

# Tailoring the Catalytic Performance of Sol–Gel-Encapsulated Tetra-*n*-propylammonium Perruthenate (TPAP) in Aerobic Oxidation of Alcohols

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**Abstract:** Sol–gel nanohybrid silica particles organically modified and doped with the ruthenium species tetra-*n*-propylammonium perruthenate (TPAP) are highly efficient catalysts for the selective oxidation of alcohols to carbonyl groups with O<sub>2</sub> at low pressure in toluene. The materials are easily prepared by a one-step sol–gel process, and their catalytic performance can be optimised by tailoring the con-

ditions of their synthesis by hydrolytic co-polycondensation of tetramethoxysilane (TMOS) and alkyltrimethoxysilanes R-Si(OMe)<sub>3</sub> in the presence of TPAP. Eventually, heterogeneous catalysts considerably more active than the

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unsupported perruthenate were obtained, while also being leach-proof and recyclable. The correlation between the materials' activity, surface polarity and textural properties suggests valuable information on the chemical behaviour of sol–gel catalytic materials in oxidation catalysis; this is of interest in view of the importance of efficient solid catalysts for the selective oxidation of alcohols with O<sub>2</sub>.

## Introduction

The selective oxidation of alcohols to carbonyl groups has a central role in synthetic organic chemistry and in the fine chemicals industry, often being a key step for the preparation of important synthons or directly affording valuable speciality and fine chemicals products such as fragrances, drugs, vitamins and hormones.<sup>[1]</sup>

Because of increasingly stringent environmental legislation,<sup>[2]</sup> traditional carbinol oxidation processes carried out stoichiometrically in organic solvents, either with toxic and hazardous chromium(vi)<sup>[3]</sup> or manganese(iv)<sup>[4]</sup> reagents or with DMSO,<sup>[5]</sup> will need to be replaced with new ecofriendly catalytic conversions using clean and atom-efficient oxidants such as O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub>.<sup>[6]</sup>

Hence, a remarkable number of new, mild aerobic processes have been reported in recent years, in which impressive levels of selective activity have been achieved mainly by use of Ru,<sup>[7]</sup> Pd<sup>[8]</sup> and Cu<sup>[9]</sup> catalytic species, and in certain cases even eliminating the use of the volatile solvents in which such conversions are generally performed<sup>[8c]</sup> (a feature also shared by a W catalyst with H<sub>2</sub>O<sub>2</sub> as primary oxidant<sup>[10]</sup>).

For all of these catalytic processes, an effective catalyst heterogenization method would be highly desirable<sup>[11]</sup> in

order to allow catalyst recycling (and easy workup of the product mixture) as well as for applications to continuous processes, which are in high demand in industry. Accordingly, many attempts are currently being directed towards the heterogenization of soluble catalytic species in solid materials in which the metallorganic moiety acts as active site and the solid provides avenues for recovery and recycling of the active species.<sup>[12]</sup>

The requirements for such catalysts, however, are demanding. They will need to be highly selective (given the number of different oxidizable groups in fine chemistry molecules) and stable over prolonged times of use. Furthermore, they should also be versatile (i.e., applicable to a vast number of structurally different alcoholic substrates).

Stability of solid catalysts in heterogenized systems is a requirement particularly difficult to achieve,<sup>[11]</sup> since many supported molecules are often labile in oxidative environments and are easily leached in the homogeneous phase, as in the case—relevant to this report—of polymer-supported perruthenate (PSP), a solid catalyst doped with the aerobic ruthenium catalyst TPAP,<sup>[7b]</sup> originally claimed to be heterogeneous,<sup>[13]</sup> but soon found to be unstable and impossible to recycle.<sup>[14]</sup>

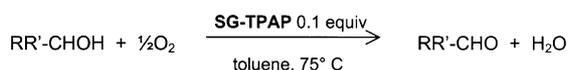
The sol–gel technology for the preparation of reactive materials, on the other hand, is increasingly being used for the preparation of efficient heterogeneous catalysts,<sup>[15]</sup> since it allows the entrapment of practically any active organic species within the vast internal porosity of porous oxides, in which the active molecules are confined and protected in nanoporous cages where they are accessible to incoming reactants.<sup>[16]</sup>

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The process is simple and highly reproducible, consisting of the room-temperature hydrolysis and polycondensation of suitable metal alkoxide precursors carried out in the presence of one or more dopant active species.<sup>[16]</sup> Most importantly, through variation of the sol composition and the condensation conditions, the structural—and thus reactivity—properties of the resulting materials can be controlled and tailored to meet the requirements of specific applications such as chemical catalysis, in which the hydrophobic/hydrophilic nature of the catalyst is often crucial.<sup>[17]</sup>

Hence, for example, excellent results have recently been demonstrated in liquid-phase catalytic esterifications<sup>[18a]</sup> and oxidations<sup>[18b]</sup> mediated by sol–gel alkylated silicas, the surface hydrophilic–lipophilic balances (HLBs) of which were shown to have a profound influence on the activity of the encapsulated molecules.

