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Transition-metal ligands bound onto the micelle-templated silica surface

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Contents

Abstract

This paper reviews recent works on the design of immobilized transition-metal ligands on solid supports. After an overview of some results concerning ligand anchorage on polymeric supports and encapsulation of transition-metal complexes inside layered or zeolitic minerals, the grafting of ligands onto the silicic wall surface of micelle-templated silicas (MTS) is reported. MTS silicas featuring a regular mesoporous system of pore-monodispersed size and exhibiting larger pores than zeolites, provide a new opportunity to allow anchorage of organic moieties through the silanation procedure. Mn(III) Salpr and *t*Salpr complexes bound onto

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the MTS surface are active in epoxidation reaction using PhIO as oxygen donor. Anchorage of (1*R*,2*S*)-ephedrine has been also investigated with the aim to obtain benefit from the MTS structure effect. These new supported chiral catalysts are active in alkylation of benzaldehyde with diethylzinc although less enantioselective than the corresponding homogeneous catalyst. The effect of dispersion of active sites and of surface passivation has been investigated and discussed in terms of the nature of the support surface.

Keywords: MCM-41 materials; Functionalization; Metal-transition complexes; Olefin epoxidation; Ephedrine; Enantioselective alkylation

1. Introduction

Transition-metal complexes are very effective and selective catalysts for a variety of organic reactions such as hydrogenation, hydroformylation, hydrosilylation, dimerization, alkylation, oxidation reactions and polymerization of unsaturated compounds for which suitable ligands and metal atoms must be associated [1].

During the 1970s, extensive research was devoted to the anchorage onto insoluble supports of homogeneous catalysts based on metal-transition complexes [2]. Heterogenized catalysts would combine the advantages of homogeneous and heterogeneous catalysts and sometimes might minimize the drawbacks of both. The catalytic phase would be well-defined from a molecular scale point of view and all metal atoms could be, in principle, effective. Activity comparable to that of the solution phase has been observed in some cases with equivalent or even enhanced selectivity. Also, easy separation of the products from the reaction medium, along with the recovery and reuse of the expensive catalyst, provide an attractive advantage over homogeneous catalysis.

Nevertheless the major drawbacks of these systems concern both their mechanical and chemical stabilities. The nature of the support, the catalytic phase and the anchorage type should be judiciously chosen to be resistant towards solvent and reactant attacks under the reaction conditions used. Some examples of metal-transition complexes supported on polymers are reported in Section 2 and the use of clays and zeolites as inorganic support is briefly reviewed in Section 3.

Among the transition-metal complexes chiefly used in recent years in catalysis, besides rhodium or palladium phosphine-type complexes which are known to be very efficient in olefin hydrogenation, manganese(III) Schiff-base complexes are currently of considerable interest to promote oxidation reactions. First developed by Jacobsen [3], manganese chiral salen complexes combined with oxygen donors such as NaOCl, constitute a valuable new family of homogeneous catalysts for enantioselective epoxidation of olefins.

β-Aminoalcohols are the most studied chiral ligands in the field of enantioselective catalysis. Despite their ability to anchor transition metals such as molybdenum and tungsten in order to promote oxidation reactions [4], they are able to greatly enhance the reactivity of dialkylzincs by zinc atom complexation during the enantioselective alkylation of the aldehyde [5].

The increasing interest devoted to these two types of ligands prompted us to investigate their immobilization onto mineral oxides. Another target of our research was the use of new nanostructured materials, called micelle-templated silicas (MTS). We have therefore developed the design of new hybrid organic–inorganic systems based on the anchorage of ligands on the MTS surface. Section 4 of this paper will focus on such investigations dealing with the grafting of salen-type ligands and of ephedrine as an example of β-aminoalcohols onto the MTS surface.

2. Transition-metal immobilization on polymers

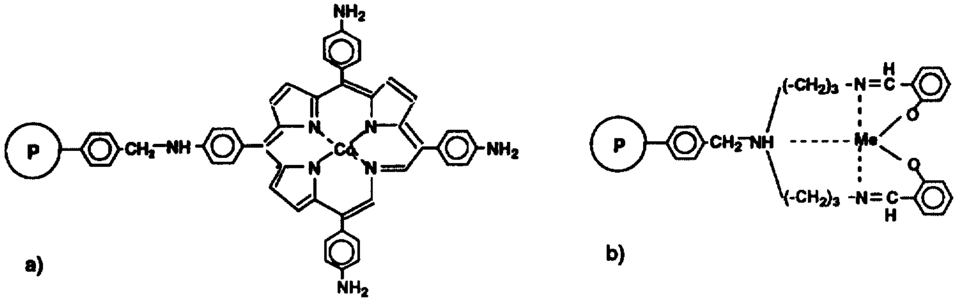
Organic polymers stand among the most used solid materials for supporting the homogeneous catalytic phase due to the wide variety of coupling reactions able to perform a covalent anchorage of the active molecules onto the polymeric framework. These coupling reactions can be achieved either on the functional polymer or on the monomeric precursors.

As regards transition metals immobilized onto polymers, various systems have been reported in the literature. Some examples concern the use of metallic salts such as vanadyl and molybdenyl cations as compensating ions of the polymeric matrix of cation-exchanged resins for achieving olefin epoxidation in the presence of *t*-butyl hydroperoxide [6,7]. Transition-metal porphyrin complexes recognized as powerful homogeneous catalysts in oxidation reactions [8] were immobilized by ionic interaction on cationic ion-exchange resins [9]. Electron donor molecules such as pyridine were also incorporated in the polymeric framework by copolymerization of vinylpyridine with ethylene, and used as liganding centres for complex transition metals (V, Fe, Mn, Co) [10,11]. The ligand moieties might also be post-synthetically introduced in the polymeric framework by modification of functionalized polystyrene resins [12]. Imidazole-containing polymers were synthesized and then loaded with Mo(VI). The resulting polymer metal complexes were used as catalysts in liquid-phase epoxidation of cyclohexene using *t*-butyl hydroperoxide as the oxygen source [13].

However, the leaching of some metal centres during the first run gave rise to homogeneous catalysis and reduced the catalytic activity on recycling. Attempts to reduce the transition metal leaching proved successful by using stronger binding ligands [14]. In this respect, Mo(VI)-loaded polybenzimidazole resins which can be reused without significant metal loss probably coordinated the metal as an anion does [13]. Similarly, acetylacetonate, porphyrins and salen based ligands were anchored to polystyrene–divinyl benzene copolymer in order to improve the robustness of the metal complexation achieved by electron donor-anionic polydentate ligands [10,15–19] (Scheme 1).

Nevertheless, the chemical stability of both polymeric support and catalytic site [15] towards oxidation reaction is not absolutely convincing to allow wide applications in heterogeneous catalysis.

Several chiral aminoalcohols have been also grafted to polymeric resins in order to perform enantioselective alkylation reaction of the aldehyde using dialkylzinc as



Scheme 1. Metal-transition complexes grafted onto polymer: (a) metalloporphyrin according Ref. [15]; (b) metal-transition salen-type according Ref. [16].

