

The Effects of Material Properties on the Activity of Sol-Gel Entrapped Perruthenate under Supercritical Conditions

Rosaria Ciriminna,^a Sandro Campestrini,^b Mario Pagliaro^{a,*}

^a Istituto per lo Studio dei Materiali Nanostrutturati, Sezione di Palermo, CNR, via Ugo La Malfa 153, 90146 Palermo, Italy

Fax: (+39)-91-680-939, e-mail: pagliaro@pa.ismn.cnr.it

^b Dipartimento di Chimica Organica, Università degli Studi, via Marzolo 1, 35131 Padova, Italy

Received: April 29, 2003; Accepted: July 15, 2003

Abstract: Silica gels organically modified and doped with the ruthenium species tetra-n-propylammonium perruthenate (TPAP) are leach-proof, selective catalysts for the aerobic oxidation of alcohols to carbonyl compounds with dioxygen at low pressure in compressed carbon dioxide. The catalytic sol-gels are recyclable and the correlation between the reactivity of the materials and their surface polarity and textural properties suggests valuable information on the chemical behaviour of sol-gel entrapped silica catalysts in oxidation catalysis which is of relevant interest

considering the importance of heterogeneous oxidative dehydrogenation of alcohols in fine chemistry. An explanation of the structure-activity relationship is proposed to provide guidelines for the further development of efficient solid oxidation catalysts for conversions in supercritical carbon dioxide.

Keywords: alcohol; catalytic aerobic oxidation; dioxygen; immobilization; ormosil; ruthenium; sol-gel; supercritical carbon dioxide

Introduction

Heterogeneous catalysts for the selective oxidation of alcohols are of primary industrial importance,^[1] carbonyl compounds being precursors of valuable commercial fine chemicals including drugs, vitamins, fragrances and important synthons for complex syntheses. Traditional industrial oxidations, in fact, are becoming obsolete processes being mainly carried out in organic solvents using as oxidants stoichiometric (*at best*) amounts of toxic chromates or manganates.^[2] Hence, the introduction of heterogeneous catalytic processes using O₂ as primary oxidant is one of the main objectives of current industrial and academic research efforts in chemistry towards sustainability.^[3]

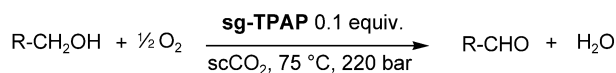
Furthermore, the replacement of the volatile organic solvents used as reaction medium with water or with other environmentally benign solvents such as ionic liquids^[4] or supercritical fluids^[5] is also desirable because, as recently remarked by researchers in the pharmaceutical industry,^[6] “solvents despite current low prices, in addition to their impacts through use and final disposal, have a considerable life cycle impact and their broader total costs are *not* cheap”.

In this context, carbon dioxide in the supercritical state (scCO₂) has emerged as a promising alternative reaction medium due to its advantageous physical and chemical properties including:^[5]

- (a) low critical temperature ($T_c = 31^\circ\text{C}$) and vapour pressure ($P_c = 73.8$ bar);
- (b) excellent *miscibility* with reagents such as O₂ and H₂;
- (c) lack of flammability in the presence of O₂;
- (d) low *viscosity* and superior mass transport properties (absence of a gas-liquid phase boundary).

In addition, *heterogeneous* catalytic conversions, that are particularly important for industry, can be efficiently carried out in scCO₂ using small, high-throughput reactors in continuous processes where the CO₂ is recycled while the substrates are converted,^[7] and at the end of reaction carbon dioxide is completely removed from the products (thanks to its high volatility) resulting in an overall “solvent-free” reaction.^[8]

Now, we report that ormosils doped with the catalytic ruthenium species TPAP are suitable catalysts for the oxidative dehydrogenation of primary alcohols in supercritical carbon dioxide with O₂ at a low partial pressure (Scheme 1).



R = alkyl, aryl, alkenyl

Scheme 1.

We show how the thorough choice of the material properties affords recyclable, selective catalysts with the pronounced selectivity of TPAP in the liquid-phase and offer an explanation of the structure-activity relationship aiming to provide guidelines for the development of efficient sol-gel oxidation catalysts under supercritical conditions.