We now wish to demonstrate how the sol–gel process can also be effectively applied to the catalysis of aerobic oxidation of alcohols, affording highly active and versatile catalysts that can be (re)used in the fast conversion of different substrates through the use of O<sub>2</sub> at ambient pressure as primary oxidant (Scheme 1).



Scheme 1. Sol–gel catalyst-based aerobic oxidation of alcohols.

The catalysts, nanohybrid silica particles organically modified and doped with TPAP, are considerably more active than unsupported perruthenate, and an explanation of the effects of variations in the materials' properties on the activity is suggested in order to establish guidelines for the development of truly efficient, solid oxidation catalysts.

## Results and Discussion

Following our original findings,<sup>[19]</sup> several catalytic ormosils (ormosils = organically modified silicates) doped with TPAP were prepared by variation of the R-substituted trimethoxy-silane (RTMS)/tetramethyl orthosilicate (TMOS) ratio in order to study more thoroughly the effect of the xerogels' surface polarity and textural properties on the activity in the hydrophobic solvent toluene.

In particular, we prepared two different batches of catalytic gels (**A** and **B**) with different water/silane/co-solvent ratios, in each case varying the relative amount and type of organo-silane employed in the polycondensation. Furthermore, to investigate the influence of the condensation process, each precursor sol in the series **A** and **B** was gelled with and without NaF (Table 1; “-F” in the materials notation indicates the employment of fluoride).

**Catalytic activity:** Surprisingly, comparison between the reactivity of TPAP unsupported and encapsulated in the 75% methylated silica matrix **A-Me3** in the toluene/oxygen oxidation protocol for benzyl alcohol shows that the sol–gel encapsulation of TPAP within a hydrophobic silica matrix

Table 1. Compositions of the sol–gel-entrapped TPAP catalytic ormosils **A** and **B**.

Batch <b>A</b>	Batch <b>B</b>	TMOS	MTMS	ETMS	PTMS
Si/H <sub>2</sub> O/MeOH 1:8:1	Si/H <sub>2</sub> O/MeOH 1:4:4	[%]	[%]	[%]	[%]
<b>A-Me0</b>	<b>B-Me0</b>	100	0	–	–
<b>A-Me1</b>	<b>B-Me1</b>	75	25	–	–
<b>A-Me2</b>	<b>B-Me2</b>	50	50	–	–
<b>A-Me3</b>	<b>B-Me3</b>	25	75	–	–
<b>A-Me4-F</b> <sup>[a]</sup>	<b>B-Me4-F</b> <sup>[a]</sup>	0	100	–	–
<b>A-Et2-F</b> <sup>[a]</sup>	<b>B-Et2-F</b> <sup>[a]</sup>	50	–	50	–
<b>A-Pr2-F</b> <sup>[a]</sup>	<b>B-Pr2-F</b> <sup>[a]</sup>	50	–	–	50

[a] Gels obtainable only by use of NaF as polycondensation catalyst. All the other gels were obtained with and without NaF.

enhances its activity (Figure 1), with the reaction going to completion much more rapidly (about six times faster) than under homogeneous conditions.

This result was thoroughly investigated and the homogeneous oxidation of benzyl alcohol with a 10 mol% catalytic amount of TPAP was carried out with<sup>[7b]</sup> and without<sup>[20]</sup> 4 Å molecular sieves. However, no significant changes were observed, and the turnover frequency of our sol–gel-entrapped silica catalyst **A-Me3** under the reaction conditions employed was considerably higher than that of homogeneous TPAP (Figure 1).

Interestingly, the heterogeneous kinetic reaction curve does not show the slow stage (probably involving RuO<sub>2</sub>,<sup>[19]</sup> which becomes a better aerobic alcohol oxidant when confined in a zeolite<sup>[7a]</sup>) following the faster stage up to 40–50% conversion typical of TPAP-catalysed alcohol oxidations, thus showing that the reaction mechanism may not necessarily be the same when dehydrogenation takes place within the sol–gel cages. In all cases the reaction mediated by the catalytic xerogels was heterogeneous in nature, since no further reactivity of the “hot” reaction filtrate was observed upon rapid filtration of the catalyst shortly after the start of the reaction (at about 50% alcohol conversion); nor was any unreactive ruthenium species leached from the solid catalyst, since no Ru was detected either in the reaction filtrate (ICP-MS, detection limit < 1 ppb) or in reaction samples withdrawn from the liquid phase during catalysis.