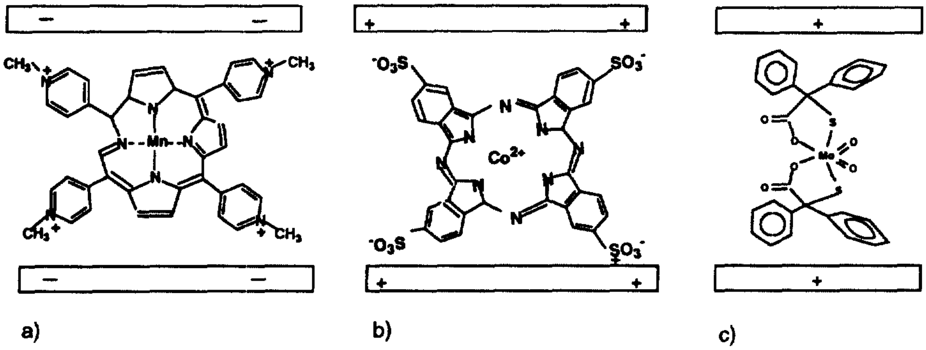
reactant [20,21] or to achieve Diels–Alder reactions using Al or Ti species as catalytic metal centres [22].

However, it should be noted that isolation of polymer-bonded ligands was controversial [23–29]. Hence, possible transition-metal complex interactions might facilitate highly probable self complex transformation such as both the dismutative reaction, leading to almost unknown species and/or to some inert metallated centres, and the self autoxidation reaction which destroys the catalytic sites.

3. Transition-metal complexes entrapped inside porous metal oxide frameworks

Mineral oxides constitute another interesting class of supports widely used to immobilize transition-metal ligands. Adsorption of manganese(III) tetracationic porphyrin on silica was first reported by Battioni *et al.* and the resulting adsorbed transition-metal complex phase was found more effective for olefin epoxidation and alkane hydroxylation than the corresponding soluble Mn-porphyrins, emphasizing the beneficial effects of a silica support [30]. Nevertheless, the nature of the complex immobilization and the origin of such a phenomenon were not well-established. In order to improve the anchorage of the transition-metal complexes, the same authors have immobilized tetracationic chloro[*meso*-tetra(4-*N*-methylpyridinio)porphyrinato]manganese(III) on montmorillonite by exchange of its interlayer cations [31] (Scheme 2(a)). Pinnavaia *et al.* [32] and Corma *et al.* [33,34] have used the same methodology for the preparation of intercalated transition-metal complexes between the interlayer space of layered double hydroxides (LDH). They used ligands possessing negative charges able to compensate the positive charges of the layer framework. Hence, cobalt phthalocyanine tetrasulphonate anions (Scheme 2(b)) and oxomolybdenum 2,2-diphenyl-2-mercaptoethanolate (Scheme 2(c)) were trapped inside this LDH host and shown to be effective catalysts for thiol oxidation.

In order to obtain a better isolation of the catalytic sites, Romanovsky has achieved the immobilization of metal transition phthalocyanine inside the microporous system of zeolites using the "ship-in-bottle" procedure [35] (Scheme 3(a)).



Scheme 2. Metal-transition complexes entrapped inside the interlayer space of clays: (a) tetracationic porphyrin into montmorillonite according Ref. [31]; (b) phthalocyanine into LDH according Ref. [32]; (c) mercaptoethanolate according Ref. [33].

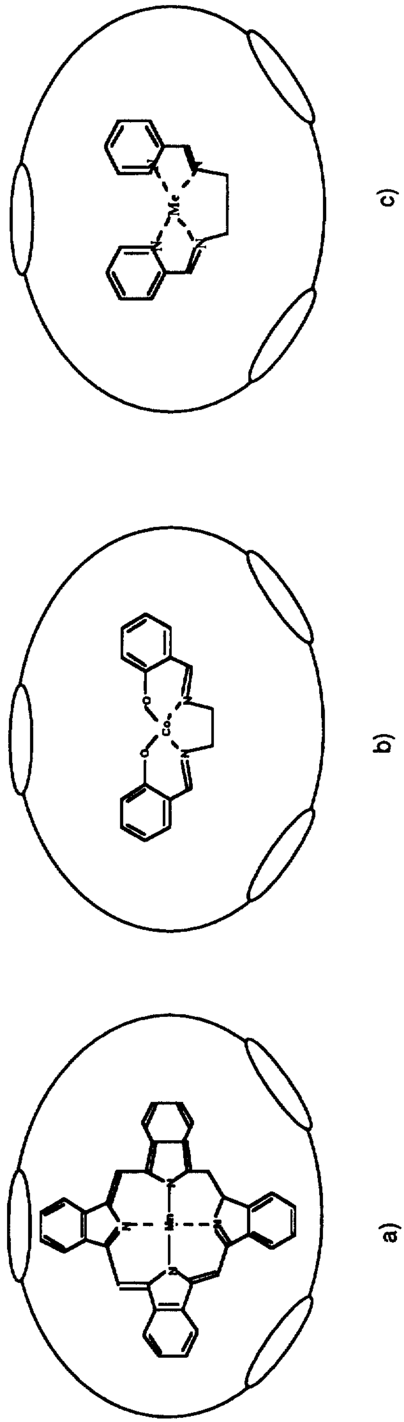
This approach has been then widely developed by several authors either for the same ligand [36–42] or for other macrocyclic tetradentate or pentadentate ligands, such as salen- and salophen-type [42–48] (Scheme 4(b)) or pyren- and acacen-type [45,48] (Scheme 3(c)) ligands. The physical encapsulation of metal complexes in the zeolite supercages could be also performed by templating the zeolite with the metal complex as reported by Balkus et al. for iron(II) perfluorophtalocyanine complex [49].

Other interesting work recently reported [50,51] concerns the intrazeolite preparation of chiral manganese(III) salen-type in order to obtain benefit from both the shape selectivity of the zeolitic structure and the high stereocontrol of this chiral complex in olefin epoxidation which was previously discovered by Jacobsen [3,52,53].

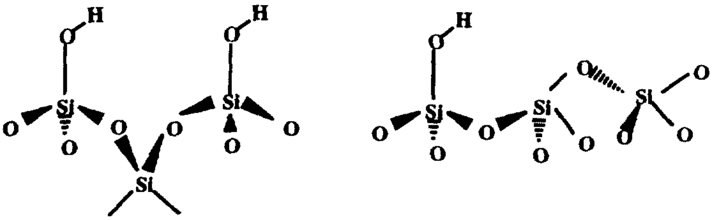
This strategy for isolation of the metal complexes can never be realized by a homogeneous system and would provide many advantages in catalysis. The metal complexes should be free to react inside the cavities as in solution but should be prevented from leaching by restrictive pore openings. Additionally, the zeolite host should provide a stabilizing effect since deactivation pathways involving dimerization and degrading of the complexes will be precluded. However, the beneficial effect of the complex encapsulation is still a matter of debate. In some cases the specific activity of the occluded catalyst was higher than that of the free complex in solution [47] but, in most cases, reaction rates were lower [44] and pore blockage led to shutdown of the reactivity after a few cycles [54]. These serious problems could be resolved in part by embedding the metal complex-containing zeolite crystals in a polymeric membrane [55,56]. Nevertheless, the use of such zeolitic materials is limited to reactions in which small organic molecules are involved.

