



New recyclable catalysts for aerobic alcohols oxidation: sol-gel ormosils doped with TPAP

Mario Pagliaro and Rosaria Ciriminna*

Institute of Chemistry and Technology of Natural Products, CNR, via Ugo La Malfa 153, 90146 Palermo, Italy

Received 10 April 2001; accepted 14 May 2001

Abstract—Novel nanoporous materials have been prepared that are recyclable catalysts for the aerobic oxidation of activated and non-activated alcohols. The catalysts are organically modified silicas (ormosils) doped with tetra-*n*-propylammonium perruthenate (TPAP) via the sol-gel process. Hydrophobicity and flexibility of the sol-gel cages were crucial in promoting catalysis. © 2001 Elsevier Science Ltd. All rights reserved.

The selective oxidation of alcohols to carbonyl compounds is a key process in organic synthesis and plays a central role in the fine chemicals industry, carbonyls being precursors of drugs, vitamins, fragrances and important synthons for complex syntheses.¹

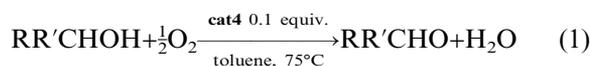
Traditional industrial alcohol oxidations, however, are stoichiometric conversions carried out in liquid-phase with toxic chromium and manganese species and their replacement with *heterogeneous catalytic* oxidations using clean, atom-efficient oxidants such as O₂ and H₂O₂ remains a primary goal of the ‘Green Chemistry’ program.¹

Besides hydroxyl groups, however, the alcoholic substrates of interest to the industry often contain other oxidisable functional groups; hence, *highly* selective oxidation catalysts are needed that also, due to the low volumes of products of the fine chemicals industry, should be *versatile*, i.e. applicable to the conversion of widely different alcoholic substrates.

Now we report that nanoporous (pore sizes <15 Å) organically modified silicas doped with tetra-*n*-propylammonium perruthenate (TPAP) by direct encapsulation of TPAP via the sol-gel process, are recyclable aerobic catalysts for the oxidation of activated and non-activated alcohols (TOF 1–13 h⁻¹ depending on the substrate).

Keywords: oxidation; heterogeneous; sol-gel cage; TPAP; ormosil; hydrophobicity.

* Corresponding author. Fax: +39 091 680 93 99; e-mail: ciriminna@ictpn.pa.cnr.it



The sol-gel process is increasingly being employed to heterogenize all kinds of molecules (including enzymes) within inorganic or inorganic–organic metal oxides.²

By simply promoting the hydrolysis and polycondensation of suitable precursors such as metal alkoxides in the presence of a solution of the dopant species highly porous, *reactive* materials are obtained with surface areas of several *hundreds* of m² g⁻¹. These materials have *higher* chemical and physical stability compared to the organic and inorganic polymers commonly employed as catalyst supports, and often afford sensitivity and selectivity superior to those of the dopant molecules in solution.^{2c}

The entrapped species are in fact homogeneously dispersed *within* the microporous cages where they are highly protected by the surface of the cages and yet accessible by external reagents (provided that the size of the approaching molecules does not exceed that of the cages).^{2c}

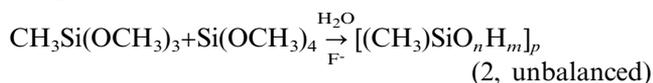
Remarkably, many structural properties (cages hydrophobicity, porosity, surface area, morphology, etc.) of doped sol-gel materials can be *tailored* to meet the requirements of the needed chemical conversion by varying the preparation conditions (types of alkoxides, catalyst, pH, water/metal ratio, additives, precursors, co-solvent, drying temperature, etc.) whose wide variability offers to chemists a *versatility* that has made the sol-gel process a viable alternative to many traditional catalyst preparation routes.³

The species tetra-*n*-propylammonium perruthenate, in this respect, was recently found⁴ to be a versatile aerobic homogeneous catalyst for the oxidative dehydrogenation of largely different alcohols with O₂ (1 atm) in the presence of molecular sieves. Looking for the preparation of recyclable oxidation catalysts we therefore decided to encapsulate TPAP within sol-gel SiO₂.

