The structural origins of superior performance in sol–gel catalysts

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Why do sol–gel catalysts often show superior performance in terms of selectivity, stability and reactivity? This work is an attempt to provide a rationale which could be used as a predictive tool in the development of novel catalysts for chemical conversions that will be crucial to achieve a more sustainable development.

1. Introduction

Catalysis by sol–gels—chemical conversions mediated by porous glasses containing catalytic species entrapped within their internal vast porosity—is a developed chemical technology[1] offering unique advantages which include ease of materials production in various forms (powder, monolith, rod, disc, thin film, coating *etc.*) and application. Enzymatic conversions 10 times faster than in solution;[2] reactions at the surface of silica-entrapped living bacteria;[3] one-pot consecutive conversions with mutually destructive reactants;[4] fast conversions in carbon dioxide;[5] selective activities higher than in solution;[6] and commercial asymmetric syntheses with full recovery of the precious catalyst[7] are only few selected examples of the new possibilities opened by these functional materials.

The common structural feature producing all these applications is the entrapment of the dopant molecules in the inner porosity of an highly porous nano- or mesostructured oxide matrix; a phenomenon which imparts unique chemical and physical properties to the resulting doped ceramic.[8]

In general, the process to obtain the sol–gel catalyst consists of the synthesis of an amorphous inorganic network by hydrolysis and polycondensation of a metal alkoxide in the presence of a solution of the catalytic species.[9] Taking silica as an optimal catalyst support[10] the overall hydrolytic polycondensation reaction can be written as in eqn. (1):

$$n\mathrm{Si(OR)_4} + m\mathrm{H_2O} \rightarrow \mathrm{Si}_n\mathrm{O}_{2n-(a+b)/2}\mathrm{(OH)}_a\mathrm{(OR)}_b + (4n - b)\mathrm{ROH} \qquad (1)$$

Alkoxides are soluble in common organic solvents and, being easily hydrolysed, provide a convenient source for "inorganic" monomers which are further condensed into polymeric species composed of metal–oxygen–metal bonds. Actually, this reaction never results in the formation of the pure oxide, and it is precisely the fact that $a \neq 0$ and that a large number of unreacted silanol groups exist at the material's surface that gives rise to the impressive variety of chemical applications of doped sol–gel materials.[8]

The structure of the sol–gel material evolves sequentially, being the product of successive and/or simultaneous hydrolysis, condensation and their reverse reactions (esterification and depolymerization). Thus, by chemical control of the mechanisms and kinetics of these reactions (namely the catalytic and reaction conditions) it is possible to tailor the textural and surface structural properties of the gel over a wide range by solution chemistry, rather than by surface or colloidal chemistry.[11]

Furthermore, organically modified oxides are easily formed co-polymerizing an organo-derived alkoxide with a fully hydrolysable precursor such as in the case of Ormosils (organically modified silicates) obtained, for instance, by copolymerization of TMOS (tetramethylorthosilicate) and methyltrimethoxysilane (MTMS):

$$\mathrm{CH_3Si(OCH_3)_3} + \mathrm{Si(OCH_3)_4} \xrightarrow[\text{cat.}]{\mathrm{H_2O,\ MeOH}} [\mathrm{(CH_3)SiO}_n\mathrm{H}_m]_p \qquad (2)$$

But why, in general, do sol–gel catalysts offer superior performance in terms of selectivity, stability and activity? What are the structural factors governing the behaviour of sol–gel entrapped catalysts? This work aims to provide a general picture of such structure—activity relationship.

In the following, results obtained with silica xerogels doped with TPAP (tetra-*n*-propylammonium perruthenate) and TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl radical) employed in oxidation catalysis are often discussed, but similar findings with different sol–gel catalysts in different chemical conversions[1] show that the conclusions can be generalized.

2. Results and discussion

Three factors play a major role in affecting the performance of sol–gel entrapped catalysts:

1. The encapsulation itself;
2. The hydrophilic–lipophilic balance (HLB) and
3. The textural properties.

2.1 Encapsulation

Figs. 1a and 1b show the SEM photographs of an organically-modified silica gel doped with TPAP obtained by co-polymerising 25% TMOS and 75% MTMS: A solid aerobic oxidation catalyst whose activity shows a 7-fold activity

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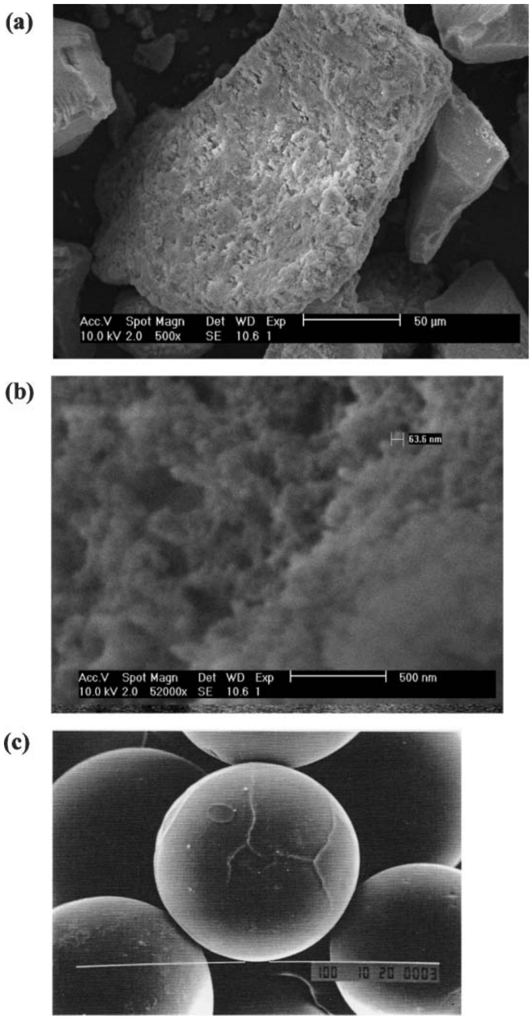