4. Transition-metal ligands anchored onto micelle-templated silicas (MTS)

Another possible strategy to immobilize transition-metal complexes deals with the design of new larger-pore hybrid materials having well-defined pore structures. We



Scheme 3. Zeolite-encapsulated metal-transition complexes: (a) phthalocyanine according Ref. [35]; (b) salen according Ref. [38]; (c) pyren according Ref. [45].



Scheme 4. Adjacent silanols, isolated silanol and siloxane groups.

have investigated in detail the grafting of transition-metal complexes by covalent linkage onto the micelle-template silica (MTS) supports. These new materials, recently discovered by Mobil's researchers [57,58], feature an ordered mesoporous system of monodispersed pore size and exhibit larger pore aperture than zeolites. They provide new opportunities for grafting catalytic phases on inorganic surfaces [59,60].

The aim of our investigation was therefore to design new hybrid solids taking special care in controlling the key aspects pointed out in Fig. 1, namely:

(1) the preservation of the textural properties of the support upon ligand grafting,

(2) the control of the nature of the anchorage of the organic moieties onto the mineral surface,

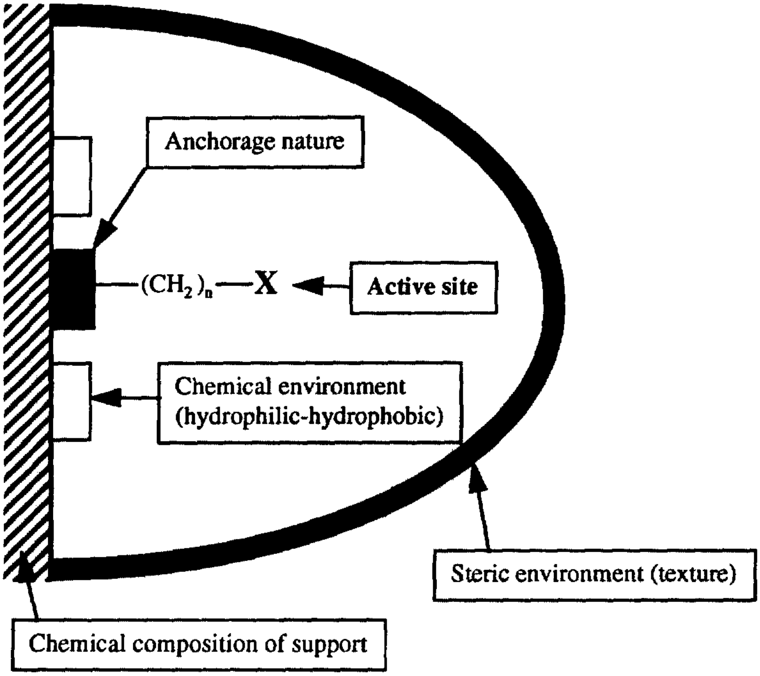


Fig. 1. Design of hybrid organic–inorganic mesoporous materials.

(3) the selective modification of the organic function,

(4) the avoidance of interaction between the catalytic sites and the uncovered surface.

Such requirements implied a thorough knowledge of the textural properties and chemical nature of the surface before and after performing the different treatments on these materials and the detailed characterization of the new properties afforded by these systems.

4.1. Preparation and physico-chemical characteristics of the parent MTS

MTS materials, mostly silicates or aluminosilicates, are obtained according to a cooperative organization of the inorganic phase and the organic micellar phase into three-dimensionally structured arrays (Fig. 2). MTS are then inorganic–organic hybrid nanomaterials which are similar to the corresponding lyotropic phases such as liquid crystals. Davis et al. [61] and Stucky *et al.* [62–66] have proposed a mechanism for MTS synthesis which starts by ion-exchange of bromide (counterion of quaternary ammonium surfactant) by silicate oligomers and the charge-density matching between silicates and surfactants organizes the micelles into a well-defined array. The silicates then polymerize in the interface region. The assembly process leading to an hexagonal array (MCM-41) would be governed by these nucleation and growing steps controlled by equilibrium displacements and dynamic interactions between the ionic charges and templating organic molecules [67]. The pore diameter of MTS can be adjusted from 1.8 to 3.5 nm depending on the chain length of the alkylammonium surfactants, from 8 to 16 carbon atoms, used in the synthesis. Larger pores can be formed by the use of mixed surfactant hydrocarbon micelles. Moreover, mineral wall thickness can be controlled by the alkalinity of the parent hydrogel. Thicker walls between pores stabilized the mesoporous system after elimination of the organic templating agent by calcination [68]. The X-ray diffraction pattern of the calcined parent support prepared with trimethylcetylammonium bro-

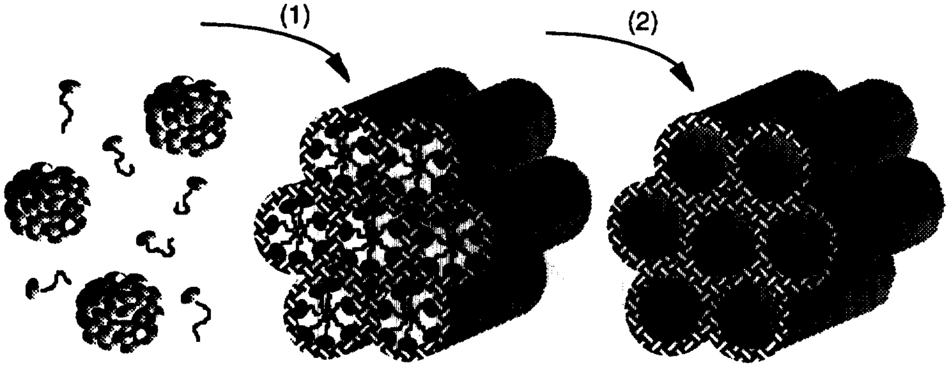


Fig. 2. Mechanism of MTS materials: (1) organization of the hexagonal array of cylindrical micelles by anion-exchange by silicate oligomers and silicate polymerization; (2) liberation of the mesoporosity by calcination of the organic surfactant.

mide as surfactant, is reported in Fig. 3 and shows three peaks in the region $2q$ 1–5° consistent with a structurally long-range hexagonal order. These three peaks are assigned to the ⟨100⟩, ⟨110⟩ and ⟨200⟩ reflections based on a hexagonal unit cell with $a = 4.8$ nm ($2d_{100}/\sqrt{3}$).

The size uniformity of these cylindrical pores is also illustrated by the nitrogen sorption isotherm (Fig. 4). Isotherms of nitrogen adsorption and desorption on MTS material are of type IV showing monolayer and multilayer adsorptions on a mesoporous surface with a typical step reversible step at p/p_0, characteristic of mesopore filling and a plateau when the pores are filled. The very narrow range of p/p_0values corresponding to mesopore filling is consistent with a monodispersed size of the mesopores. The surface area of the sample used in this study was 958 $m^2 g^{-1}$ and the mesoporous volume estimated from the nitrogen amount adsorbed at the top of the step was 10.74 $mL\ g^{-1}$. Both high surface area and accessible mesoporous volume in addition to uniform pore size distribution are relevant to applications of this raw material to the binding of organic moieties onto its surface.

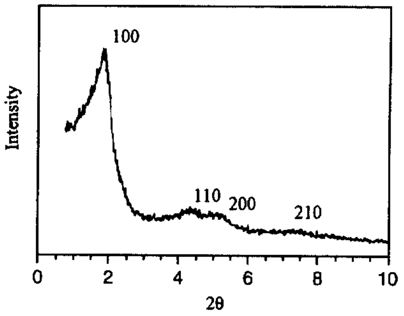


Fig. 3. X-ray diffraction spectrum of the calcined MTS.