The activity of the resulting black–green glass obtained starting from Si(OCH₃)₄ in the aerobic oxidation of benzyl alcohol, however, was rather modest; and after 6 h only 40% of the alcohol (0.2 mmol) was converted to benzaldehyde when the homogeneous reaction on the same scale is complete in ca. 30 min.⁴

Aiming at the improvement of catalytic activity, we reasoned that SiO₂ gels are highly hydrophilic materials commercially used in packaging to absorb water and preserve contents from the diffusion of O₂;⁵ moreover, we were aware of the remarkable catalytic activity of hydrophobic sol-gel silicas (ormosils) entrapped with lipases for liquid-phase esterifications.⁶

Thus, we attempted the preparation of different doped ormosils copolymerizing TMOS together with methyltrimethoxysilane (MTMS) at various ratios in the presence of TPAP:



An entirely methylated ormosil was also prepared using MTMS as unique material precursor and NaF as the condensation catalyst.^{6b}

When we tested the activity of the resulting materials (Table 1) in the aerobic oxidation of benzyl alcohol, results were very surprising and a trend analogous to that observed with encapsulated lipases^{6a} was observed (Fig. 1).

The activity of the doped xerogels was still moderate with the ormosil obtained from equimolar amounts of TMOS and MTMS (**cat2**); but was considerably higher using the 75% methylated ormosil (**cat3**), and became comparable (TOF of 13.3 h⁻¹) to that of homogeneous TPAP when the fully methylated material **cat4** was employed and reaction was complete in 45 min.

The catalyst, a grey powder with a BET specific surface area of 400 m²/g and a *narrow* pore size distribution centered around 12 Å, was 30 times more active compared to TPAP entrapped in unmodified SiO₂ (**cat0**),

Table 1. Catalysts composition

Catalyst	TMOS (%)	MTMS (%)
cat0	100	–
cat1	75	25
cat2	50	50
cat3	25	75
cat4	–	100

and in contrast to the homogeneous reaction protocol⁴ no molecular sieves were needed in the reaction.

Significantly, upon filtering the reaction mixture at 75°C, leaching of ruthenium in liquid-phase assessed by highly sensitive ICP-MS on the reaction filtrate was found to be negligible (6 ppb) and the catalyst constantly leach-proof in the subsequent three runs in which it was used.

This is of crucial importance since analogous heterogeneous aerobic oxidations were actually found to be promoted by the metal species leached in solution and then *readsorbed* by the solid support upon cooling the reaction mixture.⁷

Based on these encouraging results, we used the catalytic ormosil **cat4** in the oxidation of the non-activated primary aliphatic alcohol 1-octanol. Employing the same catalytic amount (0.1 equiv.) the substrate (0.2 mmol) was smoothly converted into octanal in good yield 70% and moderate catalytic activity (TOF 1 h⁻¹). However, negligible leaching was found to take place (60 ppb) and the catalyst was reusable with no leaching in the 3 subsequent runs in which it was used.