Results and Discussion

The comparison between the reactivity of unsupported TPAP and TPAP encapsulated in the representative sol-gel ormosils **A-Me2** (50% methylated) in the aerobic oxidation of benzyl alcohol under the supercritical conditions of Scheme 1 shows immediately that sol-gel encapsulation *enhances* its activity.

Interestingly, it may be noted that, despite the insolubility of the ionic species $(\text{Pr})_4\text{N-RuO}_4$ in the supercritical CO_2 phase,^[9] a moderate degree of activity is observed with reaction going to completion in 11 hours.

The analogous course of the reactions for unsupported TPAP and TPAP encapsulated in **A-Me2** also shows that in scCO_2 , despite a much slower rate,^[10] the

mechanism of TPAP-catalysed alcohol oxidations in organic solvent is unvaried, with a faster stage up to 40–50% conversion followed by a slower stage probably involving RuO_2 .^[11]

Indeed, the reaction mediated by gel **A-Me2** takes place within the sol-gel cages and is heterogeneous in nature since *no* ruthenium was detected in reaction samples withdrawn *during* reaction from the sc phase (with a Ru detection limit < 1 ppb).

Effects of Catalyst Hydrophobicity, Textural Properties and Preparation Conditions

Based on our recent findings on the pronounced effect of xerogels' surface polarity on their aerobic activity in organic solvent,^[10a] we prepared several sol-gel entrapped catalytic ormosils by varying the MTMS/TMOS ratio in order to study analogous effects of the xerogels' surface polarity and textural properties on the reactivity also in the non-polar CO_2 reaction medium.

Hence, we prepared 2 different batches of catalytic xerogels (**A** and **B**) with different water/silane/co-solvent ratios, varying in each case the relative amount of organosilane employed in the sol-gel polycondensation (Table 1).

In addition, to investigate the relationship between the condensation process and the reactivity of the resulting materials, each precursor sol in the series **A** and **B** was gelled with *and* without NaF as condensation catalyst and the respective activities compared. Catalytic amounts of fluoride, in fact, have a dramatic effect on the textural properties of the final xerogels by largely affecting the condensation rate of the sol-gel process.^[12]

Using benzyl alcohol as model substrate, Figure 2 clearly shows that, on average, catalysts of batch **A** are more active than those of batch **B**; while in both cases the employment of NaF as polycondensation mediator yields materials of *lower* activity, with effects that in some cases are as drastic as in the case of the 50% methylated gel **A-Me2** whose activity, when prepared in the presence of NaF, becomes lower than that of unsupported TPAP.

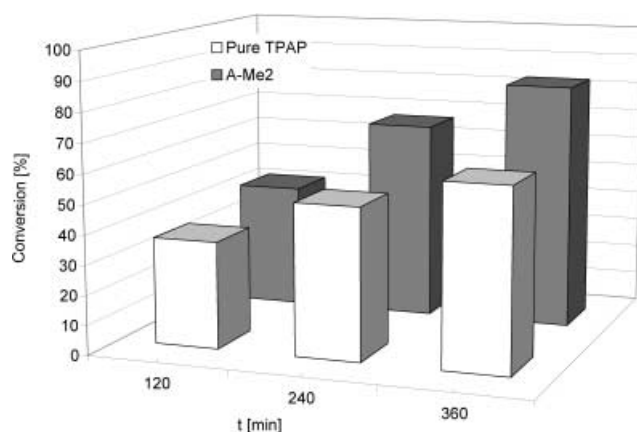


Figure 1. Conversions in the aerobic oxidation of benzyl alcohol in scCO_2 over TPAP unsupported (white) and entrapped in gel **A-Me2** (grey).

Table 1. Composition of the sol-gel entrapped TPAP catalytic ormosils.

Batch A Si:H ₂ O:MeOH = 1 : 8 : 1		Batch B Si:H ₂ O:MeOH = 1 : 4 : 4	TMOS (%)	MTMS (%)
A-Me0	B-Me0		100	0
A-Me1	B-Me1		75	25
A-Me2	B-Me2		50	50
A-Me3	B-Me3		25	75
A-Me4 ^[a]	B-Me4 ^[a]		0	100

^[a] Fully methylated gels are obtainable only using NaF.