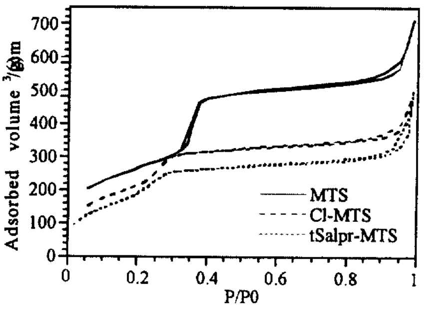


Fig. 4. Nitrogen adorption–desorption isotherms of parent MTS (———), Cl–MTS (– – –) and *t*Salpr–MTS (- - -) samples.

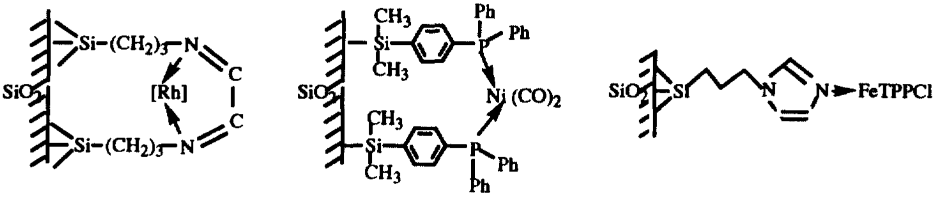
4.2. Hydrophobic and hydrophilic behaviour of MTS surface

Studies of water–MTS surface interaction by microcalorimetry and infrared spectroscopy and comparison with the results of water–usual silica systems [69–73] have shown a unique behaviour of MTS silicas [74]. The MTS surface shows hydrophobic and hydrophilic patches as a result of the particular channel geometry. This site distribution is responsible for the low water uptakes on MTS similar to those obtained in pyrogenic silica, considered as a hydrophobic material. On the contrary, adsorption heats are higher than those observed on the more hydrophilic silicas such as cristobalite. The hydrophilic patches are constituted by clustered, H-bonded silanols, such as adjacent silanol groups shown in Scheme. 4, whereas hydrophobic patches correspond to siloxanes and non-interacting silanol groups resulting from condensation of silanols during the calcination step. This distribution is in agreement with a lower silanol content on MTS than on the classical silica surface (more than 5 OH per nm^2). Llewellyn et al. [75] and Zhao et al. [76] have proposed 1.2 OH groups per nm^2 and between 2.5 and 3 OH groups per nm^2, respectively. This different distribution is also consistent with the limited mobility of adsorbed water on the MTS walls and the longer relaxation times (T_1) of the Q^3 silicon nucleus observed by MAS-NMR by comparison with those characteristic of amorphous silica gel [77].

The coexistence of two well-defined patches provides ideal configuration for the determination of the sites where anchorage of organic moieties takes place during the grafting reactions.

4.3. Grafting of Mn(III) N,N′-bis-(3-salicylidenaminopropyl)amine (Salpr) and Mn(III) N,N′-bis-[3-(3,5-di-tert-butyl salicylidenamino)propyl]amine (tSalpr) complexes

Anchorage of neutral ligands onto silica through covalent Si–O–Si bonds has been already achieved in order to complex transition metals [78–83]. The neutral ligands were mainly amine or phosphine functions directly grafted to the silica surface by silanation procedure. Such ligands achieved direct complexation of transition metals as shown in Scheme 5(a) [79] and Scheme 5(b) [82] or permitted immobilization of metal complexes such as porphyrin through apical coordinative ligation on the metal centres (Scheme 5(c)) [80]. Ligands of this type have also been



Scheme 5. Metal-transition complexes anchored onto silica surface: (a) rhodium complex according Ref. [79]; (b) nickel complex according Ref. [82]; (c) iron porphyrin according Ref. [80].

anchored on silica by a coupling reaction on previously grafted functional organic moieties [83]. The same procedure was also followed for the immobilization of anionic ligands such as acetate [84], phthalocyanines [85] and porphyrins [86].

The grafting procedure consisted in the treatment of activated MTS solid with a refluxing anhydrous toluene solution of a functional alkyltrialkoxysilane, followed by washing of the separated solid with a mixture of diethylether–dichloromethane in a Soxhlet apparatus.

Calorimetric and FTIR analyses of the interaction of water with the MTS surface grafted with either propyl chains or 3-aminopropylsilane chains, suggested the preservation of the hydrophilic patches of the MTS surface and the decrease of the isolated silanol groups during the grafting procedure. These results were in agreement with an anchorage of the silane chains taking place mainly onto the hydrophobic patches. Hence, a fraction of siloxane bridges was also involved in the grafting of functional alkylsilane through nucleophilic substitution at the silicon atom [87]. As a consequence of this mechanism, anchored alkylsilane chains are surrounded by uncovered hydrophilic parts consisting of hydrogen-bonded silanol groups.

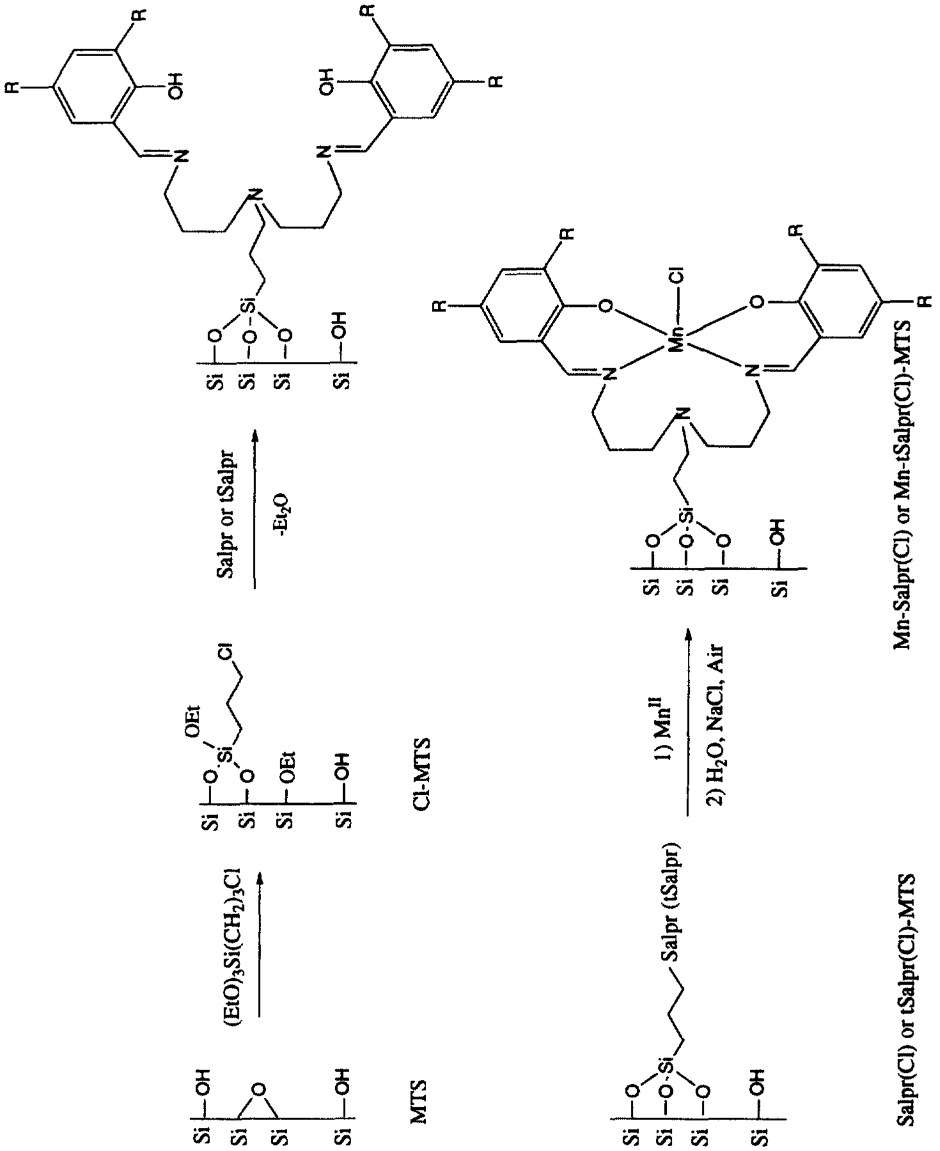
In order to covalently anchor salen-type ligands, 3-chloropropylsilane chains were previously grafted onto the MTS surface leading to Cl–MTS (Scheme 6).