**Catalyst recyclability, selectivity and applicability:** To assess the catalyst's stability, comparison of the intermediate activities of the methylated silica matrix **A-Me3** in sequential reaction runs (which truly measures a catalyst's stability<sup>[21]</sup>) shows that, besides a slight loss of activity after the first reaction run (ca. 5%, probably due to formation of RuO<sub>2</sub>), the catalyst reactivity—which in the case of absolute stability should remain constant—does indeed remain practically unvaried. Hence, the valuable compound TPAP, impossible to recycle under homogeneous conditions, gradually yielding a black sol precipitate,<sup>[20]</sup> is physically and chemically stabilized upon encapsulation in a sol–gel hydrophobic silica matrix<sup>[16a]</sup> and can be recycled with no loss of precious ruthenium.

The known stability of metal “onium” ion pairs physically encapsulated in sol–gel materials towards leaching<sup>[15b]</sup> was

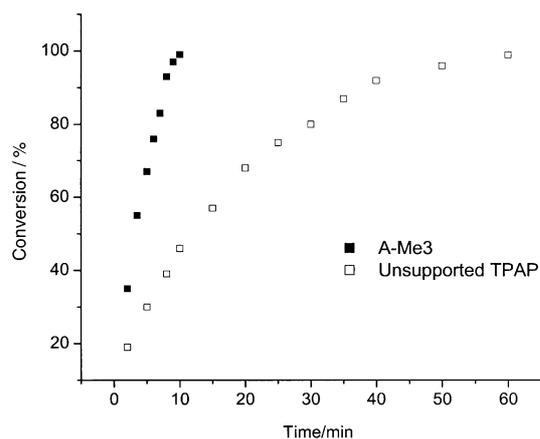


Figure 1. Oxidation kinetics in the aerobic conversion of benzyl alcohol in toluene mediated by 10 mol % TPAP encapsulated in the sol–gel hydrophobic matrix **A-Me3** (■) and unsupported (□).

thus also confirmed for TPAP. Accordingly, the reaction filtrate obtained upon “hot” filtration of the catalyst (i.e., carried out rapidly at the reaction temperature to prevent any possible perruthenate readsorption<sup>[11]</sup>) at 50 % reaction completion was kept at 75 °C under O<sub>2</sub>, and no further oxidation was observed even after 12 h. This should be compared to the complete leaching in a single reaction run of RuO<sub>4</sub><sup>−</sup> physically supported in the mesoporous channels of MCM-41 silica.<sup>[14]</sup>

Finally, in order to confirm the generality of the method, the same catalytic hydrophobic silica gel **A-Me3** was also used in the conversion of less easily oxidizable aliphatic and allylic alcohols (Table 2).

Hence, cyclohexanol (entry 2, Table 2), which could not be oxidised over MCM-41-supported TPAP,<sup>[10]</sup> was now smoothly converted over the hydrophobic silica gel **A-Me3** to yield a 45 % conversion into cyclohexanone after 6 h and a maximum 58 % conversion; this is the same as observed when the reaction is carried out with unsupported TPAP.

Nor was such excellent activity following encapsulation in a hydrophobic matrix limited to cyclic substrates, as shown by the rapid, high-yielding oxidation of the aliphatic substrate

Table 2. Aerobic oxidation of alcohols mediated by sol–gel-entrapped TPAP **A-Me3**.<sup>[a]</sup>

Entry	Substrate	Product	Conv. [%]	Time [h]
1	benzyl alcohol	benzaldehyde	96	0.16
1	1-phenylethanol	acetophenone	98	3
2	cyclohexanol	cyclohexanone	45	6
3	1-octanol	octylaldehyde	96	5
4	<i>trans</i> -cinnamyl alcohol	<i>trans</i> -cinnamaldehyde	99	2

[a] Reaction conditions: 0.2 mmol of substrate, 10 mol % entrapped TPAP, 4 mL of solvent, 75 °C, O<sub>2</sub> atmosphere.

1-octanol (Entry 3, Table 2), which in five hours afforded a 96 % yield of octylaldehyde, also confirming the pronounced versatility of these materials.

Full retention of the selectivity of TPAP in solution<sup>[20]</sup> is demonstrated by the lack of oxidation of the olefinic double

bonds when *trans*-cinnamyl alcohol was chosen as substrate (Entry 4, Table 2). In the presence of 10 mol % TPAP entrapped in the same **A-Me3** gel, this was rapidly (2 h) converted in high yields into *trans*-cinnamaldehyde (99 %).