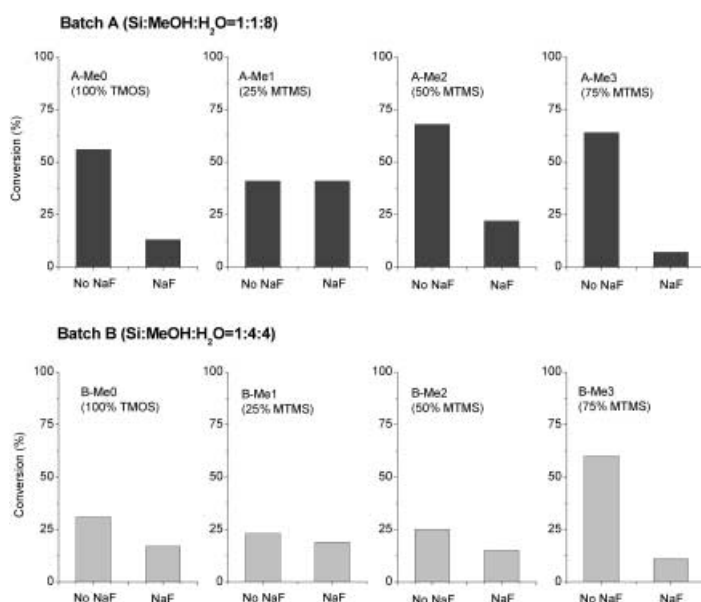


Figure 2. Conversions after 4 h in the aerobic oxidation of benzyl alcohol in scCO_2 over different gels prepared without (left bars) and with NaF (right bars).

Catalyst Stability and Applicability

To test the catalyst stability, each gel was recovered and reused at the end of several consecutive reaction runs showing full retention of the selective activity in each case. Indeed, the *intermediate* yields in said consecutive runs (which truly measures a catalyst's stability)^[13] were remarkably constant; and no leaching of perruthenate during catalysis was observed since no ruthenium was detected in samples withdrawn *during reaction* from the homogeneous supercritical phase.

Notably, upon each reaction run the catalysts appeared clean and macroscopically unmodified and *no* post-reaction physical or chemical treatment was necessary to ensure retention of their activity, which is in contrast with the behaviour of sol-gels in liquid solvents where pore clogging by adsorbed reactants often occurs, requiring a mild treatment of the used catalyst with ultrasound, hot solvents or aqueous bicarbonate to remove the adsorbates and reopen the pores.^[14]

Finally, in order to prove the generality of the method, the catalytic gel **B-Me3** (prepared without NaF) was used also in the conversion of less easily oxidisable aliphatic and alkenyl alcohols (Table 2).

Notably, the gel proved again to be leach-proof and selective with *no* oxidation of the olefinic double bonds occurring, generally showing lower activities but with reaction proceeding to the same extent as observed in toluene for each substrate.

To explain the marked variations in the catalytic behaviour of these materials in scCO_2 , the correlation amongst N_2 -BET surface area/porosity, degree of matrix

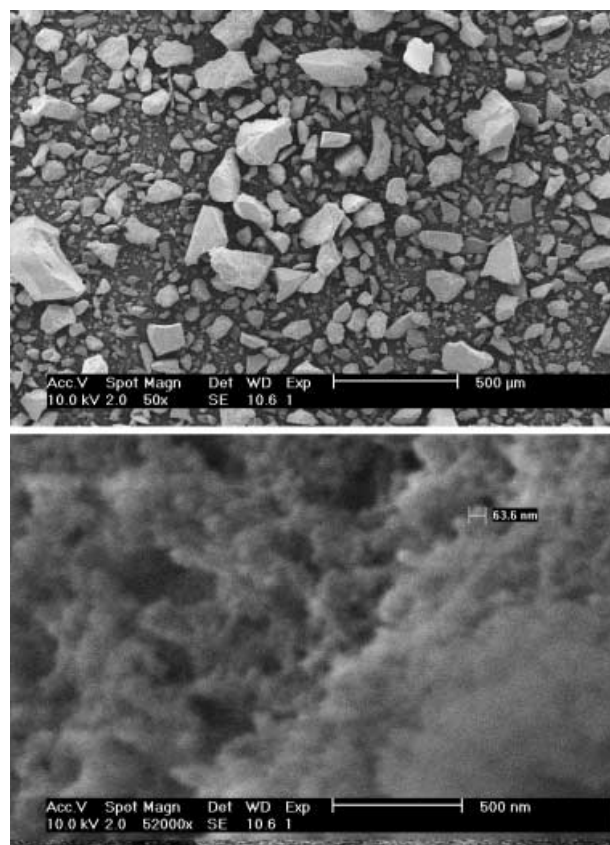


Figure 3. A typical TPAP-doped ormosil (here are shown SEM micrographs of the fully methylated gel **B-Me4**) is made of silica particles (*above*) that upon magnification ($52,000\times$) reveal a nanostructured spongy morphology (*below*). No changes are observed after reaction in scCO_2 .