The chloro atoms of Cl–MTS were further replaced by Salpr or *tert*-Salpr molecules [88]. These pentadentate ligands possess a secondary amine group which allowed the partial nucleophilic displacement of the chlorine atom. Moreover this amine function may act as an additional apical ligand usually added to tetradentate salen complexes in order to improve their catalytic activity [89] (Scheme 7).

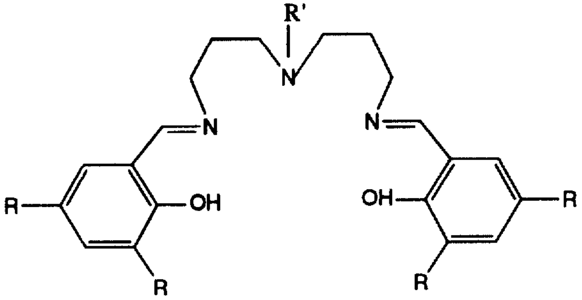
Identification of the grafted organic chains was achieved by FTIR, ^{13}C NMR and UV–Vis spectroscopies by comparison of the spectra of modified MTS solids with those of the corresponding molecules in solution. The infrared spectra of Salpr–MTS and *t*Salpr–MTS exhibited the characteristic signals of Salpr and *t*Salpr molecules, respectively, in addition to the C–H vibration bands of the propyl chains. The vibration band characteristic of ethoxy groups was not observed besides the bands assigned to the methylene groups of the propyl silane chains. Disappearance of these alkoxy groups could be explained by a third Si–O–Si bonding formation during the coupling reaction (Scheme 6). This supplementary Si–O–Si anchorage probably resulted from further alkoxysilane substitution catalyzed by nucleophilic assistance by the amine function of the Salpr or *t*Salpr. This result is in agreement with previous work concerning the nucleophilic or basic assistance for silicon substitution reported by Corriu *et al.* [90,91] and Leyden *et al.* [92,93].

^{13}C MAS-NMR spectra of Salpr–MTS and *t*Salpr–MTS samples showing the characteristic signals of the corresponding ligands in solution are in good agreement with the occurrence of the coupling reaction by a partial substitution of the chlorine.

Textural properties of the materials were analyzed by both X-ray diffraction and nitrogen adsorption measurements. Fig. 4 shows nitrogen adsorption and desorption isotherms of the parent MTS and Cl–MTS, Salpr–MTS and *t*Salpr–MTS samples. The isotherms of the modified MTS always featured the type IV isotherm characteristic of the uniform pore size. These analyses indicated the preservation of the textural properties of the mineral support during the grafting experiments. Nevertheless,



Scheme 6. Mn(III) Salpr complex grafting on MTS materials.



R' = H , R = H : Salpr
R' = H , R = tBu: tSalpr
R' = CH_3, R = H : Smdpt

Scheme 7. Structure of Salpr, *t*Salpr and Smdpt ligands.

surface area and mesoporous volume decreased at each stage of the modification (Table 1). The changes observed were consistent with progressive homogeneous lining of the pore walls by the anchored organic chains reducing the accessible diameter of the pores estimated by the ratio $4V_{meso}/S$. On the other hand, the value of the BET parameter, C_{BET}, decreases from the parent MTS to Salpr–MTS or *t*Salpr–MTS via Cl–MTS. Such a variation suggested a decrease in the average polarity of the surface as this parameter is related to the adsorption enthalpy of nitrogen adsorption ($\Delta H_{ads} = \Delta H_L + RT \ln C_{BET}$) due to the quadrupolar moment of the nitrogen molecule.

The metal chelation process was adapted to avoid the loss of the ordered porosity of the MTS support. Hence, manganese atoms were introduced by means of mild exchange between Mn(II)$(acac)_2$ and the grafted salen-type ligands under inert atmosphere.

The success of the complexation reactions was monitored by dosing of the 2,4-pentadione formed during the ligand exchange and by EPR spectroscopy of grafted Mn(II) Salpr or Mn(II) *t*Salpr which showed a strongly distorted sextuplet signal at $g = 2$, typical of an unsymmetrical complex. Moreover, the comparison of

Table 1
Textural properties of parent and modified MTS

Solid	S_{BET} ($m^2 g^{-1}$)	V_{meso} ($mL g^{-1}$)	C_{BET}	Pore diameter ($4V_{meso}/S_{BET}$) (nm)
MTS	947	0.72	121	3.2
Cl–MTS	790	0.47	60	2.4
Salpr–MTS	648	0.37	49	2.3
*t*Salpr–MTS	671	0.39	51	2.3
Mn–Salpr–MTS	624	0.37	52	2.3
Mn–*t*Salpr–MTS	672	0.41	55	2.4

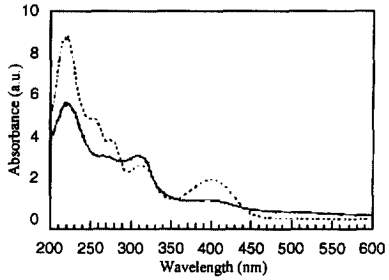


Fig. 5. UV–Vis spectra of Salpr–MTS (- - -) and Mn(II)Salpr–MTS (———).

the UV–Vis spectra of the metallated and the parent *t*Salpr–MTS after air oxidation in brine of Mn(II) centres into Mn(III)Cl showed the efficiency of the complexation (Fig. 5). The patterns of these spectra, which are very similar to those of the corresponding Mn(III)(Cl)Smdpt complex and Smdpt ligand, respectively, were in agreement with such an assumption. Organic moieties and manganese contents of the modified MTS are summarized in Table 2. These results confirm that the substitution of each ligand molecule from the chlorine atoms was partial. Nevertheless, the yield of substitution is higher for the less hindered ligand. But the complexation yield is higher for the bulkier ligand. That suggested control of the first reaction by steric hindrance and a higher accessibility of the metallated reactant to the ligand when it is more dispersed. Hence, homogeneous distribution of the grafted chains would result from the use of anhydrous and apolar solvent which would avoid an island-type grafting. On the contrary, this latter coverage would be favoured by wet conditions and polar solvent through a polymerization reaction induced by hydrolysis of the alkoxy group of the silanating agent.