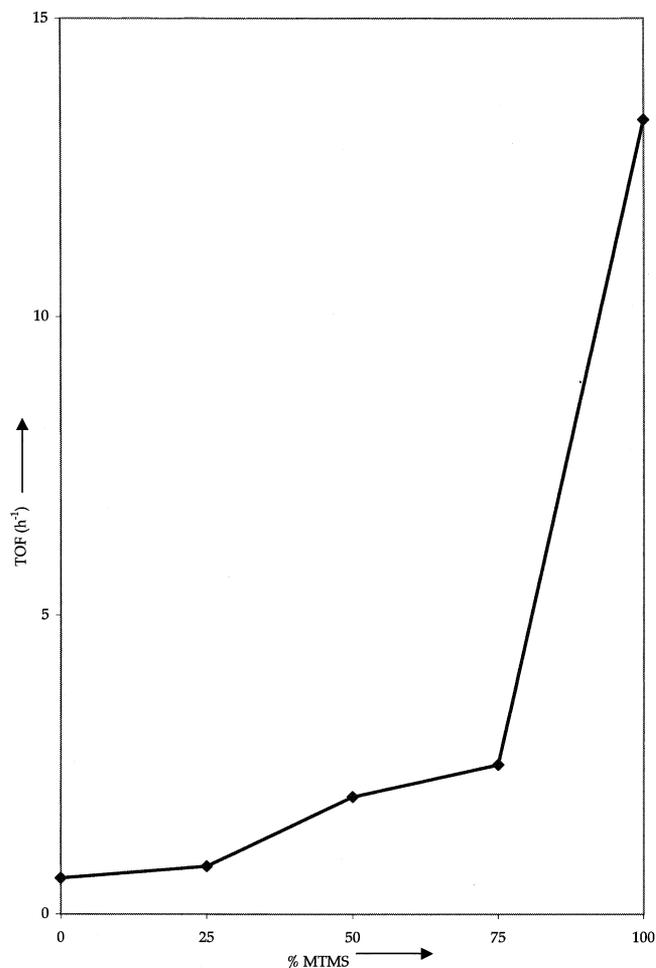


Figure 1. Dependence of the activity (mmol h⁻¹ (mmol TPAP)⁻¹) of entrapped TPAP in TMOS/MTMS mixed gels versus gel composition.

Table 2. Aerobic oxidation of alcohols mediated by doped ormosil **cat4**¹²

Alcohol	Product	Conversion (%)	Time (h)	TOF (h ⁻¹)
Benzyl alcohol	Benzaldehyde	100	0.75	13.3
(<i>R,S</i>)-1-Phenylethanol	Acetophenone	90	3	3.0
Cinnamyl alcohol	Cinnamaldehyde	90	5	1.8
1-Octanol	<i>Octyl aldehyde</i>	70	7	1.0

We also used **cat4** for the oxidation of (*R,S*)-1-phenylethanol and of cinnamyl alcohol. With both substrates (Table 2) the catalyst was found active and leach-proof with activities (TOF 3.0 h⁻¹ for (*R,S*)-1-phenylethanol; 1.8 h⁻¹ for cinnamyl alcohol) higher than that observed with 1-octanol. Lack of leached ruthenium confirmed the heterogeneous nature of the aerobic oxidations demonstrating that sol-gel ormosils doped with TPAP are selective catalysts for the oxidation of activated and non-activated alcohols.

These results extend what was recently reported when the perruthenate ion RuO₄⁻ was tethered (through Si(CH₂)₃NH₃⁺ groups) to the *inner* mesoporous channels of sol-gel silica MCM-41. Indeed, the latter material was found to be a truly recyclable catalyst suitable for the oxidation of allylic and benzylic alcohols,⁸ but the direct entrapment of perruthenate by simple *impregnation* of MCM-41 with KRuO₄ yielded a material giving complete leaching upon a single aerobic oxidation run.⁸

In fact, many of the traditional heterogenization methods of catalytic species on inorganic and organic polymers are *surface derivatizations* that leave the anchored molecules unprotected at the polymer surface, and are unsuccessful on a technological scale due to loss in activity and selectivity upon leaching of the supported species in solution.^{1b} Similarly, RuO₄⁻ supported over an ion exchange polystyrene resin was initially claimed to be an effective heterogeneous catalyst⁹ but was soon found to be 'unstable probably due to oxidative degradation of the polystyrene support'.⁸

The sol-gel entrapment, on the other hand, highly protects the entrapped species within the cages of the doped xerogel and it is relevant to this report to notice that in order to ensure recyclability many transition metal catalysts^{2c} were encapsulated in leach-proof catalysts using the corresponding onium ion pairs, a structural feature shared by the species (CH₃CH₂CH₂)₄NRuO₄ employed in our direct entrapment procedure.

Finally, to explain the superior catalytic activity of the doped ormosil compared to TPAP encapsulated within unmodified SiO₂, it may be noted that in the sol-gel process, substituted silanes R'Si(OR)₃ condense to the network formed by the faster hydrolysis and condensation of Si(OR)₄ mostly modifying the *surface* of the cages.¹⁰ This enhances the hydrophobicity of the cages and, correspondingly, the diffusion rates within the porous network of the hydrophobic O₂ and alcohol molecules.

However, in liquid-phase the cages of sol-gel materials are *rapidly* filled by the hosting liquid and the polarity *sensed* by the encapsulated molecules is largely determined¹¹ by the liquid in which the material is hosted (toluene in our case). It is the higher *flexibility* of the cages obtained by diminishing the amount of hindering intra-cage Si-OH groups that is crucial for the reactivity of doped sol-gel materials; in fact, in many chemical applications of doped sol-gel materials, it has been observed^{2b,6a} that a *compromise* between cage protectability and flexibility must be reached to ensure optimal reactivity.