Fig. 1 SEM photographs of a 75% methyl-modified silica gel doped with TPAP (**TP-Me3**, a and b) compared to a polystyrene-supported metal catalyst (c, photo courtesy of Prof. Anthony Barrett).

enhancement compared to perruthenate in solution (70 h^{-1} *vs.* 10 h^{-1} in terms of TOF).[12]

Entrapped in this Ormosil, NPr_4RuO_4 does not leach in solution and smoothly mediates the conversion of a variety of structurally different alcoholic substrates in the presence of 1 bar O_2 at 70–80 °C:

$$\mathrm{RR'-CHOH+1/2O_2}\xrightarrow[\text{toluene, 75 °C}]{\textbf{ormosil-TPAP}\text{ 0.1 equiv.}}\mathrm{RR'{-}CHO+H_2O} \quad (3)$$

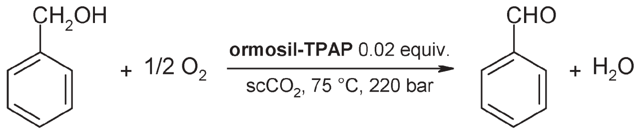
On the other hand, in the same aerobic oxidation perruthenate supported at the surface of polystyrene beads is unstable towards leaching and cannot be reused,[13a] whereas RuO_4^- ionically bound to the mesoporous channels of crystalline MCM-41 silica (a molecular sieve) can be reused for the conversion of benzylic and allylic alcohols only.[13b]

Comparison between the SEM photograph of an analogous metal catalyst supported over polystyrene beads (Fig. 1c)[14] with photographs in Figs. 1a and 1b clearly reveals that the nanostructured spongy shape of the aggregate of organosilica particles in the sol–gel catalyst is completely different compared to the non-porous, smooth surface of the organic polymer bead. Indeed, instead of bearing the active species tethered at the *external* surface of an inorganic or organic material, the sol–gel organosilica entraps and protects the dopant molecules within its internal porosity, with important consequences for either the reactivity and the applicability of the catalyst.

The XPS analysis of the same Ormosil doped with 1.7 wt% TPAP (Fig. 2), for instance, is not capable of detecting the entrapped ruthenium even upon two minutes sputtering of the surface with Ar^+ ions accelerated at 4 keV to remove contaminants, showing indirectly how deep is the encapsulation of Ru in this catalyst (Table 1).

The sol–gel entrapment has three main consequences. First, a sol–gel (silica) matrix physically and chemically *stabilizes* the dopant, which is of crucial importance in catalytic applications where long-term stability of the catalyst is required. Second, it alters the catalyst *selectivity* since it dictates the approach of incoming reactants to the active center. Third, it enhances the *reactivity* due to extreme dispersion of the dopant in the ceramic matrix.

Again, this is shown by the sol–gel Ormosil-entrapped TPAP and TEMPO. Employed in the oxidative dehydrogenation of benzyl alcohol in supercritical CO_2, the 75%-methyl modified catalyst **TP-Me3** has one of the highest turnover number (140) thus far reported for a Ru-based aerobic catalyst:[15]



(4)

The material can be reused in consecutive reaction runs, while in organic solvent the precious TPAP catalyst cannot be recycled due to association of the reduced Ru species gradually yielding a black sol precipitate;[16] a chemical process which here is *intrinsically* prevented by the encapsulation of the $[NPr_4]^+[RuO_4]^-$ ion pair within the organosilica cages (electronic spectrum unchanged prior and upon reaction).

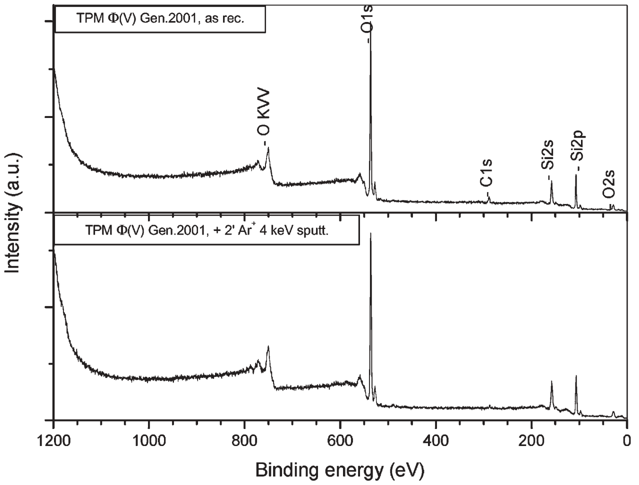


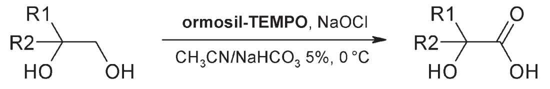
Fig. 2 XPS spectrum of the 75% methyl-modified Ormosil doped with 1.7 wt% TPAP (**TP-Me3**).

