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Stabilization of catalytic sol–gel entrapped perruthenate

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Abstract

A combination of more stable counter-cation (tetraphenylphosphonium in place of tetrapropylammonium), of local basic microenvironment, and of a non-solubilizing reaction medium (supercritical CO_2) improves the life-cycle and reusability of catalytic ORMOSILs doped with perruthenate in the oxidation of alcohols with O_2. A number of different bases were co-entrapped and their effect on catalysis assessed in the oxidative dehydrogenation of benzyl alcohol in dense phase carbon dioxide at 22 MPa and 75 °C. The optimized catalyst retains most of its activity after five consecutive runs when a normal ORMOSIL-entrapped TPAP has become inactive. Deactivation of TPAP could be ascribed by EPR analysis to the formation of catalytically inactive RuO_2.

Keywords: TPAP; Oxidation; Heterogeneous; Sol–gel; ORMOSIL; Aerobic; Stabilization

The demand from industry and society for more efficient and environmentally benign processes for chemical transformations of primary industrial importance such as alcohols oxidation to carbonyl compounds is rapidly growing.[1] Carbonyl compounds are precursors of diverse valuable fine chemicals including drugs, dyes, vitamins, and fragrances,[2] and the design of simple, safe, and effective synthetic routes in place of stoichiometric industrial processes based on toxic metal oxidants such as dichromate and permanganate employed in volatile organic solvents[3] is a central theme of contemporary chemical research. Terms such as atom efficiency and waste minimization are now central requirements for both commercial and research focused synthesis. The principles of 'green chemistry'[3] applied to an oxidative process may be expressed as follows: (i) the ultimate oxidant must be environmentally neutral and preferably end up entirely incorporated into the final product; (ii) the catalyst must be highly active, selective, reusable, and easily recoverable to minimize the energetic requirements of the overall process; and, (iii) the use of auxiliary substances such as solvents or separation agents should be avoided to minimize waste stream.

To meet these requirements, a variety of reagents and techniques have been lastly proposed. Clearly, oxygen is the ideal terminal oxidant also in the case of alcohols dehydrogenation (in this case the oxidant cannot be incorporated into the final products, but is found in totally innocuous water by-product, Eq. 1).

$$\mathrm{RR'{-}CHOH} + 1/2\mathrm{O_2} \longrightarrow \mathrm{RR'{-}CO} + \mathrm{H_2O} \qquad (1)$$

In recent years, a number of highly selective metal-based catalytic processes employing Ru,[4] Pd,[5] Cu,[6] Co,[7] V,[8] Os,[9] Ni,[10] and Au[11] derivatives have been reported.[12] Most of these methods, however, suffer from some drawbacks, and in most cases either relatively large amount of expensive catalysts are needed (and in some cases the stoichiometric consumption of a sacrificial reactant) or high reaction temperatures are required.

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The Ru(VII) derivative tetra-*n*-propylammonium perruthenate (TPAP) rapidly emerged as a commercial catalytic oxidant, thanks to its pronounced selectivity in the aerobic oxidation of primary, secondary, benzyl, and allyl alcohols.[13,14] Indeed, many other oxidizable functional groups such as carbon–carbon double bond, epoxy, indol, acetal, etc. remain unaffected by TPAP whereas high yields of carbonyl compounds are obtained.[15]

The major drawbacks of the TPAP/O_2 oxidative system in conventional organic solvents such as toluene lie both in the scarce turnover numbers (TON) observed (ca. 20) and in the impossibility of catalyst recycling.[15] The use of supercritical carbon dioxide ($scCO_2$) as an alternative reaction solvent exhibits some distinct advantages[16] including stability under oxidative conditions and excellent oxygen solubility and diffusivity. This enables one-pot isolation and purification of the products from the reaction mixture by simple control of the density of the supercritical phase eliminating the need of auxiliary substances (e.g., extracting solvents, separation agents) and of expensive distillation.

In this context, we recently reported that ORMOSILs[17] doped with TPAP are suitable catalysts for the aerobic oxidation of alcohols in $scCO_2$.[18] Aiming at improving catalyst stability, we now describe the effects of tetrapropylammonium (NPr_4^+) cation replacement by tetraphenylphosphonium (NPh_4^+) as well as of the employment of base in the sol–gel polycondensation process used to synthetize the active ORMOSILs. Benzyl alcohol was chosen as a model substrate but we have already shown that similar ORMOSIL-entrapped TPAP materials can be used for the oxidation of a variety of largely different substrates.[18]

The catalysts were prepared by sol–gel entrapment of TPAP or TFF (tetraphenylphosphonium perruthenate) in hybrid organic–inorganic silica glasses obtained using methyltrimethoxysilane (MTMS) and tetramethylorthosilicate (TMOS) as precursors of the final xerogel. All (analytical grade) chemicals employed were supplied by Aldrich. Previous analysis indicates that the best performing catalysts in $scCO_2$ require both a high degree of surface hydrophobicity as well as high amounts of water in the sol–gel polycondensation process.[19] Hence, we prepared two catalysts, namely, TFF-Me3A (a xerogel prepared with 75% of MTMS containing 5.0×10^{-3} mmol of tetraphenylphosphonium perruthenate per 100 mg of catalyst) and TPAP-Me3A (a xerogel prepared with 75% of MTMS containing 5.0×10^{-3} mmol of tetrapropylammonium perruthenate per 100 mg of catalyst). Ru load was measured by ICP-MS. A batch of catalysts with the same molar composition of TPAP-Me3A was also prepared adding to the sol mixture a base chosen among potassium carbonate, *N*-methyl morpholine (NMM), tetrabutylammonium hydroxide (TBAOH), and tetramethylammonium hydroxide (TMAOH) in 5×10^{-5} mol/g amount.