Remarkably, such retention of the selectivity of TPAP was further confirmed on testing of the material's selectivity for primary versus secondary hydroxy groups—an important property of perruthenate-mediated oxidations<sup>[22]</sup>—when the oxidation of a 1:1 mixture of benzyl alcohol and 1-phenylethanol was carried out in one-pot fashion over the same hydrophobic gel **A-Me3**.

Hence, after 10 min all the primary benzyl alcohol had been converted, whereas only 19 % of 1-phenylethanol had been dehydrogenated to form acetophenone. However, in sharp contrast to perruthenate heterogenized on polystyrene resin,<sup>[13]</sup> all the secondary alcohol left in solution could be further oxidised just by prolonging the reaction time, thus showing the potential of these materials for combinatorial applications, in which such selectivity and versatility are in high demand.<sup>[23]</sup>

The gel proved to be leach-proof and recyclable with all substrates, requiring only a washing step with CH<sub>2</sub>Cl<sub>2</sub> at reflux between each consecutive reaction run.

#### Effects of catalyst hydrophobicity, textural properties and preparation conditions:

As reported in our original communication,<sup>[19]</sup> the catalytic activity of TPAP-doped ormosils increases with the relative amount of alkyl groups, while, independently of the preparation protocol used, the unmodified SiO<sub>2</sub> glasses derived from pure TMOS show the lowest reactivities. However, the study of TPAP-doped nanohybrid silica gels prepared under different conditions affords materials that are more active than homogeneous TPAP and provides deeper insights in the behaviour of sol–gel materials in oxidation catalysis.

Interestingly, such results are remarkably analogous to those observed with entrapped lipase enzymes in organic solvents (in which these enzymes are poorly soluble), which become more active upon encapsulation in a hydrophobic silica matrix,<sup>[18a]</sup> with TPAP alone being similarly insoluble in toluene (even at reflux) and with the alcohol providing the solubility needed through RuO<sub>4</sub><sup>−</sup> complexation.<sup>[20]</sup>

Tables 3 and 4 show that, on average, catalysts of batch **A** are more active than those of batch **B**, and that the best performing catalyst is the 75 % methylated **A-Me3** obtained without sodium fluoride from a precursor sol with molar ratios Si/H<sub>2</sub>O/MeOH 1:8:1.

In both preparation protocols, the employment of NaF generally yields materials of considerably lower activity, while also<sup>[18a]</sup> in aerobic oxidations, increasing the length of the alkyl group in the organosilane generally enhances the material's activity to an extent apparently related to the material's preparation conditions (requiring NaF to promote gelation in all cases).

Hence, under conditions **A** the employment of ethyl- and propyltrimethoxysilane in place of MTMS yields 50 % alkylated ormosils of higher reactivity (in relation to that of their methylated analogues, Table 3). The gel **A-Et2-F**, for instance, is more active than **A-Pr2-F**, but still less efficient than the

Table 3. Activity<sup>[a]</sup> and textural properties of sol–gel catalytic ormosils doped with TPAP of batch **A**.<sup>[b]</sup>

Catalyst	Conv. [%]	Time [h]	SSA [m <sup>2</sup> g <sup>-1</sup> ]	PSV [cm <sup>3</sup> g <sup>-1</sup> ]
<b>A-Me0</b>	28	1	445	0.95
<b>A-Me1</b>	59	1	530	0.83
<b>A-Me2</b>	54	1	646	1.47
<b>A-Me3</b>	100	0.16	251	0.24
<b>A-Me0-F</b>	5	1	272	0.86
<b>A-Me1-F</b>	93	1	405	0.65
<b>A-Me2-F</b>	19	1	507	0.72
<b>A-Me3-F</b>	95	1	430	1.00
<b>A-Me4-F</b>	96	0.75	223	0.20
<b>A-Et2-F</b>	91	1	470	0.76
<b>A-Pr2-F</b>	84	1	288	0.56

[a] Reaction conditions: 0.2 mmol of benzyl alcohol, 10 mol % entrapped TPAP, 4 mL of solvent, 75 °C, O<sub>2</sub> atmosphere. [b] Gels prepared from a sol with molar ratio Si/H<sub>2</sub>O/MeOH 1:8:1

Table 4. Activity<sup>[a]</sup> and textural properties of sol–gel catalytic ormosils doped with TPAP of batch **B**.<sup>[b]</sup>