alkylation, and catalytic activity suggests valuable information.

Addressing first the gels of the **A** series (Figure 4), it is seen how, in contrast to what happens in the liquid phase,^[15] for reactions mediated by sol-gels in compressed CO_2 the N_2 -penetrability measured by the BET experiment at -196°C seems to be of relevance also to the reactivity of other molecules adsorbed under different conditions.

Hence, for example, the catalyst with the biggest pore volume and surface area (**A-Me2** prepared without

Table 2. Aerobic oxidation of alcohols mediated by TPAP encapsulated in 75% methylated gel **B-Me3**.^[a]

Alcohol	Product	Conversion (%) at 4 h
Benzyl alcohol	Benzaldehyde	60
1-Octanol	Octylaldehyde	30
9-Decen-1-ol	9-Decenal	8
4-Hexen-1-ol	4-Hexenal	4

^[a] Gel obtained without NaF.

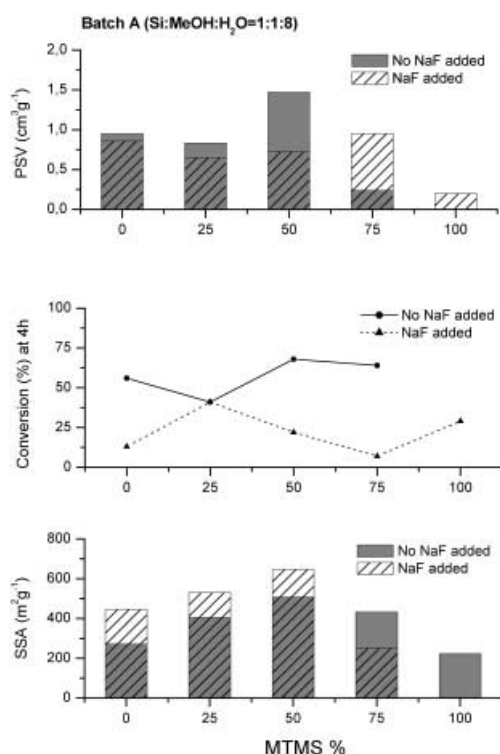


Figure 4. Dependence of the activity of encapsulated TPAP in MTMS/TMOS mixed gels (batch **A**) on the gel composition, specific surface area (SSA) and pore specific volume (PSV).

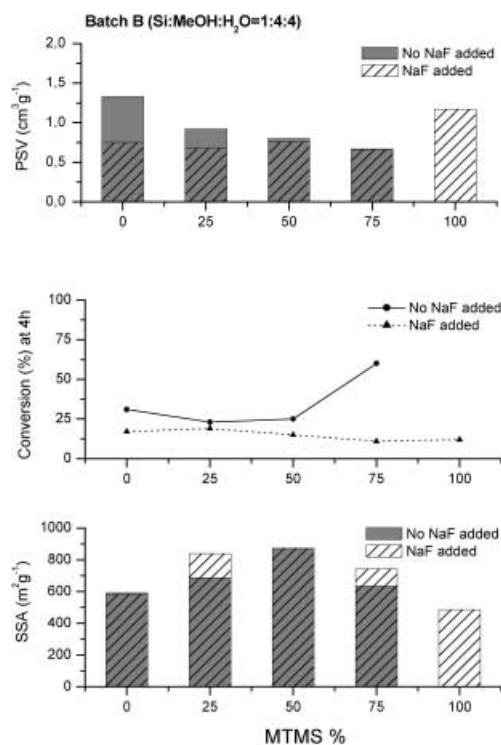


Figure 5. Dependence of the activity of encapsulated TPAP in MTMS/TMOS mixed gels (batch **B**) on the gel composition, specific surface area and pore volume.