The catalytic oxidation of benzyl alcohol was performed in a stainless steel 10 mL reaction vessel (connected to a restrictor through a 6-way HPLC valve for sample withdrawing) at a final total pressure of 22 MPa and at 75 °C, in the presence of O_2 (0.1 MPa at 25 °C) and TPAP-Me3A or TFF-Me3A. The molar ratios of the components of reaction mixtures were approximately TPAP/alcohol/oxygen = 1/10/350; in which the oxygen excess and the final pressure of 22 MPa were used to ensure, respectively, a complete conversion of benzyl alcohol and complete solubility of the substrate. Reaction was monitored by GC. Samples withdrawn through the stainless steel restrictor (kept at 90 °C) were trapped in dichloromethane prior to GC analysis. When the reaction was complete (reaction times ranging from 7 to 35 h, depending on the catalyst), 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 used as such in a subsequent reaction run. The rate constants for the catalytic processes ($k_{cat.}$) were obtained from the slope of integrated pseudo first-order plots, that is, $\ln([\text{aldehyde}]_{t=\infty}\text{-}[\text{aldehyde}]_{t=t})$ versus time, which are linear up to ca. 90% reaction. TOF values were determined at complete conversion. The EPR spectra of untreated and used catalysts at 110 K were recorded on a Bruker ER 200 D spectrometer equipped with a nitrogen flow Bruker ER 4121 variable temperature system, for the measurement in the range 100–350 K. Typical parameters for the acquisition of the spectra were modulation amplitude 5 G, microwave power 10 mW, sweep width 5 G, sweep time 80 s, and time constant 50 ms. The simulations of the EPR spectra have been performed using Bruker SimFonia program. The EPR spectrum was simulated with a rhombic *g*-tensor whose principal values are $g_{xx} = 1.92$, $g_{yy} = 2.01$, $g_{zz} = 2.27$ and a anisotropic linewidth of 250, 150, and 250 G along the *x*, *y*, *z* directions of the *g*-tensor.

Table 1 summarizes the results of the experiments aimed at evaluating the effect of tetrapropylammonium cation replacement by tetraphenylphosphonium on the efficiency of the resulting doped ORMOSILs in the aerobic benzyl alcohol oxidation. Indeed, tripropylamine is detected among the byproducts in the stoichiometric oxidation of alcohols by TPAP in liquid phase,[15] so that the replacement of the NPr_4^+ species by a cation less prone to undergo

Table 1
Oxidation of benzyl alcohol (4.83×10^{-2} mmol) with oxygen (1.0×10^5 Pa at 25 °C) catalyzed by TPAP-Me3A and TFF-Me3A (content of perruthenate: 0.5×10^{-2} mmol per 100 mg of ORMOSIL), in $scCO_2$ at 22.0 MPa and 75 °C

Entry	Catalyst	Age (Months)	$k_{cat.} \times 10^2$ min^{-1}
1	TPAP-Me3A	1	0.49
2	TPAP-Me3A	18	4.0
3	TFF-Me3A	0	0.16
4	TFF-Me3A	5	0.25
5	TFF-Me3A	8	0.34
6	TFF-Me3A	14	0.58

Hofmann's elimination should in principle help in preventing catalyst degradation.

Clearly, the activity of the TFF-based catalyst is lower than that of TPAP-based material.[20] However, TFF-Me3A and TPAP-Me3A exhibit a qualitatively similar temporal behavior in enhancing their activities along with the xerogel's aging. This phenomenon has been already observed in the case of aerobic alcohol oxidations with TPAP-Me3A carried on in both $scCO_2$ and toluene.[21] However, in the case of TFF-Me3A the aging effect results much less pronounced as evidenced by Figure 1 (negative values in the graph are shown only for visual clarity).

As usual for ORMOSIL-entrapped TPAP no leaching of Ru was observed during reaction (by ICP-MS analysis of reaction samples withdrawn *during* reaction). Since the reactivity enhancement upon xerogel aging stems from the migration of the entrapped ion pairs from aggregates partially buried into sol–gel cages to the newly accessible pores being formed upon further hydrolysis and condensation of the unreacted –Si(OR) groups,[21] it appears that the more sterically hindered PPh_4^+ ion pairs exhibit a lower mobility in the inner nanoenvironment of the cages.