Catalyst	Conv. [%]	Time [h]	SSA [m <sup>2</sup> g <sup>-1</sup> ]	PSV [cm <sup>3</sup> g <sup>-1</sup> ]
<b>B-Me0</b>	9	1	590	1.33
<b>B-Me1</b>	21	1	688	0.92
<b>B-Me2</b>	36	1	866	0.80
<b>B-Me3</b>	96	0.5	635	0.66
<b>B-Me0-F</b>	10	1	584	0.75
<b>B-Me1-F</b>	14	1	839	0.68
<b>B-Me2-F</b>	28	1	874	0.76
<b>B-Me3-F</b>	38	1	743	0.67
<b>B-Me4-F</b>	78	1	487	1.17
<b>B-Et2-F</b>	23	1	610	0.51
<b>B-Pr2-F</b>	50	1	324	0.35

[a] Reaction conditions: 0.2 mmol of benzyl alcohol, 10 mol % entrapped TPAP, 4 mL of solvent, 75 °C, O<sub>2</sub> atmosphere. [b] Gels prepared from a sol with molar ratio Si/H<sub>2</sub>O/MeOH 1:4:4

75 % methylated gel **A-Me3**; however, this order is inverted under gelation conditions **B** (Table 4) and the 50 % propylated silica **B-Pr2-F** is more active than the ethylated matrix **B-Et2-F**.

To explain such marked variations, the correlation between N<sub>2</sub>-BET surface area/porosity, degree of matrix alkylation and catalytic activity of the methylated ormosils yields valuable information and shows that enhanced diffusivity alone (due to the hydrophobicity and larger pore size) does not fully explain the general structure–activity relationship observed with the doped ormosils.

Addressing first the gels of the **A** series (Table 3), it can be seen how, similarly to what happens in analogous liquid-phase hydrobrominations<sup>[24]</sup> and esterifications<sup>[18a]</sup> mediated by sol–gels, under aerobic oxidations the material's N<sub>2</sub>-penetrability measured by the BET experiment at –196 °C seems to be of minor relevance to the reactivity of other molecules adsorbed under different conditions.

The catalyst **A-Me3**, for example, shows the best activity, despite its relatively low porosity, and is followed by the most hydrophobic ormosil **A-Me4-F**, which has the smallest pore volume in the series (0.20 cm<sup>3</sup>g<sup>-1</sup>). The picture changes dramatically when TPAP is encapsulated in gels prepared at lower water/silane ratios (batch **B**, Table 4).

First, it is seen that the effect of the employment of NaF both on the textural properties and on the activity is less pronounced than in catalysts of batch **A**. Thus, independently of its addition during the preparation process, the 50 % methylated gels **B-Me2** and **B-Me2-F** have almost identical porosity/surface areas and show similarly moderate reactivity.

It can also be seen how, on going from TPAP encapsulated in the unmodified SiO<sub>2</sub> matrix **B-Me0** to the half-methylated silica gel **B-Me2**, the activity increases only slightly. Then, however, the 75 % methylated gel **B-Me3** shows a jump in the activity, converting most (96 %) of the added benzyl alcohol to benzaldehyde in only 30 minutes.

On the basis, therefore, of a predominant hydrophobic effect, one might expect to observe the highest activity in the series with the fully methylated gel **B-Me4-F** (obtainable only by employment of NaF). This, however, shows a good activity, but lower than that of the 75 % methylated gel **B-Me3** prepared without F<sup>-</sup>, despite having pores almost two times bigger (1.17 vs 0.66 cm<sup>3</sup>g<sup>-1</sup>).

These results can be interpreted in the light of the structural characteristics of doped sol–gel materials in general,<sup>[16]</sup> and of ormosils in particular,<sup>[25]</sup> by considering that the final material microstructure is mainly a result of the initial polycondensation conditions. One might first recall that the use of organoalkoxysilanes R'Si(OR)<sub>3</sub> in the sol–gel polycondensation affords nanohybrid hydrophobic porous silicas with the organic groups distributed through the whole polymeric network and mostly at the cage surface;<sup>[25a]</sup> and it is precisely the considerably lesser proportion of hindering *intra-cage* hydrogen-bonding silanols (Si–OH)<sup>[16a]</sup> that is crucial in enhancing the reactivity of encapsulated dopant molecules (and thus the gels' catalytic activities)<sup>[18]</sup> by promoting their mobility within the cages.