Table 1 Surface elemental composition of **TP-Me3** from XPS analysis before and upon 2 min sputtering with Ar^+ at 4 keV

	O1s (%)	Si2p (%)	C1s (%)	O/Si
As rec. (pellet)	64.2	26.8	9.0	2.4
Upon sputtering	66.1	33.9	—	1.9

There is a clear activity enhancement upon encapsulation since now a 2 mol% catalytic amount of Ormosil-entrapped TPAP can be efficiently employed affording high yields of dehydrogenated product (eqn. (4)), in contrast to the optimal 10 mol% amount of TPAP required under homogeneous conditions.[16] Finally, the first-order kinetics for the catalyst (Fig. 3) shows another unique feature of sol–gel entrapped catalysts compared to traditional solid catalysts obtained by heterogenization of a material's external surface, which in general do not show a first-order rate law dependence for the catalyst.

The relevant effect of encapsulation on the selectivity of the entrapped catalyst is clearly shown by the radical TEMPO, which in solution is an unselective mediator of aminodiol oxidation with hypochlorite whereas, entrapped in a 100% methyl-modified Ormosil matrix, it turns into a highly selective catalyst affording high yields of valuable aminohydroxy-acids.[17a] Again, the result is general and other compounds with potent biological activity such as α-hydroxy acids can be synthesised from diols using the same hydrophobized silica matrix doped with TEMPO:[17b]



(5)

The sol–gel encapsulation of the nitroxyl radical markedly improves its chemical stability relative to TEMPO tethered to the external surface of commercial silica, in which deterioration occurs due to intermolecular quenching of the radical moieties left unprotected at the material surface.[18a] Entrapped within the silica cages, intermolecular quenching is prevented leading to a remarkably high chemical and physical stability as proved by full retention of its (high) chemical reactivity and by ESR and FTIR spectroscopies.[18b]

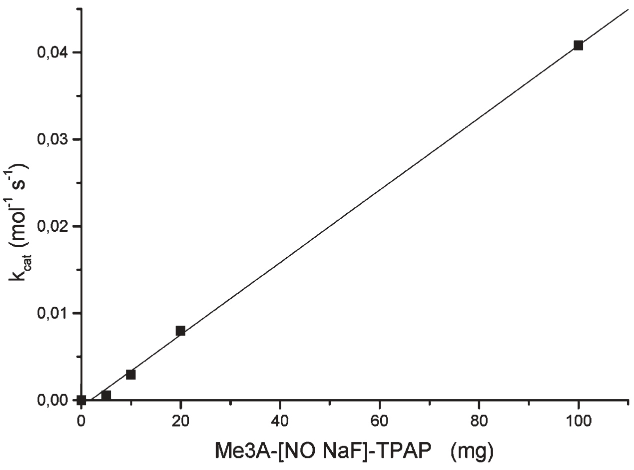
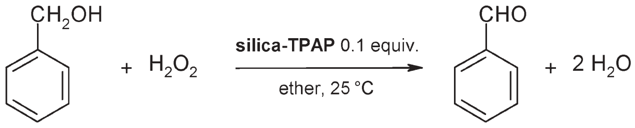


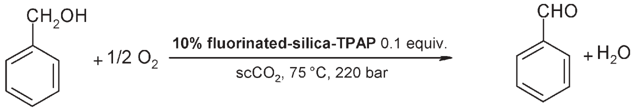
Fig. 3 Kinetic order in catalyst in the oxidation of benzyl alcohol with O_2 catalysed by 75% methyl-modified Ormosil **TP-Me3** in CO_2 at 75 °C and 22 MPa.

2.2 HLB

As expected, chemical affinity between the matrix and hydrophobic organic substrate/product favours diffusion through the porous network but the effects of the hydrophilic–lipophilic balance of the sol–gel matrix on the reactivity of the resulting material are subtle, and other factors besides enhanced diffusivity must be taken into consideration. For example, while alcohols oxidation with hydrophilic H_2O_2 proceeds best over an unmodified SiO_2 gel doped with TPAP (eqn. (6)),[19a] the optimal aerobic process in supercritical CO_2 requires a 10% fluorinated silica matrix (eqn. (7)).[19b]



(6)



(7)

Similarly, a 5% methyl-modified silica matrix doped with Rh is required to promote the catalytic hydrogenation of organic substrates emulsified in water,[20] with more hydrophobic matrices retaining the substrate/product within the pores, and more hydrophilic xerogels being *too* polar to promote the required spilling of the substrate into the cages entrapping the catalyst.

