miranbeigi, *J. Hazard. Mater.* **2011**, 192, 1667–1674.
- [60] X. Zhang, Z. Qu, X. Li, Q. Zhao, X. Zhang, X. Quan, *Mater. Lett.* **2011**, 65, 1892–1895.
- [61] R. Yan, J. Xu, Y. Zhang, D. Wang, M. Zhang, W. Zhang, *Chem. Eng. J.* **2012**, 200–202, 559–568.
- [62] H. Liu, D. Ma, R. A. Blackley, W. Zhou, X. Bao, *Chem. Commun.* **2008**, 2677–2679.
- [63] a) H. S. Kibombo, R. T. Koodali, *J. Phys. Chem. C* **2011**, 115, 25568–25579; b) X. Zhang, Z. Qu, J. Jia, Y. Wang, *Powder Technol.* **2012**, 230, 212–218.
- [64] a) A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* **2002**, 102, 3757–3778; b) C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, *Chem. Rev.* **2005**, 105, 1025–1102; c) Y. Yin, A. P. Alivisatos, *Nature* **2005**, 437, 664–670.
- [65] C. Aprile, A. Abad, H. Garcia, A. Corma, *J. Mater. Chem.* **2005**, 15, 4408–4413.
- [66] M. Alvaro, C. Aprile, H. Garcia, C. J. Gómez-García, *Adv. Funct. Mater.* **2006**, 16, 1543–1548.
- [67] a) G. Budroni, A. Corma, *Angew. Chem.* **2006**, 118, 3406–3409; *Angew. Chem. Int. Ed.* **2006**, 45, 3328–3331; b) G. Budroni, A. Corma, H. Garcia, A. Primo, *J. Catal.* **2007**, 251, 345–353.
- [68] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, *J. Chem. Soc. Chem. Commun.* **1994**, 801–802.
- [69] S. Banerjee, V. Balasanthiran, R. T. Koodali, G. A. Sereda, *Org. Biomol. Chem.* **2010**, 8, 4316–4321.
- [70] a) X. Duan, C. M. Lieber, *Adv. Mater.* **2000**, 12, 298–302; b) A. M. Morales, C. M. Lieber, *Science* **1998**, 279, 208–211.
- [71] a) P. Yang, S. Gai, J. Lin, *Chem. Soc. Rev.* **2012**, 41, 3679–3681; b) Y.-S. Lin, C. L. Haynes, *Chem. Mater.* **2009**, 21, 3979–3981; c) K. Ariga, A. Vinu, J. P. Hill, T. Mori, *Coord. Chem. Rev.* **2007**, 251, 2562–2591; d) J. Font, P. de March, F. Busqué, E. Casas, M. Benitez, L. Temel, H. García, *J. Mater. Chem.* **2007**, 17, 2336–2343.
- [72] a) H. Li, Y. Fu, L. Zhang, X. Liu, Y. Qu, S. Xu, C. Lü, *Microporous Mesoporous Mater.* **2012**, 151, 293–302; b) J. L. Vivero-Escoto, I. I. Slowing, C. W. Wu, V. S. Y. Lin, *J. Am. Chem. Soc.* **2009**, 131, 3462–3468; c) L. D. Carlos, R. A. S. Ferreira, V. Z. Bermúdez, S. J. L. Ribeiro, *Adv. Mater.* **2009**, 21, 509–534; d) A. L. Pénard, T. Gacoin, J. P. Boilot, *Acc. Chem. Res.* **2007**, 40, 895–902.
- [73] a) D. Aiello, A. M. Talarico, F. Teocoli, E. I. Szerb, I. Aiello, F. Testa, M. Ghedini, *New J. Chem.* **2011**, 35, 141–148; b) F. Carniato, C. Bisio, G. Paul, G. Gatti, L. Bertinetti, S. Coluccia, L. Marchese, *J. Mater. Chem.* **2010**, 20, 5504–5509; c) T. Nakamura, Y. Yamada, H. Yamada, K. Yano, *J. Mater. Chem.* **2009**, 19, 6699–6705; d) K. Binnemans, *Chem. Rev.* **2009**, 109, 4283–4374; e) B. H. Han, I. Manners, M. A. Winnick, *Chem. Mater.* **2005**, 17, 3160–3166.
- [74] a) K. Mori, K. Watanabe, Y. Terai, Y. Fujiwara, H. Yamashita, *Chem. Eur. J.* **2012**, 18, 11371–11378; c) D. B. A. Raj, S. Biju, M. L. P. Reddy, *J. Mater. Chem.* **2009**, 19, 7976–7983; d) G. Alberto, I. Miletto, G. Viscardi, G. Caputo, L. Latterini, S. Coluccia, G. Martra, *J. Phys. Chem. C* **2009**, 113, 21048–21053.
- [75] a) N. Mizoshita, T. Tani, S. Inagaki, *Chem. Soc. Rev.* **2011**, 40, 789–800; b) T. Tami, N. Mizoshita, S. Inagaki, *J. Mater. Chem.* **2009**, 19, 4451–4456; c) J. Feng, H. J. Zhang, C. Y. Peng, J. B. Yu, R. P. Deng, L. N. Sun, X. M. Guo, *Microporous Mesoporous Mater.* **2008**, 113, 402–410.
- [76] S. Perruchas, N. Desboeufs, S. Maron, X. F. Le Goff, A. Fargues, A. Garcia, T. Gacoin, J. P. Boilot, *Inorg. Chem.* **2012**, 51, 794–798.

Received: December 19, 2012

Published online on March 11, 2013