NaF) is more active than the corresponding more hydrophobic gel **A-Me3**, while the fully methylated gel **A-Me4** with the smallest pores size in the series (and which can be prepared *only* using NaF) shows again moderate activity. This a picture that changes dramatically when TPAP is encapsulated in gels prepared at lower water/silane ratio (batch **B**, Figure 5).

First, it is seen that the effect of the addition of fluoride on the textural properties and on the activity is *less* pronounced than for catalysts of batch **A**. For example, the 50% methylated gels **B-Me2** have almost identical porosity/surface area and activity independently of NaF addition.

Moreover, going from TPAP encapsulated in unmodified SiO₂ (**B-Me0**) to the 50% methylated silica gel (**B-Me2**) the activity is apparently *independent* of surface hydrophobicity and of textural properties; then, however, the 75% methylated gel **B-Me3** prepared *without* fluoride shows a jump in the activity converting 60% of benzyl alcohol to benzaldehyde in 4 hours. Based therefore on a predominant hydrophobic effect, one might expect to observe the highest activity with the fully methylated gel **B-Me4** which, however, shows again a *moderate* activity similar to that shown by all the remaining gels in the **B** series obtained employing NaF as condensation mediator.

These results provide new, valuable information on the catalytic behaviour of doped sol-gel materials in supercritical CO₂. First, the highest activities are now observed over *partly* methylated silica gels; moreover, TPAP encapsulated in unmodified SiO₂ (**A-Me0**, prepared without NaF), which in toluene was practically inactive,^[10a] in compressed CO₂ shows a pronounced catalytic activity that is, for comparison, 2 times higher than that of the most active alcohol oxidation catalyst in scCO₂ reported so far (Pt supported over fluorinated graphite, yielding a maximum benzyl alcohol conversion of 63% after 24 h).^[16a]

The enhanced reactivity of the SiO₂ doped gel **A-Me0** is likely to be due to the largely enhanced *diffusivity* of the substrate and product molecules dissolved in the supercritical medium through the vast accessible porosity (0.95 cm³ g⁻¹) of the gel that accelerates the transfer of molecules from the internal and external catalyst surface;^[5b] and yet, such enhanced diffusivity does not explain the general structure-activity relationship observed with the doped ormosils.

Indeed, one might remember that in contrast to traditional supported catalysts that bear the catalytic species unprotected at the support surface, doped sol-gel materials are chemical *sponges* with the dopant molecules encapsulated *within* nanoporous cages with

chromatographic properties (i.e., which adsorb and concentrate the reactants at their surface).^[17] On the other hand, the employment of organo-alkoxysilanes $R'Si(OR)_3$ in the sol-gel process yields hydrophobic silica gels with the organic groups mostly concentrated at the cage surface^[18] in which the considerable lesser proportion of hindering *intra-cage* hydrogen-bonding silanol groups is crucial in enhancing the reactivity of encapsulated dopants (by promoting mobility within the cages).^[17,10,13b]

Accordingly, the graphics in Figure 4 show that at high values of water/silane molar ratio (r), a compromise amongst the sol-gel cages *accessibility* and *hydrophobicity* may be in action that ensures optimal reactivity with the most active material (**A-Me2**) having both large porosity ($1.47 \text{ cm}^3 \text{ g}^{-1}$) and good surface hydrophobicity (50% alkylated).

However, the data reported in Figure 5 show that using a lower water/silane ratio and an higher amount of co-solvent, the most active catalyst is the 75% methylated gel **B-Me3** prepared *without* F^- which, despite having pores almost 2 times smaller ($0.66 \text{ vs. } 1.17 \text{ cm}^3 \text{ g}^{-1}$), is 5 times more active than the fully methylated gel **B-Me4** prepared *with* NaF.

To explain these complex observations, one should consider that the employment of fluoride as catalyst of the sol-gel process strongly enhances the rate of the condensation by multiple F^- coordination to the silane Si centres,^[12] while a lesser amount of H_2O diminishes the rate and extension of the silane monomer hydrolysis favouring condensation which in the case of ormosils^[19] takes place only *via* elimination of water, and *not* by alcohol formation.