On the other hand, highly hydrophobic (75 to 100% organically modified) sol–gels impart a 100 to 800% rise in activity which are typically observed on going from TMOS- to MTMS-derived gels (eqn. (2)) for entrapped lipases[2] or for entrapped TPAP[12] employed in organic solvent. However, such large activity enhancements are *not* due to significant differences in cross-linking;[21] but rather to the enhancement of the mobility of the dopant molecules within the hydrophobic cages, as a consequence of the reduction of the constraints imposed by the strong hydrogen bonding silanols at the surface of unmodified silica cages.[2,8,12]

Indeed, the distribution of the organic residues attached to the Si centers is inhomogeneous, with the organic groups concentrating at the pore's surface.[22] In contrast to entirely amorphous SiO_2 glasses, for example, the X-ray diffractogram of the amorphous 75% methyl-modified silica glass doped with TPAP (Fig. 4) shows *two* maxima at $2\theta \sim 23°$ and $2\theta \sim 8°$ pointing to two Bragg *d*-spacings (d_1 = 9.61 Å and d_2 = 3.91 Å) which originate, respectively, from the constant nearest silicon atoms in the siloxane Si–O–Si units and from the discrete structural units (mostly 4-ring and 6-ring siloxanes)[11] in the xerogel matrix.[23]

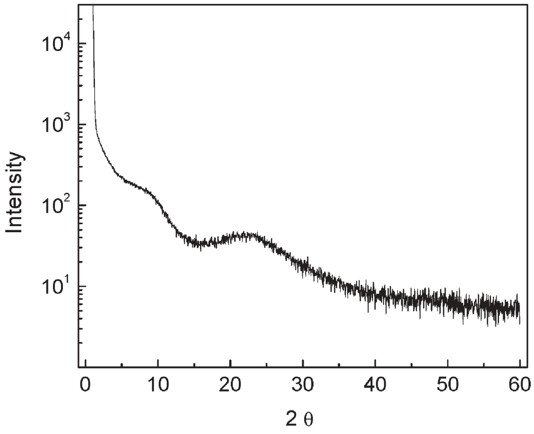


Fig. 4 The X-ray diffractogram of the 75% methyl-modified Ormosil doped with TPAP shows two maxima.

2.3. Textural properties

The surface structural differences between the perruthenate-doped silica (**TP-Me0**) employed to catalyse the reaction in eqn. (6) and the 75% methyl-modified organosilica (**TP-Me3**) used to mediate the conversion in eqn. (4) are evident also in the diffuse reflectance infrared Fourier transform (DRIFT)[11] spectra reported in Fig. 5.

Whereas that of the methyl-modified Ormosil **TP-Me3** has the fingerprints of Si–CH_3 groups within the silica network (assigned in Table 2), that of **TP-Me0** is a typical silica xerogel spectrum: The νO–H band is shifted to higher wavenumbers ($\sim$110 cm^{-1}), narrower and much weaker than in the unmodified silica's spectrum; and the position and band shape of the silica ν_{as}Si–O–Si mode are clearly different in the organically modified gel.

As expected, the spectrum clearly points to a much higher degree of lipophilicity in the Ormosil network: the pore surfaces not only contain hydrophobic groups but are also *defective* in hydrophilic ones explaining the greater affinity of TPAP to the hydrophobized cages. The lower relative intensity of the νO–H band in fact suggests that this catalyst is depleted of silanol groups, and such conclusion is complemented by the observed shift and lower relative intensity of the νSi–O_d band (Si–dangling oxygens in the silica network) which contains contributions from νSi–OH and νSi–O^- modes (at $\sim$950 and 910 cm^{-1}, respectively)[11] with the shift from 955 to 916 cm^{-1} corroborating the decreased proportion of silanol groups. Furthermore, adsorbed water in the Ormosil cages is residual, as indicated by the extremely low intensity of the δH–O–H band.

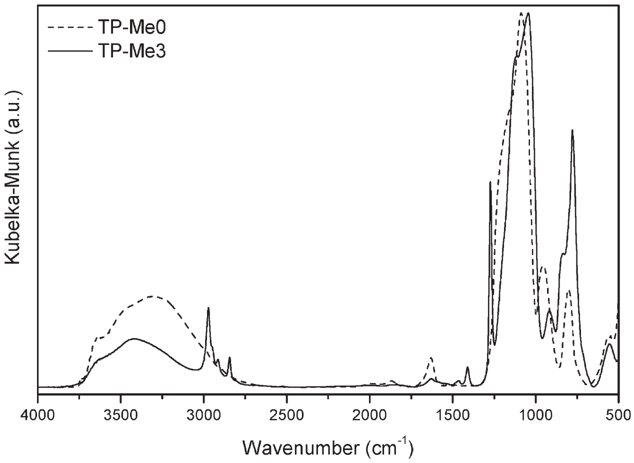


Fig. 5 DRIFT spectra of catalysts **TP-Me0** and **TP-Me3**, normalized to the maximum of the ν_{as}Si–O–Si band.

Table 2 Main band assignments in the DRIFT spectra of xerogels **TP-Me0** and **TP-Me3**

	TP-Me0	**TP-Me3**
Mode assignment	Wavenumber	
νO–H	3309	3423
$\nu_{as}CH_3$	—	2973
ν_sCH_2 (from TPAP)	—	2913
ν_sCH_3	—	2844
δH–O–H	1631	1628
δ_sCH_3	—	1273
ν_{as}Si–O–Si	1088	1045
νSi–O_d	955	916
ρCH_3	—	842
ν_sSi–O–Si	802	—
νSi–C	—	779

Finally, although the concentration of TPAP is low (1.7 wt%), its entrapment may be confirmed by a characteristic feature of the propyl groups, the CH_2 symmetric stretching mode, which is clearly observed in the Ormosil spectrum, at 2913 cm^{-1}; while in the spectrum of unmodified SiO_2 doped with TPAP this is not possible, since the νO–H band is strong and broad, masking any bands in the C–H stretching region.