Both activity and stability of the immobilized complexes were studied in the styrene epoxidation using different oxygen donors [94]. The results are summarized in Table 3. Reaction carried out in the same experimental conditions as the homogeneous reaction reported by Jacobsen [95] and Katsuki [96], using NaOCl in a buffered solution, failed due to the collapse of the inorganic mesoporous skeleton by hydrolysis of Si–O–Si bridges followed by silica recondensation in alkaline conditions.

Table 2
Content in organic moieties and manganese complexes of modified MTS

Solid	3-Chlorosilane 10^{-4} (mol g^{-1})	Salpr or *t*Salpr 10^{-4} (mol g^{-1})	Mn–Salpr or *t*Salpr 10^{-4} (mol g^{-1})
Cl-MTS	10.0	–	–
Salpr–MTS	7.0[a]	3.0	–
*t*Salpr–MTS	9.0[a]	1.0	–
Mn(III)–Salpr–MTS	7.0[a]	1.3[b]	1.7
Mn(III)–*t*Salpr–MTS	9.0[a]	0.0[b]	1.0

[a] 3-Chlorosilane content after ligand grafting or metal complexation.

[b] Non-complexed ligand content after metal complexation.

Table 3
Epoxidation of styrene using various oxygen donors on MTS-based catalysts

Catalyst	Solvent	Oxygen donor	Conversion (%)	Selectivity (%)
Mn(III)–Salpr–MTS	Buffered solution, pH = 11.3	NaOCl	0	–
Mn(III)–Salpr–MTS	Acetonitrile	H_2O_2	0	–
None	Acetonitrile	PhIO	0	–
Mn(III)–Salpr–MTS	Acetonitrile	PhIO	53	58
Mn(III)–*t*Salpr–MTS	Acetonitrile	PhIO	44	24

Unfortunately, reactions achieved using H_2O_2 as oxidant donor led to peroxide decomposition according a Fenton's type reaction around the metallic centre. Moreover, addition of imidazole, known to favour heterolytic cleavage of the peroxo bond [97], failed to inhibit the autoxidation of the oxidant.

Indeed, Manganese(III) salen-type complexes are known to be efficient catalysts when iodosyl arenes are used as an oxygen source [98,99]. With PhIO as oxygen donor, Mn(III)(Cl)Salpr–MTS and Mn(III)(Cl)*t*Salpr–MTS exhibited reasonable activities under the used experimental conditions (styrene/PhIO/Mn = 80/160/1; solvent: acetonitrile). The relatively low selectivity in epoxide formation resulted from the formation of by-products, mainly adsorbed on the catalyst surface. This phenomena would explain the lower epoxystyrene selectivity observed with the bulkier system Mn(III)(Cl)*t*Salpr. The preparation of MTS supports with larger pore diameters and passivation of the residual surface silanol groups which are probably the adsorption sites of the final catalysts are in progress in order to improve their catalytic efficiency.

Another possible route deals with the research of H_2O_2 resistant complexes. In this respect, interesting results were reported in the literature by De Vos et al. [100] concerning the use of the manganese complex of the triamine 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn) as catalyst for highly selective epoxidation of many alkenes with an efficient use of H_2O_2. This triamine ligand, synthesized according to an improved Richman–Atkins procedure [101] was also encapsulated inside Mn faujasite and led to higher selectivity in styrene, cyclohexene and norbornene epoxidations using *t*BuOOH or H_2O_2 as oxygen donors [102]. Finally 1,4,7-triazacyclononane (tacn) ligand was also grafted onto the MTS surface via surface glycidation and subsequent additional *N*-alkylation with a hydroxyethyl group according Hancock *et al.* [103] and Bolm *et al.* [104]; such a material was revealed to be an excellent catalyst to achieve styrene and cyclohexene epoxidation in the presence of $Mn(SO_4)_2$ and H_2O_2 [105,106]. This result hence emphasized that the possible application of such well-ordered hybrid materials can be developed. Moreover, immobilization of the transition-metal complexes inside the mesoporous volume thanks to covalent linkage onto the surface allows a stronger anchorage and a better dispersion of the catalytic phase than single impregnation [107,108] or exchange [109,110].

4.4. (−)-Ephedrine bound onto MTS surface and application in enantioselective alkylation of benzaldehyde by dialkylzinc

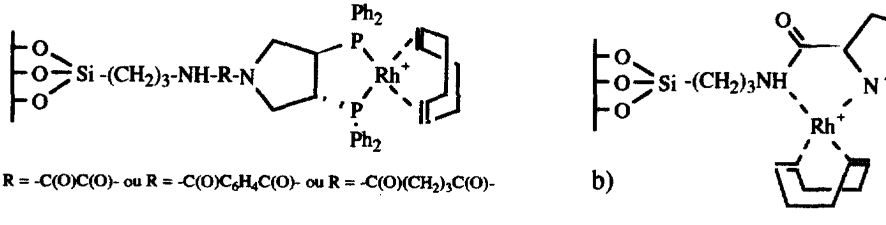
The design of chiral solids able to perform enantioselective catalysis constitutes an important target in chemical synthesis [111–115]. The first application of silica-supported optically-active transition-metal complexes was reported by Nagel et al. [116] on the stereospecific catalysis hydrogenation of α-(acetyl-amino) cinnamic acid and its methyl ester, in the presence of rhodium complexes of 4-(*R*,*R*)-bis(diphenylphosphino)pyrrolidine bound covalently to silica (Scheme 8(a)).

Corma *et al.* have anchored Rh(I), Ru(II), Co(II) and Ni(II) chiral complexes based on β-aminoalcohols such as (L) prolinol onto silica and modified USY-zeolites (Scheme 8(b)) to perform catalytic hydrogenation of prochiral alkenes [117]. The higher enantioselectivity obtained on the zeolite-supported complex than either silica-supported or unsupported complexes suggested an important role for steric constraints induced by the confined species of zeolite supermicropores (1.2–3.0 nm) [118].

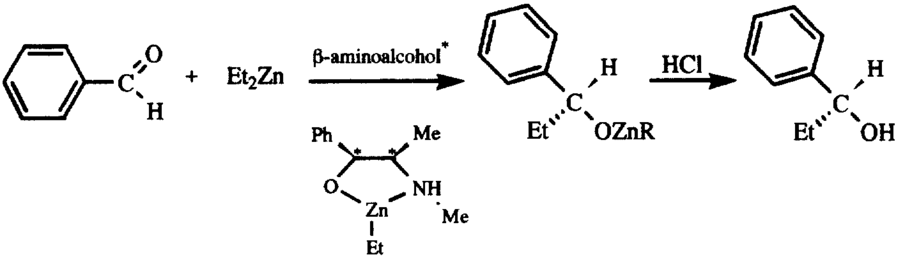
On the other hand, chiral dioxoacetylacetonate Mo(VI) complexes derived from (L) proline and (L)-*trans*-4-hydroxyproline grafted inside USY-zeolite were also active in the enantioselective epoxidation reaction of alkenes with *tert*butyl hydroperoxide as an oxygen source. The increase of enantioselectivity, though low, when the complexes are incorporated into zeolites is a systematic finding [119].