The resulting overall effect is that slowly generated $R-Si(OH)_3$ monomers rapidly condense in micellar-like structures^[15a] that are typical of the very early stages of the sol-gel process in which hydrolysed monomers tend to arrange themselves with the polar $-Si(OH)_3$ groups at the forefront of the growing sol-gel material, and the hydrophobic non-polymerisable R residue orientating away from the interfacial strongly hydrogen bonding solvent (water/methanol).^[15a] In the presence of the hydrophobic TPAP molecules this results in the partial *burying* of the catalytic ion pair in the core of the micelles and eventually in the bulk of the resulting silica xerogel where they are *inaccessible* for catalysis.

This hypothesis explains the inhibiting effect of fluoride on the materials activity and the higher reactivities of catalysts of batch **A**. In the latter case, indeed, the higher amount of H_2O (and lesser of MeOH) favours the hydrolysis and slows down the condensation, so that rapid aggregation of the early sol particles is prevented and MTMS can *fully hydrolyse* to $CH_3-Si(OH)_3$ and this copolymerises with the $Si(OH)_4$ monomers obtained by the hydrolysis of TMOS. An open network is eventually formed in which most of the added TPAP molecules are encapsulated at the *surface*

of the resulting (hydrophobic) silica cages, where they are accessible for catalysis resulting in gels that are generally more active than those of batch **B**.

In all cases the remarkably high stability of the doped ormosils in $scCO_2$ is consistent with both the considerably higher solubilities of organic molecules in supercritical carbon dioxide (that prevents catalyst deactivation by the adsorbed species acting as cage blocking agents), and with the stability towards leaching of metal “onium” ion pairs encapsulated in sol-gel materials.^[14]

Finally, scanning electron micrography (Figure 3) reveals the catalysts morphologies showing that the materials are constituted of silica aggregates and that these are *nanostructured* which – given that the surface geometry experienced by the approaching reactant molecules has a profound effect on the materials reactivity,^[20] and that the sol-gel methodology allows one to tailor such geometry^[21] – may be a relevant subject for further investigations aimed at optimization of the materials catalytic performance.

Conclusions

In conclusion, sol-gel silica gels doped with TPAP and organically modified are leach-proof selective catalysts suitable for the aerobic conversion of alcohols into valuable^[5,7] carbonyl compounds in supercritical CO_2 . The best performing catalysts require both a high degree of surface hydrophobicity as well as high amounts of water and co-solvent in the sol-gel polycondensation process employed for the catalyst preparation.

Under the batch experimental conditions applied, their activity in the supercritical phase is still considerably lower than in the liquid phase:^[10a] However, a general interpretation of the structure-activity relationship observed is offered to provide guidelines for the development of efficient solid catalysts for oxidative dehydrogenations which – considering the commercial and synthetic relevance of carbonyl compounds along with the versatility of doped sol-gel materials^[21] and the technical and environmental advantages offered by continuous reactions in supercritical phase^[7] – might soon lead to practical applications capable to meet the industrial requirements of catalyst versatility (including combinatorial applications)^[22] and process sustainability.^[6]

Experimental Section

Materials

Methyltrimethoxysilane (MTMS), tetramethyl orthosilicate (TMOS), tetra-*n*-propylammonium perruthenate (TPAP), benzyl alcohol, 9-decen-1-ol, 4-hexen-1-ol, and *n*-decane were purchased from Sigma-Aldrich and used without further

purification. Methanol and NaF were purchased from Fluka. Ultra pure water (Millipore Type 1 quality) was used in all the preparations.

Instruments

The reaction system employed for oxidations in scCO_2 (a modified Carlo Erba SFC 3000) was described elsewhere.^[23] The stainless steel 10-mL high pressure vessel is connected to a restrictor through a 6-way HPLC valve for sample withdrawing.

The carbonyl product content was determined by GC analysis on a Shimadzu chromatograph equipped with a Supelcowax 10 capillary column (30 m, 0.25 mm ID) using the internal standard method (with previously calculated response factors). The N_2 -BET textural values were obtained with a Carlo Erba Instruments Sorptomatic 1900 powder analyzer, and the Ru content in catalysts and reaction samples assessed by ICP-MS on an HP 4500 spectrometer.