The *disordered* structure of sol–gel glasses implies a range of porosity that makes it possible the access to external reactants of different size and shape.[24] Therefore, as mentioned above, while perruthenate entrapped within the 26 Å hexagonal channels of crystalline silica MCM-41 is active only with benzyl and allylic alcohols,[13b] TPAP-doped Ormosils are selectively active in the oxidation of a multiplicity of substrates.[5,12]

Accordingly, the BET analysis of 75% methyl-modified xerogel doped with TPAP prepared at high water and co-solvent amounts (Si : H_2O : MeOH = 1 : 8 : 8, in molar terms) shows a type II isotherm typical of a non-porous material whose pore size distribution, shown on Fig. 6, points to the presence of a micropore population.[25] Indeed, the material's large BET surface area (486 m^2 g^{-1}) and inner porosity (0.58 cm^3 g^{-1}) are capable of adsorbing a considerable volume of cryogenic nitrogen ($\sim$500 cm^3 g^{-1}).

These results show the pronounced connectivity present in the organosilica matrix, indicating that the decrease of surface area and pore volume, due to the reduction of the silica network connectivity upon the incorporation of Si nuclei with lower functionality, is effectively *counteracted* by the reduction of the capillary tension at the cage solid–liquid interface (which mitigates the collapse of the network commonly observed in the alcogel → xerogel transition).

Besides hydrophobicity, which is mainly dictated by the relative amount of organosilane, the choice of silane : water : cosolvent ratio in the material preparation largely affects the

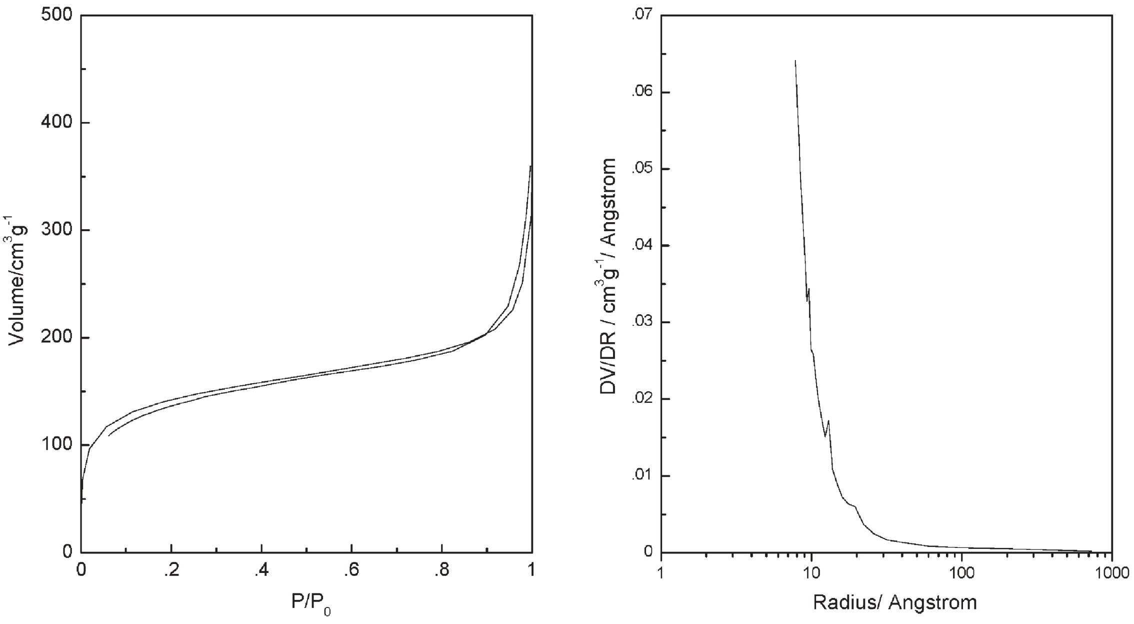


Fig. 6 N_2-BET isotherm and pore size distribution of a 75% methylated Ormosil prepared from a sol containing high amounts of water and co-solvent (Si : H_2O : MeOH = 1 : 8 : 8).

reactivity of the final material. Having to do with the entrapment of a lipophilic metal ion pair it is important to choose reaction conditions that ensure extended hydrolysis of the alkoxide monomers in order to minimise the presence of micellar-like structures in the sol precursor mixture, with part of the (hydrophobic) catalytic species eventually ending segregated into the bulk of the resulting polymeric matrix, and thus inaccessible for catalysis.[12]

Furthermore, the gel obtained in the sol–gel process described in eqn. (1) is chemically unstable, since its alkoxy (OR) groups are subject to further hydrolysis by the presence of unreacted water. Consequently, the dry gel (xerogel) obtained by removal of the residual solvent is also unstable, since the remaining hydroxyl (OH) groups can further condense by exposure to moisture resulting in a "living" material that undergoes structural modifications, even months after preparation. Indeed, when the catalytic 75% methylated Ormosil is prepared starting from a sol containing a low amount of water and co-solvent (Si : H_2O : MeOH = 1 : 4 : 4) a 10-fold increase in reactivity is observed upon 8 months of aging the xerogel at room temperature, due to the migration of the buried Ru active species at the surface of the newly formed porosity.[15]