Several methods have been reported for asymmetric alkylation of aldehydes with dialkylzincs using chiral aminoalcohols as catalysts, either in homogeneous [5,120–123] or heterogeneous conditions (Scheme 9) [20,21,123–126]. *N*-alkylephedrines, *N*,*N*-dialkylnorephedrines, 3-*exo*-(dimethylamino)isoborneol and cinchona alkaloids were investigated as β-aminoalcohols. The active catalytic site consisting in zinc complex, as shown in Scheme 8, was proposed from separation and recycling experiments when it was supported on polymers [20] and from *ab initio* molecular orbital study [127].

The only example of chiral aminoalcohol grafted on mineral supports to achieve enantioselective alkylation of aldehyde concerns ephedrine anchored onto the alumina and silica surface [126]. Nevertheless enantiomeric excesses (*ee*%) were relatively low compare to the results obtained in homogeneous catalysis or with the corresponding polymer-supported catalysts (*ee* 74–81%).



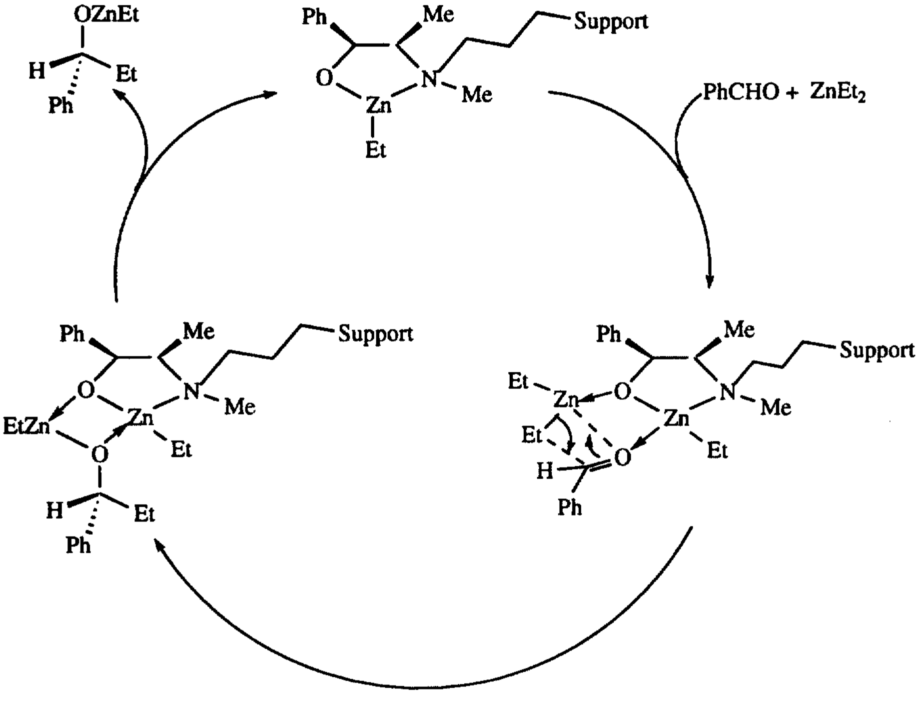
Scheme 8. Chiral rhodium complexes ancored onto mineral oxide surface: (a) silica surface according Ref. [116]; (b) modified USY-zeolite according Refs. [117,118].



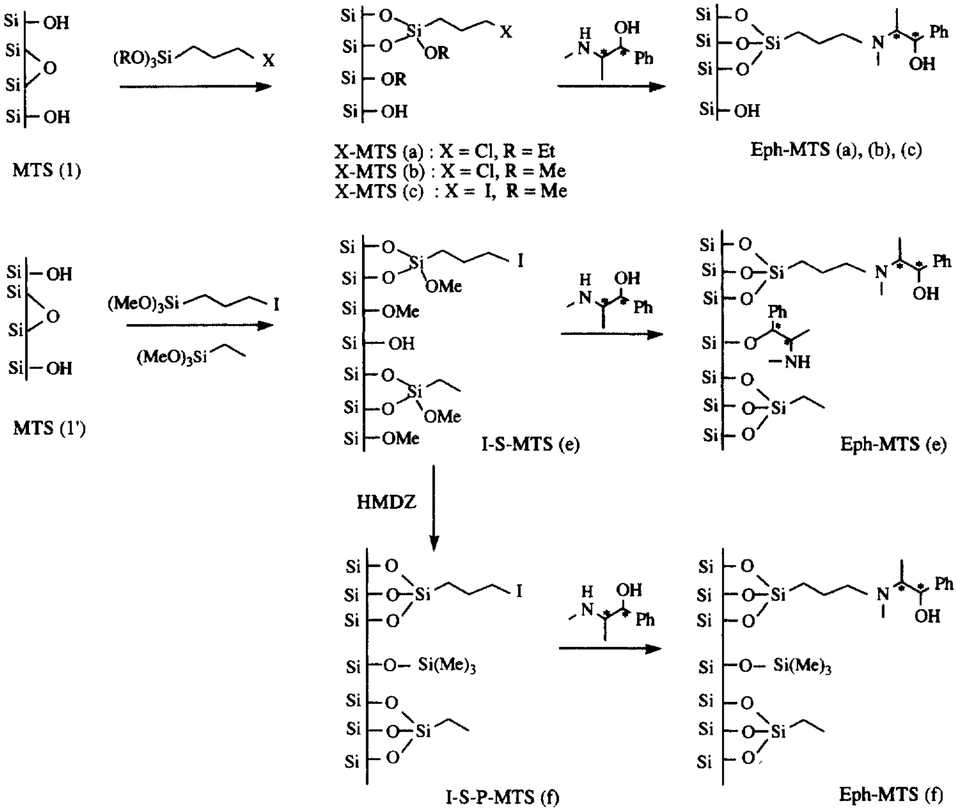
Scheme 9. Enantioselective alkylation of benzaldehyde with diethylzinc using chiral ephedrine.

Taking into account the possible beneficial effect of confinement induced by supermicropores of Y zeolite during other enantioselective catalysis and heterogeneous distribution of the grafted chiral centres on the silica surface, we have investigated the ephedrine grafting onto the MTS surface with the aim to take benefit of both the probable homogeneous distribution of the catalytic sites and textural properties of the support during the catalytic cycle shown in Scheme 10.

The immobilization of (1*R*,2*S*)-ephedrine has been carried out over two types of silicas — MTS (1) and MTS (1′) — by a coupling reaction performed on a previously anchored 3-halogenopropyl silane onto the MTS surface



Scheme 10. Catalytic cycle during the enantioselective alkylation of benzaldehyde with diethylzinc.



Scheme 11. Surface modification and ephedrine grafting of MTS materials.

(Scheme 11) [128,129]: Cl–MTS (a) resulted from MTS functionalization using 3-chloropropyltriethoxysilane, whereas Cl–MTS (b) and I–MTS (c), obtained from MTS (1) and I–MTS (d) obtained from MTS (1′), corresponded to the same treatment with 3-chlorotrimethoxysilane and 3-iodopropyltrimethoxysilane, respectively. Nucleophilic substitution of the halogen led to the Eph–MTS samples.