Catalyst Preparation

Several doped ormosils were prepared by sol-gel hydrolysis and co-polycondensation of MTMS and TMOS in the presence of TPAP dissolved in methanol with and without NaF as polycondensation catalyst and varying the relative amounts of water, co-solvent (batch A, $\text{Si}:\text{MeOH}:\text{H}_2\text{O} = 1:8:1$; batch B, $\text{Si}:\text{MeOH}:\text{H}_2\text{O} = 1:4:4$), and the organosilane/silane ratio.

A typical catalyst of batch A obtained with NaF (A-Me1, Table 1), was prepared by adding 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 followed by the addition of H_2O (5.70 mL) and NaF (765 μL , 1 M) under 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 catalytic xerogel thus obtained was powdered, washed under reflux ($\text{CH}_2\text{Cl}_2 \times 2$, 40°C) and dried at 50°C prior to use.

A typical catalyst of batch B such as **B-Me3** was obtained by 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 as reported above. A typical catalytic load was 0.05 mmol TPAP/g ormosil.

Typical Oxidation Procedure

Benzyl alcohol (5 μL , 0.5 mmol) and 0.1 equiv. of catalyst **A-Me1** (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 (Scheme 1) in the homogeneous supercritical phase. In order to do so, we dissolved 0.5 mmol of substrate and 0.5 mmol of product along with the internal standard decane in 10 mL CH_2Cl_2 , analysing its content at GC, prior to charging the reactor with the same amounts of substrate, product and internal standard. Keeping constant the

reaction vessel temperature at 75°C , and assuming complete dissolution of the hydrophobic decane, we varied the CO_2 pressure inside the reactor from 140 to 240 bar while analysing the content at GC in order to check the substrate and product dissolution which was complete at 220 bar.

Hence, after purging with oxygen (1 bar partial pressure at ambient temperature), the reaction vessel was sealed and placed into an oven thermostatted 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; and when the reaction was complete, the heating was stopped and the system allowed to cool to ambient temperature. The reactor was thus opened and the CO_2 gradually vented off in CH_2Cl_2 . When the total pressure inside the reactor reached the atmospheric value, the product was extracted with a further amount of CH_2Cl_2 and the recovered catalyst was dried and reused *as such* in a subsequent reaction run.

Acknowledgements

We thank the CNR for a short-term mobility scholarship to R. C. that allowed her stay at Reading University Catalysis Research Centre and Dr. S. C. E. Tsang for his kind hospitality. Thanks are due to Dr. Giuseppe Marci at the University of Palermo for the SEM pictures.

References and Notes

- [1] R. A. Sheldon, M. Wallau, I. W. C. E. Arends, U. Schuchardt, *Acc. Chem. Res.* **1998**, *31*, 485.
- [2] B. M. Choudary, M. Lakshmi Kantam, P. Lakshmi Kantam, *Catal. Today* **2000**, *57*, 17.
- [3] For selected recent examples, see: a) D. R. Jensen, J. S. Pugsley, M. S. Sigman, *J. Am. Chem. Soc.* **2001**, *123*, 7475; b) G. J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636; c) J. Takagi, M. Aoki, R. Noyori, *Tetrahedron Lett.* **1998**, *39*, 7549; d) A. Dijkman, A. Marino-González, A. Mairata i Payaras, I. W. C. E. Arends, R. A. Sheldon, *J. Am. Chem. Soc.* **2001**, *123*, 6826; e) G. Csajnyik, A. H. Éll, L. Fadini, B. Pugin, J. E. Bäckvall, *J. Org. Chem.* **2002**, *67*, 1657; f) I. E. Markó, P. R. Giles, M. Tsukazaki, I. Chellé-Regnault, C. J. Urch, S. M. Brown, *J. Am. Chem. Soc.* **1997**, *119*, 12661.
- [4] For a recent account, see: M. Freemantle, *Chem. Eng. News* **2001**, *79* (1), 21.
- [5] a) S. R. Oakes, A. A. Clifford, M. C. Rayner, *J. Chem. Soc. Perkin Trans. 1* **2001**, 917; b) A. Baiker, *Chem. Rev.* **1999**, *99*, 453; c) S. Kainz, W. Leitner, *Catal. Lett.* **1998**, *55*, 223.
- [6] A. D. Curzons, D. J. C. Constable, D. N. Mortimer, V. L. Cunningham, *Green Chem.* **2001**, *3*, 1.
- [7] a) N. J. Meehan, A. J. Sandee, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, M. Poliakoff, *Chem.*