3. Conclusions

The sol–gel process allows the fabrication of high-performing heterogeneous catalysts capable of meeting the requirements of widely different conversions in similarly various reaction media by proper tailoring of the materials' structural properties. This opens the way to the efficient heterogenization of many homogeneous catalytic systems which thus far could not be commercialized due to difficulties associated with separating the products from the catalyst[26] with the unfortunate result that, still today, *only 20% of the fine chemicals production processes are catalytic* and the remaining 80% of industrial processes normally generate 15–20 kg of by-products for each kg of useful product.[27] The general picture of the structural reasons providing the behaviour of sol–gel entrapped catalysts described in this report provides a unified rational framework of the main factors affecting their chemical behaviour. Hopefully, this will be used as a predictive tool in the development of novel sol–gel catalysts for chemical conversions that will be crucial to achieve a more sustainable development.[28]

4. Experimental

Materials preparation

Methyltrimethoxysilane (MTMS) and tetramethyl-orthosilicate (TMOS), tetra-*n*-propylammonium perruthenate (TPAP), benzyl alcohol, methanol and *n*-decane were purchased from Sigma-Aldrich. Ultra pure water (Millipore Type 1 quality) was used in all the preparations.

Ormosil-TPAP

A typical catalytic Ormosil doped with TPAP such as **TP-Me3** was obtained adding MTMS (4.90 mL) and TMOS (1.95 mL) to a solution of TPAP (55.5 mg) in MeOH (7.30 mL) cooled in an ice bath followed by the addition of H_2O (2.65 mL) under fast stirring. The sol gelled slowly and the alcogel thereby obtained was sealed, left to age at room temperature for 48 h and eventually dried at 50 °C for 5 days. The resulting powder xerogel was washed three times with Et_2O under reflux. A typical catalytic load was 500 μmol TPAP per g Ormosil.

Fluorinated Ormosil-TPAP

Several fluorinated xerogels were prepared by sol–gel processing a fluoro-alkyl containing monomer (3,3,3-trifluoropropyltrimethoxysilane, TFPTMOS, purchased from Fluka) with tetramethylorthosilicate (TMOS) in the presence of TPAP dissolved in methanol, and keeping constant the Si : MeOH : H_2O molar ratio at 1 : 8 : 4. A typical 10% fluoro-propyl doped silica gel was synthesised by adding TMOS (2.68 mL) and TFPTMOS (0.39 mL) to a solution of TPAP (24.5 mg) in MeOH (6.45 mL) cooled in an ice bath, followed by the addition of H_2O (1.44 mL). The mixture was stirred for 30 min when it gelled, yielding a black alcogel which was sealed and left to age at room temperature for 24 h prior to drying at 50 °C (5 days). The grey xerogel thus obtained was powdered, washed under reflux (Et_2O × 2) and dried to 50 °C prior to use.

Ormosil-TEMPO catalysts preparation

The radical species 4-oxo-TEMPO (1 g, 7 mmol) was added to a solution of 3-aminopropyltrimethoxysilane (5 mL, 28 mmol) containing $NaBH_3CN$ (0.220 g, 4 mmol) dissolved in methanol (18 mL). The reaction solution was stirred for 40 h and then the unreacted cyanoborohydride destroyed by the addition of HCl 7 M (1 mL).

The precursor mixture thereby obtained was equally divided in seven portions and each vessel added with different amounts (in subsequent order) of MeOH, alkyl-trimethoxysilane, TMOS and H_2O to yield gels with the chosen total molar ratios Si : H_2O : MeOH = 1 : 8 : 2 or 1 : 8 : 3. Sodium fluoride was added as condensation catalyst in the ratio Si : F = 1 : 0.017 for the preparation of the gel obtained from methyltrimethoxysilane (MTMS) alone. Hence, for example, the gel SG-TEMPO-2 with Si : H_2O = 1 : 2 was obtained adding one vessel of the precursor mixture mentioned above with MeOH (1 mL), MTMS (5.82 mL) and H_2O (5.35 mL). The resulting sol was stirred using a Vortex shaker prior to the addition of aqueous NaF (0.750 mL, 1 M) under fast stirring that resulted in fast gelation. Likewise, all the other sols gelled rapidly yielding elastic alcogels that were left sealed to age for 20 h at room temperature prior to being opened and densified at 60 °C for 3 days during which time the gels further shrank to about half of the initial volume reaching constant weight. The resulting xerogels isolated as pale orange coloured powders, were washed with boiling CH_2Cl_2 (3 × 20 mL, 50 °C) under reflux, dried and used as such in the oxidations.

Representative oxidation procedures. In $scCO_2$

Benzyl alcohol (5 μL, 0.5 mmol) and 0.1 equiv. of fluorinated catalyst (100 mg) were added along with *n*-decane (5 μL, 1 mmol) as internal standard to the reaction vessel and the reaction conditions chosen to ensure complete solubility of the alcohol and of the aldehyde in the homogeneous supercritical phase. Hence, after flushing the oxygen (1 bar partial pressure at ambient temperature), the reaction vessel was sealed and placed into an oven thermostated at 75 °C. Liquid CO_2 was then pumped into the autoclave using a cryogenic pump to bring the reactor pressure at 220 bar while the reaction mixture was kept under stirring at 400 rpm (by means of an alternating magnetic field stirrer) at the set temperature for the desired reaction time. Samples withdrawn through the stainless steel restrictor (kept at 90 °C) were trapped in dichloromethane prior to GC analysis.