In conclusion, we have found that sol-gel modified silicas doped with TPAP are recyclable heterogeneous catalysts for the aerobic oxidation of alcohols with a remarkable hydrophobic effect. Considering the vast number of available organically modified alkoxides and the vastness of controllable parameters of the sol-gel process mentioned above,² these findings might open the way to the introduction of clean and cost-effective aerobic oxidation catalysts, especially considering that for practical applications like continuous processes where long-term stability is crucial, the mechanical stability of doped sol-gel ormosils can be increased by attaching the gel to the surface of sintered glass beads^{6a} or of similar materials.

Acknowledgements

This paper is dedicated with deep affection to Professor David Avnir. We thank him for continuing to share his intelligence and his humanity with us throughout recent years. We would also like to thank Dr. Filippo Saiano (ITAF Department, University of Palermo) for the ICP-MS measures and Dr. Salvatore Catania (Bromatos Laboratory, Palermo) for their generous assistance.

References

- (a) Choudary, B. M.; Lakshmi Kantam, M.; Lakshmi Kantam, P. *Catal. Today* **2000**, *57*, 17–32; (b) Sheldon, R. A.; Arends, I. C. W. E.; Dijkstra, A. *Catal. Today* **1999**, *57*, 157–166.
- (a) Avnir, D.; Blum, J.; Lev, O. In *Encyclopedia of Materials Science and Technology*; Buschow, K. H. J., Ed. Molecular composite sol-gel materials with reactive organic and bio-organic dopants.; Pergamon: Oxford, 2001; pp. 224–237; (b) Avnir, D. *Acc. Chem. Res.* **1995**,

- 28, 328–334; (c) Blum, J.; Avnir, D.; Schumann, H. *Chemtech* **1999**, 29 (2), 32–38.
3. Predieri, G.; Cauzzi, D. *La Chim. l'Industria*, **2000**, http://www.bias-net.com/chimica/pdf/lug_predieri.pdf
4. Markó, I. E.; Giles, P. R.; Tsukazaki, M.; Chellé-Regnaut, I.; Urch, C. J.; Brown, S. M. *J. Am. Chem. Soc.* **1997**, 119, 12661–12662.
5. Brody, A. *Plast. Packaging* **1989**, 22–25.
6. (a) Reetz, M. T. *Adv. Mater.* **1997**, 9, 943–954; (b) Reetz, M. T.; Zonta, A.; Simpelkamp, J. *Biotechnol. Bioengin.* **1996**, 527–534.
7. Sheldon, R. A.; Wallau, M.; Arends, I. W. C. E.; Schuchardt, U. *Acc. Chem. Res.* **1998**, 31, 485–493.
8. Bleloch, A.; Johnson, B. F. G.; Ley, S. V.; Price, A. J.; Shephard, D. S.; Thomas, A. W. *Chem. Commun.* **1999**, 1907–1908.
9. Hinzen, B.; Lenz, R.; Ley, S. V. *Synthesis* **1998**, 977–979.
10. Husing, N.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1998**, 37, 22–35.
11. Rottman, C.; Grader, G. S.; De Hazan, Y.; Avnir, D. *Langmuir* **1996**, 12, 5505–5508.
12. Representative experimental procedures: **CAUTION**, add TPAP to MeOH **slowly** and **portionwise** to prevent sudden formation of **flames**. The catalyst **cat4** was prepared

adding MTMS (3.65 mL) to a solution of TPAP (34 mg) in MeOH (1 mL) containing 0.45 μ L of NaF 0.1 M. The resulting solution was added with 3.6 mL of H₂O under fast stirring and sealed.

The mixture gelled rapidly and the alcogel was left sealed to age for 1 day at room temperature then opened and dried for 5 days at 40°C (*aging* 1 day the sealed alcogel improved the activity of the final xerogel). The resulting xerogel (**cat4**) is a soft grey powder (1.3 g) that was washed under reflux (CH₂Cl₂×3, 60°C), dried at 40°C and used as such in the aerobic reaction runs.

A solution of substrate alcohol (0.2 mmol) in toluene (4 mL) was added with 0.1 equiv. **cat4** (270 mg) and the suspension brought to 75°C in an oxygen atmosphere; the reaction mixture was kept sealed during reaction in order to avoid product loss at the reaction temperature. Aliquots were periodically withdrawn and the carbonyl content assessed by gas chromatography; upon each withdrawal oxygen was reflushed, 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 CH₂Cl₂ (×3, 60°C), dried and used as such in the subsequent reaction runs according to the same oxidation protocol.