The employment of fluoride as a catalyst of the sol–gel process, in its turn, strongly enhances the condensation rate through multiple F<sup>-</sup> coordination to the silane Si centres,<sup>[25b]</sup> promoting linear aggregation of the growing silica particles (similarly to what happens with acid-catalysed silica gels<sup>[26]</sup>); finally, a smaller amount of H<sub>2</sub>O diminishes rate and extension of the silane monomers hydrolysis, thus favouring condensation (which in the case of ormosils takes place only through elimination of water, and not by alcohol formation).<sup>[27]</sup>

The resulting overall effect is that slowly generated R-Si(OH)<sub>3</sub> monomers rapidly condense in micellar-like structures typical of the very early stages of the sol–gel process, in which these hydrolysed monomers tend to arrange themselves with the polar heads made of –Si(OH)<sub>3</sub> groups at the forefront of the growing sol–gel material, and the hydrophobic nonpolymerizable residue R orientated away from the interfacial solvent water/methanol (strongly hydrogen bonding).<sup>[24]</sup>

In the presence of hydrophobic molecules, such as the TPAP ion pair, this results in the partial burying of the catalytic perruthenate moieties in the core of the transient micelles and eventually in the bulk of the final hybrid silica xerogel, where they are inaccessible for catalysis. This hypothesis would explain the inhibiting effect of NaF on the

materials' activities and why catalysts of batch **A** are generally more active than those of batch **B**.

In the former case, indeed, the greater amount of H<sub>2</sub>O (and smaller of MeOH) favours the hydrolysis of the alkoxide monomers and slows down the condensation, so that rapid aggregation of the early sol particles is prevented and MTMS can fully hydrolyse to CH<sub>3</sub>–Si(OH)<sub>3</sub> and, thus, copolymerize with the Si(OH)<sub>4</sub> monomers from the faster TMOS hydrolysis. An open network is eventually formed, resulting in gels in which most of the added TPAP molecules are encapsulated at the surfaces of the (hydrophobic) silica cages, accessible for catalysis, while the compromise between the sol–gel cage accessibility and hydrophobicity ensures optimal reactivity for the material **A-Me3**.

The hypothesis is also verified by the shape of the N<sub>2</sub>-adsorption isotherms of the fully methylated ormosils (Figure 2).

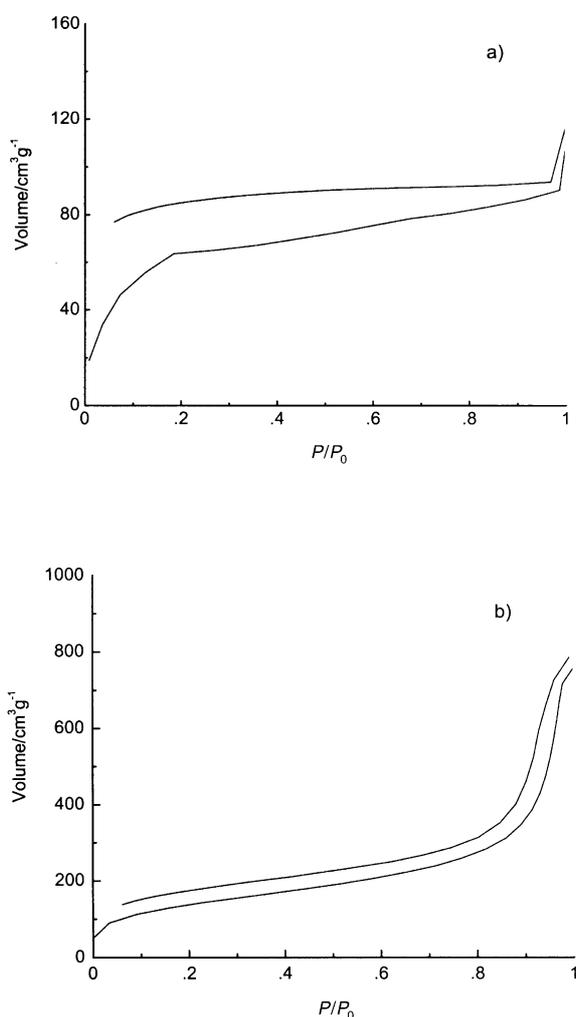


Figure 2. N<sub>2</sub> adsorption-desorption isotherms of fully methylated gels **A-Me4-F** (a) and **B-Me4-F** (b).

Hence, the type I isotherm of the fluoride-catalysed gel **A-Me4-F** (Figure 2a) is typical of a purely microporous material<sup>[28]</sup> with a narrow pore size and a relatively low maximum adsorbed volume ( $V_{\text{ads}} = 150 \text{ cm}^3 \text{ g}^{-1}$ ), whereas the type IV isotherm of the gel **B-Me4-F** (Figure 2b) clearly indicates a

mesoporous material<sup>[28]</sup> able to adsorb a considerable volume of cryogenic nitrogen ( $860 \text{ cm}^3 \text{ g}^{-1}$ ).