The dispersion of the active sites has been investigated in order to study the effect of site proximity on the catalytic activity, the selectivity in 1-phenyl-propan-1-ol and the enantioselectivity of the reaction. This goal was performed by dilution of 3-halogenopropyltrialkoxysilanating agent with ethyltrimethoxysilane during the silanation step to lead to the I–S–MTS (e) sample, where S stands for spacers. This modified solid was then treated by ephedrine to yield the Eph–MTS (e) sample.

Moreover, in order to passivate the residual silanol groups which can interact with the OH group of ephedrine during the coupling reaction, I–S–MTS (e) was treated with hexamethyldisilazane (HMDZ) [130] forming I–S–P–MTS (f) before halogen substitution by ephedrine to yield the functionalized Eph–MTS (f). The textural characteristics, composition of supported MTS and amounts (mol g^{-1}) of

Table 4
Characterization of supported MTS silicas

Grafted CPS					Grafted chiral ephedrine				
	Solids	N_X (mol g^{-1}) $\times 10^4$	S (m^2 g^{-1})	V_{mp} (mL g^{-1})	Eph–MTS	N_X $\times 10^4$	N_E $\times 10^4$	S_{BET} (m^2 g^{-1})	V_{meso} (mL g^{-1})
MTS	(1)		962	0.74					
Cl–MTS	(a)	12.8	739	0.42	(a)	2.9	8.8	631	0.29
Cl–MTS	(b)	14.3	701	0.41	(b)	6.1	8.3	620	0.28
I–MTS	(c)	16.1	608	0.27	(c)	4.8	11.3	311	0.13
MTS	(1′)		630	0.40					
I–MTS	(d)	8.8	571	0.23	(d)	0.6	9.4	373	0.16
I–S–MTS	(e)	4.6	598	0.30	(e)	0.4	5.8	576	0.27
I–S–P–MTS	(f)	4.3	563	0.24	(f)	0.9	3.4	554	0.26

grafted moieties for solids bearing either a halogen function or an ephedrine function, N_X and N_E, respectively, are listed in Table 4.

Whatever the solid, the substitution of the halogen atom by ephedrine was not quantitative. In most of the cases, conservation of the total number of grafted species was observed, which confirms that, in most cases, ephedrine essentially substituted the halogen atom. Nevertheless, in the case of Eph–MTS (e) for which this number was higher, the excess of total grafted species was explained by the presence of ephedrine directly bound to the silica surface through hydroxyl group attack, as shown in Scheme. 11. This direct linkage of the ephedrine molecule was explained by the higher accessible surface of the Cl–MTS (e) sample than the one of Cl–MTS (c). This may be due to the lower surface coverage by the layered organic chains, occurring with shorter chains of the spacers [131].

The surface area and mesoporous volume of X–MTS decreased with an increase of the number of functions grafted and substitution of the halogen by ephedrine led to a further decrease of both surface area and available mesoporous volume.

The catalytic activities and selectivities of the supported (−)-ephedrine in the enantioselective addition of diethylzinc are reported in Table 5.

The results clearly showed that supported catalysts are considerably less active and selective than in homogeneous conditions. Toluene (entries 0–2, 4, 5) or hexane (3, 6–9) have been used as solvents. Comparison of entries 2 and 3 for example, shows that higher rates are obtained with hexane. The (*R*)-1-phenyl-propan-1-ol is obtained with moderate enantiomeric excess. Moreover, an increase of the rate is observed when spacers are present (entry 8) and when passivation of the surface is carried out. In order to rationalize this variation, initial rates were fitted as a function of the density of the catalytic sites expressed by N_E/S (mol m^{-2}) in Fig. 6.

The regular increase of the initial rate is consistent with a better accessibility to catalytic sites. Hence the modification with spacers of these modified MTS reduced diffusional limitations. Nevertheless, the rate increase related to the dispersion of the catalytic sites did not favour the enantioselectivity as expected. This was explained by the grafting of (−)-ephedrine through the hydroxyl group for the catalyst

Table 5
Results of asymmetric ethylation of benzaldehyde

Entries	Catalyst	*ee* (%)	Selectivity (%)	r_0 (mol L^{-1} h^{-1}) × 10^3
0	Without[a]	0	45	0.6
1	(−)-Ephedrine[a]	67	97	97.7
2	(a)[b]	37	87	5.0
3	(a)[c]	35	90	11.3
4	(b)[b]	37	84	5.5
5	(c)[b]	23	58	2.9
6	(c)[c]	23	61	3.9
7	(d)[c]	33	84	6.4
8	(e)[c]	26	85	13.6
9	(f)[c]	33	89	19.0

[a] Homogeneous conditions in toluene; [b] toluene as solvent (8 mL); [c] hexane as solvent (9 mL). Benzaldehyde: 1 mmol; Et_2Zn: 2.3 mmol; catalyst: 0.085 mmol. Temperature 0 °C.

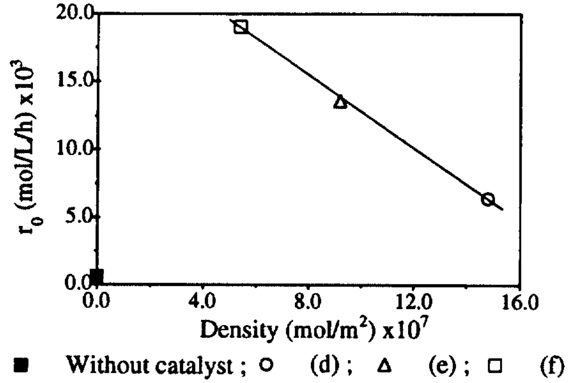


Fig. 6. Variation of initial rate with density of ephedrine moieties.

Eph–MTS (e) which induced a decrease of the enantiomeric excess when the reaction is performed at a constant number of catalytic sites. It is noteworthy that passivation of residual silanols slightly enhanced the enantiomeric excess as shown by comparison of entries 8 and 9 probably by means of the reduction of the ephedrine–surface interactions or reaction.

Future studies are aimed at better monitoring of the interactions between the active catalytic phase and its local environment. Work by using MTS silica with higher pore diameters is also in progress to examine possible diffusional problem.

5. Conclusion

MTS materials featuring an ordered mesopore system of monodispersed pore size and exhibiting larger pores than zeolites, revealed promising opportunities as catalyst supports. Moreover, their surface shows particular distribution of silanol and siloxane groups leading to the coexistence of hydrophilic and hydrophobic patches. This particular chemical nature of their surface hence provides ideal configuration to allow anchorage of organic moieties by silanation procedure. The hybrid materials thus obtained show well-defined organic chains homogeneously dispersed on their surface in addition to preserved textural properties of the support.

The grafting of salen-type complexes onto the wall surface allows the design of new oxidation catalysts which may constitute an alternative to encapsulation of transition-metal complexes inside the microporous voids of zeolites. This strategy was further adapted to the preparation of new adsorbents for heavy metals [132,133].

Immobilization of organic chains possessing chiral centres in the new environment of the catalytic sites provides new supported chiral catalysts effective in enantioselective synthesis.

Nevertheless, interaction between active sites and the solid surface deserves further study and recycling of immobilized catalysts should be investigated to allow wide applications of these new nanostructured materials in heterogeneous catalysis.

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