In toluene

A solution of substrate alcohol (0.2 mmol) in toluene (4 mL) was added with 0.1 equiv. **TP-Me3** (270 mg) and the suspension brought to 75 °C in an oxygen atmosphere kept sealed in order to avoid product loss at the reaction temperature (oxygen balloon). Aliquots were periodically withdrawn and the carbonyl content assessed by GC, and when reaction was complete the mixture was filtered at 75 °C with the filtrate tested for ruthenium by ICP-MS. The recovered catalyst was washed with CH_2Cl_2 (×3, 60 °C), dried and used as such in the subsequent reaction runs according to the same oxidation protocol.

The reaction with entrapped TEMPO was performed in a glass tube with a cooling mantle equipped at the bottom with a ceramic filter plate and a stopcock to allow easy separation of the catalyst from the reaction mixture. The tube was thus added with a solution of the diol (1 mmol) in water (6 mL)–acetonitrile (6 mL) was then placed in a thermostated reaction vessel, with 135 mg of Ormosil-supported TEMPO (0.1 mmol of TEMPO, according to microanalysis). After the reaction mixture was cooled to 0 °C, an aqueous solution of NaOCl (2.5 mL, ca. 13% w/w) was buffered to a pH of 9.1 by further addition of 5% $NaHCO_3$ (2 mL). The reaction mixture was vigorously shaken until all substrate was consumed (TLC of reaction mixture samples). After filtration, the filtrate was acidified adding 10 mL of a 1 M tartaric acid solution, and the resulting solution extracted with ethyl acetate (3 × 15 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*, and the crude product was purified by column chromatography on silica gel using a CH_2Cl_2–ethyl acetate mixture as eluent.

Structural analyses

The N_2-BET textural values were obtained with a Carlo Erba Instruments Sorptomatic 1900 powder analyzer, and ruthenium contents were measured by ICP-MS on a HP 4500 spectrometer. The surface Ru/Si molar ratio was determined from elemental analysis of the surface, carried out with a JEOL JXA-8600 electron probe microanalyzer equipped with a NORAN Vantage automation system. This method gave the ratio between the external surface-bonded ruthenium and surface Si atoms to a depth of 1 μm. Sample powders were analyzed by powder XRD using Cu Kα radiation ($\lambda = 1.542$ Å). The molecular structure of the xerogels was analysed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, by using a Mattson RS1 FTIR spectrometer with a Specac selector, in the range 4000 to 400 cm^{-1} (wide band MCT detector), at 4 cm^{-1} resolution.

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References

1 For a recent review on the topic, see: R. Ciriminna and M. Pagliaro, *Curr. Org. Chem.*, 2004, **8**, 1851.

2 M. T. Reetz, P. Tielmann, W. Wiesenhofer, W. Konen and A. Zonta, *Adv. Synth. Catal.*, 2003, **345**, 717.

3 N. Nassif, O. Bouvet, M. N. Rager, C. Roux, T. Coradin and J. Livage, *Nat. Mater.*, 2002, **1**, 42.

4 (*a*) F. Gelman, J. Blum and D. Avnir, *Angew. Chem., Int. Ed.*, 2001, **40**, 3647; (*b*) F. Gelman, J. Blum and D. Avnir, *New J. Chem.*, 2003, **27**, 205.

5 R. Ciriminna, S. Campestrini and M. Pagliaro, *Adv. Synth. Catal.*, 2003, **345**, 1261.

6 A. Adima, J. J. E. Moreau and M. Wong Chi Man, *Chirality*, 2000, **12**, 411.

7 Sol–gel organic–inorganic hybrid silica gels doped with chiral complexes are commercialised with the trademark CTIS-CACHy (Chiral Technologies Interface System – Catalytic Asymmetric CyanoHydrin) by the British fine chemicals manufacturer Avecia upon licensing of the sol–gel technology from Johnson Matthey. These catalysts allow efficient heterogeneous conversion of aldehydes and ketones into chiral cyanohydrins, high value building blocks and useful pre-cursors for hydroxyamino acids and amino alcohols.

8 D. Avnir, *Acc. Chem. Res.*, 1995, **28**, 328.

9 Pioneering work on catalysis by aerogels and xerogels was carried out by the team of Teichner at Lyon's University starting in the mid 1970s. For an account on some of the most interesting (photochemical) applications, see: M. Formenti and S. J. Teichner, Heterogeneous Photo-Catalysis, in *Catalysis, A Specialist Periodical Report*, eds. C. Kemball and D. A. Dowden, The Chemical Society, London, 1978, pp. 87–106.

10 Functionalized silica gels are commercial functional materials with a rapidly growing market. Doped silica gels offer several technical advantages over well-known organic resins being solvent-independent (rigid porous structure and no swelling), no non-specific binding, and with an high density of functional groups (small volume of gel required). Silica works in all solvents (organic and aqueous), is easy to weigh and handle, mechanically stable and prone to scale-up. A variety of functionalized silica gels are commercialized by the Canadian company SiliCycle Inc. See also the URL: http://www.silicycle.com/.