These experimental results indicate that the covalently bounded methyl groups in **A-Me4-F** are much more homogeneously distributed in the silica network than in **B-Me4-F**. Indeed, the decrease in surface area and pore volume due to the reduction of the silica network connectivity upon the incorporation of Si nuclei with lower functionality is counteracted by the reduction of the capillary tension at the cage solid–liquid interface, which prevents collapse of the gel during drying.<sup>[25a]</sup>

If there were micellar-like structures such as those mentioned above in the sol mixture precursor of gel **B-Me4-F**, one would expect to observe maximum connectivity in the final ormosil, and, thus, higher surface area and pore volume, with part of the catalytic perruthenate eventually being segregated into the bulk of the polymeric matrix and, hence, inaccessible for catalysis. In fact, despite having almost double the surface area and a pore size six times larger, the gel **B-Me4-F** is almost half as active as its fully alkylated analogue gel **A-Me4-F** (Tables 3 and 4).

It thus emerges from this hypothesis that, along with high hydrophobicity, higher amounts both of water (to promote hydrolysis) and of methanol (to promote homogeneity and disrupt the micellar-like structures) are desirable for optimal reactivity; this was also precisely the case in our original report,<sup>[19]</sup> in which the catalytic ormosils were prepared from a sol mixture with Si/MeOH/H<sub>2</sub>O 1:5:6 molar ratios, with the fully methylated gel showing the highest activity.

Finally, sol–gel encapsulation also explains the higher reactivity and versatility of these materials in comparison with TPAP confined in crystalline MCM-41, in which the perruthenate anions are ionically bound at the internal surfaces of the silica mesopores.<sup>[14]</sup>

Sol–gel ormosils doped with TPAP are, in fact, chemical sponges<sup>[16a]</sup> (see below) with the perruthenate ions encapsulated within nanoporous cages showing chromatographic properties (i.e., which adsorb and concentrate the hydrophobic O<sub>2</sub> and substrate molecules at their similarly hydrophobic surface, promoting faster diffusion of the reactant and product molecules through the vast accessible internal porosity).

Furthermore, being amorphous and with a distribution of porosities,<sup>[16]</sup> they differ from zeolites such as MCM-41 in that they do not strictly exclude different molecules from entering the porous network and also in that they do not impart a geometric order to the entrapped molecule; accordingly, our ormosils were also applicable to the conversion of alcohols such as cyclohexanol or long-chain aliphatic alcohols, which simply cannot be converted over MCM-41 doped with TPAP.<sup>[14]</sup>

Scanning electron microscopy indeed reveals the catalysts' morphology (Figure 3): the materials are made up of amorphous continuous glass-like silica aggregates, which are in their turn nanostructured with a pronounced internal microporosity typical of sol–gels prepared under acidic conditions.<sup>[25b]</sup>

Since the material surface geometry encountered by the approaching reactant molecules has relevant effects on the

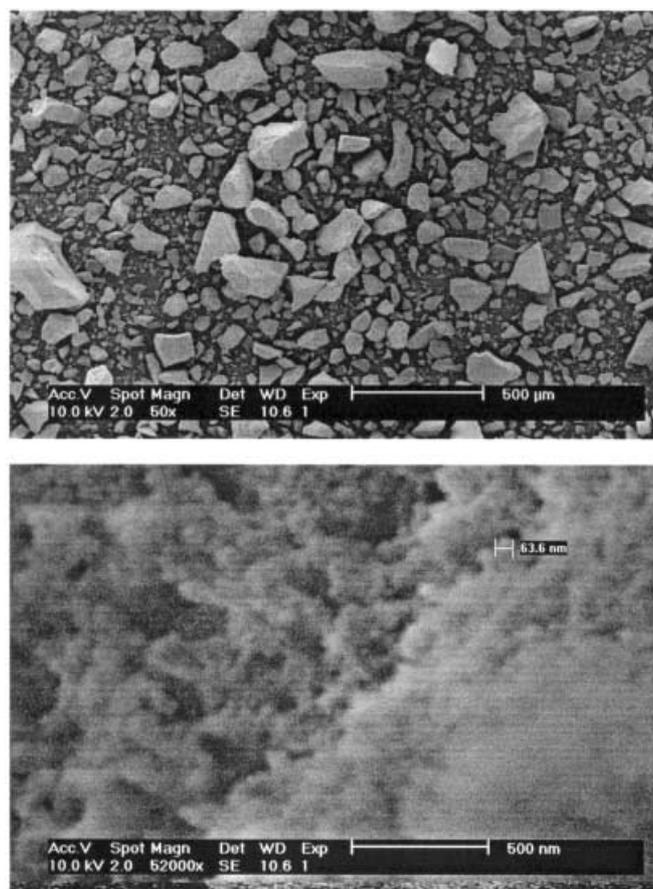


Figure 3. A typical TPAP-doped ormosil (SEM micrographs of the fully methylated gel **B-Me4** are shown here) is made of silica particles (top) that upon magnification ( $52000\times$ ) reveal a nanostructured spongy morphology (bottom).

material reactivity,<sup>[29]</sup> and since the sol–gel methodology allows such geometries to be tailored and controlled,<sup>[16]</sup> this is likely to be a relevant subject of further development efforts aimed at optimization of the catalytic performance.