- Commun.* **2000**, 1497; b) M. G. Hitzler, M. Poliakoff, *Chem. Commun.* **1997**, 1667.
- [8] For example, catalytic conversions in scCO_2 are now finding industrial applications in the UK: M. Freemantle, *Chem. Eng. News* **2001**, 79 (22), 30.
- [9] E. R. Birnbaum, R. M. Le Lacheur, A. C. Horton, W. Tumas, *J. Mol. Catal. A: Chemical* **1999**, 139, 11.
- [10] a) M. Pagliaro, R. Ciriminna, *Tetrahedron Lett.* **2001**, 42, 4511; b) similar results were reported for nanostructured $\text{R}_4\text{NX-Pd}$ -clusters encapsulated in sol-gel ormosils: M. T. Reetz, S. A. Quaiser, *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 2240.
- [11] M. Hasan, M. Musawir, P. N. Davey, I. V. Kozhevnikov, *J. Mol. Catal. A: Chemical* **2002**, 180, 77.
- [12] a) I. C. Tilgner, P. Fischer, F. M. Bohnen, H. Rehage, W. F. Maier, *Microporous Mater.* **1995**, 5, 77; b) R. Winter, J. B. Chan, R. Frattini, J. Jona, *J. Non-Cryst. Solids* **1988**, 105, 214.
- [13] a) T. Fey, H. Fischer, S. Bachmann, K. Albert, C. Bolm, *J. Org. Chem.* **2001**, 66, 8154; b) R. Ciriminna, C. Bolm, T. Fey, M. Pagliaro, *Adv. Synth. Catal.* **2002**, 344, 159.
- [14] a) J. Blum, D. Avnir, H. Schumann, *Chemtech* **1999**, 29 (2), 32; b) H. Sertchook, D. Avnir, J. Blum, F. Joó, Á. Kathó, H. Schumann, R. Weimann, S. Wernik, *J. Mol. Catal. A: Chemical* **1996**, 108, 3754.
- [15] a) H. Frenkel-Mullerad, D. Avnir, *Chem. Mater.* **2000**, 12, 3754; b) and similar higher reactivities in gels with lower porosities were found by Reetz: M. T. Reetz, *Adv. Mater.* **1997**, 9, 943.
- [16] a) A. Steele, J. Zhu, S. C. E. Tsang, *Catalysis Lett.* **2001**, 73 (1), 9; b) previous results using carbon-supported metal catalysts were reported in: G. Jenzer, D. M. Sœur, T. Mallat, A. Baiker, *Chem. Commun.* **2000**, 2247.
- [17] D. Avnir, *Acc. Chem. Res.* **1995**, 28, 328.
- [18] B. M. De Witte, D. Commers, J. B. Uytterhoeven, *J. Non-Cryst. Solids* **1996**, 202, 35.
- [19] M. J. van Bommel, T. N. M. Bernards, A. H. Boonstra, *J. Non-Cryst. Solids* **1991**, 128, 231.
- [20] A. Sery-Levy, D. Avnir, *Surf. Sci.* **1991**, 248, 258.
- [21] a) D. Avnir, J. Blum, O. Lev in *The Encyclopedia of Materials: Science and Technology*, (Eds.: K. H. J. Buschow, M. C. Flemings, E. J. Kramer, R. W. Cahn, B. Ilschner, S. Mahajan), Elsevier, Amsterdam, **2001**, pp. 8040–8049; b) J. D. Wright, N. A. J. M. Sommerdijk, *Sol-Gel Materials: Chemistry and Applications*, Gordon and Breach Science Publishers: Amsterdam, **2001**; c) C. J. Brinker, G. W. Scherer, *Sol-Gel Science and Technology*, Academic Press: Boston, MA, **1990**.
- [22] S. V. Ley, I. R. Baxendale, R. N. Bream, P. S. Jackson, A. G. Leach, D. A. Longbottom, M. Nesi, J. S. Scott, R. I. Storer, S. J. Taylor, *J. Chem. Soc. Perkin Trans. 1* **2000**, 23, 3815.
- [23] S. Campestrini, U. Tonellato, *Adv. Synth. Catal.* **2001**, 343, 819.