11 A. Fidalgo and L. M. Ilharco, *Chem.—Eur. J.*, 2004, **10**, 392.

12 R. Ciriminna and M. Pagliaro, *Chem.—Eur. J.*, 2003, **9**, 5067.

13 (*a*) B. Hinzen, R. Lenz and S. V. Ley, *Synthesis*, 1998, 977. Perruthenate tethering to the inner surface of porous silica has proved to be an effective strategy to achieve a reusable heterogeneous catalyst as shown by its attachment to MCM-41 which affords a reusable composite catalyst thanks to the reduced possibility of forming oxidation inactive colloidal RuO_2; (*b*) A. Bleloch, B. F. G. Johnson, S. V. Ley, A. J. Price, D. S. Shephard and A. W. Thomas, *Chem. Commun.*, 1999, 1907.

14 Photo courtesy of Prof. Anthony Barrett. The picture refers to a polystyrene-supported metallocene prepared as described in: A. G. M. Barrett and Y. R. de Miguel, *Chem. Commun.*, 1998, 2079.

15 TOF = $[\text{mol(alcohol)/mol(Ru)}]\text{h}^{-1}$ calculated assuming full accessibility of the Ru active centers in the Ormosil matrix, as described in: R. Ciriminna, S. Campestrini, M. Carraro and M. Pagliaro, *Adv. Funct. Mater.*, 2005, **15**, 846.

16 M. Hasan, M. Musawir, P. N. Davey and I. V. Kozhevnikov, *J. Mol. Catal. A*, 2002, **180**, 77.

17 (*a*) A double yield of the desired reaction product (from 31 to 62% in the case of chloramphenicol) and half of unselective cleavage product (from 37% to 20%) are typical, as reported in: M. L. Testa, R. Ciriminna, C. Hajji, E. Zaballos Garcia, M. Ciclosi, J. Sepulveda Arques and M. Pagliaro, *Adv. Synth. Catal.*, 2004, **346**, 655. Typically, while the homogeneous oxidation of an aromatic diol yields 24% of α-hydroxy acid, the heterogenous oxidation using a 100% methyl-modified silica xerogel doped with TEMPO leads to an inversion of selectivity with an acid–ketone ratio of 60 : 40, as reported in: (*b*) P. Gancitano, R. Ciriminna, Alexandra Fidalgo, M. Ilharco Laura, M. L. Testa and M. Pagliaro, *Org. Biomol. Chem.*, 2005, **3**, 2389.

18 (*a*) T. Fey, H. Fischer, S. Bachmann, K. Albert and C. Bolm, *J. Org. Chem.*, 2001, **66**, 8154; (*b*) R. Ciriminna, C. Bolm, T. Fey and M. Pagliaro, *Adv. Synth. Catal.*, 2002, **344**, 159.

19 (*a*) S. Campestrini, M. Carraio, R. Ciriminna, M. Pagliaro and U. Tonellato, *Tetrahedron Lett.*, 2004, **45**, 7283; (*b*) R. Ciriminna, S. Campestrini and M. Pagliaro, *Adv. Synth. Catal.*, 2004, **346**, 231.

20 (*a*) R. Abu-Reziq, J. Blum and D. Avnir, *Chem.—Eur. J.*, 2004, **10**, 958; (*b*) R. Abu-Reziq, D. Avnir and J. Blum, *Angew. Chem., Int. Ed.*, 2002, **4**, 4132.

21 The differences in the degree of crosslinking between Ormosils and silica gels derived from pure TMOS in fact are small: M. T. Reetz, *Adv. Mater.*, 1997, **12**, 943.

22 (*a*) B. M. De Witte, D. Commers and J. B. Uytterhoeven, *J. Non-Cryst. Solids*, 1996, **202**, 35; (*b*) L. He, K. Powers, R. H. Baney, L. Gower, R. S. Duran, P. Sheth and S. R. Carino, *J. Non-Cryst. Solids*, 2001, **289**, 97.

23 The relative intensity of the $2\theta \sim 8^\circ$ peak increases as the glass becomes more organically modified due to the increase in the structure long range order, as explained in: (*a*) S. L. B. Lana and A. B. Seddon, *J. Sol–gel Sci.*, 1998, **13**, 461. For a brilliant X-ray structural analysis of Ormosils, see also: (*b*) P. W. Schmidt, D. Avnir, D. Levy, A. Hoehr, M. Steiner and A. Roell, *J. Chem. Phys.*, 1991, **94**, 1474.

24 Geometrical imperfection of the surface is a major contributor to the many applications of sol–gel porous materials due to the variability in the accessibility of the dopant to external reagents through the complex geometry of the pore network. For a thoughtful reflection on the role of imperfection in materials chemistry, see: D. Avnir, in *The History of Colloid and Surface Chemistry in Japan*, ed. K. Sakamoto, The Chemical Society of Japan, Tokyo, 2001, p. 16–17.

25 G. Leonfanti, M. Padovan, G. Tozzola and B. Venturelli, *Catal. Today*, 1998, **4**, 207.

26 D. J. Cole-Hamilton, *Science*, 2003, **299**, 1702.

27 B. M. Choudary, M. Lakshmi Kantam and P. Lakshmi Kantam, *Catal. Today*, 2000, **57**, 17.

28 For a thorough analysis of the economic and social relevance of catalysis, see the report *Catalytic Process Technology*, National Academies Press, Washington, 2000; freely available at the URL: http://www.nap.edu/catalog/10038.html (last time accessed: June 25, 2005).