## Conclusion

Organically modified silica gels physically doped with TPAP are highly efficient and versatile catalysts for the selective oxidation of different alcohols with  $O_2$  at ambient pressure in toluene. The preparation of such materials is simple and reproducible, consisting of a one-step sol–gel polymerization process; this allows the catalytic performance to be optimised by tailoring of the material's surface polarity and textural properties to yield catalysts up to six times more active than unsupported perruthenate.

The best performing catalysts require both a high degree of surface hydrophobicity and large quantities of water and co-solvent in the sol–gel polycondensation. A general interpretation of the results is offered in order to provide guidelines for the development of efficient ruthenium-based solid oxidation catalysts, which—in view of the commercial and synthetic relevance of alcohol dehydrogenation<sup>[6]</sup> and the

advantages of the applications of sol–gel materials to catalysis<sup>[30]</sup>—might soon find practical applications.

## Experimental Section

**Materials:** Methyltrimethoxysilane (MTMS), ethyltrimethoxysilane (ETMS), propyltrimethoxysilane (PTMS), tetramethyl orthosilicate (TMOS), tetra-*n*-propylammonium perruthenate (TPAP), benzyl alcohol, cinnamyl alcohol, 1-phenylethanol and *n*-decane were purchased from Sigma–Aldrich and were used without further purification. Methanol and NaF were purchased from Fluka. Ultra-pure water (Millipore Type 1 quality) was used in all the preparations.

**Preparation of the modified sol–gel-entrapped catalysts:** Several doped ormosils were prepared by sol–gel hydrolysis and co-polycondensation of RTMS and TMOS in the presence of TPAP dissolved in methanol with and without NaF as polycondensation catalyst and with variation of the relative amounts of water, co-solvent (batch **A**, Si/MeOH/ $H_2O$  1:8:1; batch **B**, Si/MeOH/ $H_2O$  1:4:4), and the organosilane/silane ratio.

A typical batch **A** catalyst obtained with NaF (**A-Me1-F**, Table 1) was prepared by addition of MTMS (1.65 mL) and TMOS (5.90 mL) to a solution of TPAP (55.5 mg) in MeOH (1.80 mL) cooled in an ice bath (to prevent ignition), followed by the addition of  $H_2O$  (5.70 mL) and NaF (765  $\mu$ L, 1M) with fast stirring. The sol gelled rapidly and the resulting alcogel was sealed and left to age at room temperature for 48 h prior to drying in an oven at 50 °C until reaching constant weight (5 days). The obtained catalytic xerogel was powdered, washed at reflux ( $CH_2Cl_2 \times 2$ , 60 °C) and dried at 50 °C prior to use.

A representative catalyst of batch **B**, such as **B-Me3**, was obtained by addition of 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) with fast stirring. The sol gelled slowly and the alcogel 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 as described above. A typical catalytic load was 500  $\mu$ mol TPAP  $g^{-1}$  ormosil.

**Typical oxidation procedure:** A solution of cinnamyl alcohol (26.2  $\mu$ L, 0.5 mmol) in toluene (4 mL), maintained at 75 °C in a silicon oil bath, was added to sol–gel-entrapped catalyst **A-Me3** (430 mg, 0.02 equiv) in the presence of *n*-decane (26.2  $\mu$ L, internal standard). Oxygen was passed through, and the reaction mixture was kept under an oxygen atmosphere ( $O_2$  balloon) with fast stirring by use of an alternating magnetic field stirrer. The reaction was followed by GC, and when the reaction was complete the catalyst was filtered off (Whatman filter paper, type 1), with washing with  $CH_2Cl_2$  at reflux, dried at 50 °C and used as such in subsequent reaction runs. Allowance was made for slight material losses by equivalent reductions in substrate to keep the catalyst/substrate ratio constant (10% mol).

**Instruments:** The GC analyses were carried out on a GC-17A Shimadzu chromatograph equipped with a Supelcowax 10 capillary column (30 m, 0.25 mm ID) by the internal standard method (with previously calculated response factors). The ICP-MS ruthenium analyses were conducted with a HP 4500 mass spectrometer and the  $N_2$ -BET textural values were obtained on a Carlo Erba 1900 Sorptomatic analyzer for powders. The SEM photographs were taken with a Philips XL 30 ESEM microscope.

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