When the same batch of TPAP-Me3A catalyst is recycled several times, its grade of reusability depends on the solvent nature used for recovering and washing the ORMOSIL. In particular, dichloromethane, which is a good solvent for unsupported TPAP, leads to a very rapid catalyst deactivation and after the very first recycle the catalyst becomes almost inactive.[18] On the other hand, Figure 2 shows that the efficiency decay for TFF-Me3A in DCM is noticeably slower and the catalyst could be reused several times.

The reason of the scarce catalytic activity of TPAP in conventional organic solvents resides in the irreversible formation of colloidal RuO_2, which, under the usual experimental conditions, is a hardly active and non-selective catalyst for aerobic alcohols oxidation.[15] This could be clearly demonstrated measuring the EPR spectra of the catalyst Me3A-TPAP prior to use and after two recycles (washing it with DCM between the runs). The spectrum (black line, Fig. 3, top) of the fresh materials is fully compatible with that simulated (red line) for the Ru(VII) species with a single unpaired electron. The spectrum in Figure 3 (bottom) of the material after two recycles, on the other hand, is that of a ferromagnetic material with a typical signal drift analogous to that of RuO_2 in the crystalline structure of rutile,[22] in agreement with the behavior of catalytic perruthenate in toluene.[15]

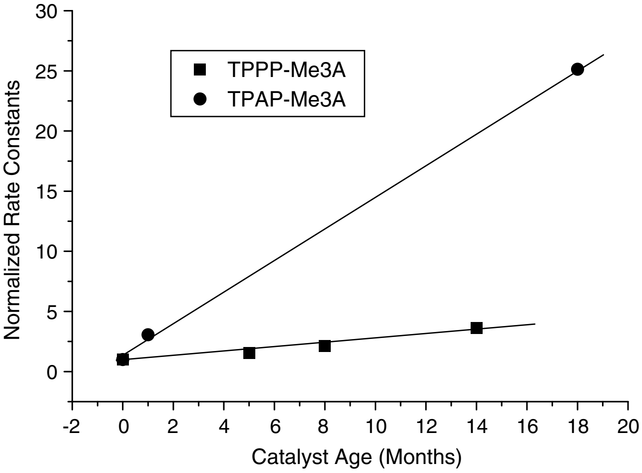

Fig. 1. Dependence of rate constants for benzyl alcohol (4.83×10^{-2} mmol) oxidation with O_2 (1 bar at 25 °C) catalyzed by 100 mg of TPAP and TFF-Me3A (content of perruthenate: 0.5×10^{-2} mmol per 100 mg of ORMOSIL), in $scCO_2$ at 22.0 MPa and 75 °C, as a function of catalyst aging.

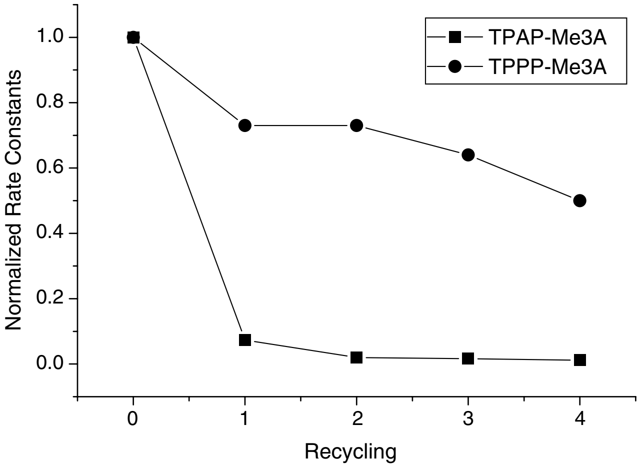

Fig. 2. Dependence of rate constants for benzyl alcohol (4.83×10^{-2} mmol) oxidation with O_2 (1 bar at 25 °C) catalyzed by 100 mg of TPAP and TFF-Me3A (content of perruthenate: 0.5×10^{-2} mmol per 100 mg of ORMOSIL), in $scCO_2$ at 22.0 MPa and 75 °C, as a function of catalyst recycling with DCM as washing solvent.

Since the perruthenate anion is highly stable in aqueous solutions in the pH range 8–12,[23] we reasoned that the realization of a basic microenvironment around the [cation] [RuO_4^-] ion pairs entrapped in the inner porosity of the sol–gel glassy matrix could limit perruthenate degradation in the course of the catalytic process. Hence, we prepared several catalysts by sol–gel co-entrapment of TPAP starting from basic mixtures of MTMS and TMOS as precursors of the final xerogel. To this aim both inorganic and organic bases were tested by conducting the sol–gel perruthenate encapsulation process in the presence of an equimolar amount of base. Both inorganic (potassium carbonate) and organic (tetrabutylammonium hydroxide, TBOH; tetramethylammonium hydroxide, TMAOH; *N*-methylmorfoline, NMM) bases were tested. The results for the aerial oxidation of benzyl alcohol carried out with the xerogels thereby obtained are shown in Table 2.

The experimental conditions for reactions summarized in Table 2 differ from those reported in Table 1 and Figures 1 and 2. In particular, a much higher substrate/catalyst was employed to thoroughly estimate the catalytic ability also in terms of the maximum number of catalytic *cycles* obtainable and not only in terms of reaction rate.

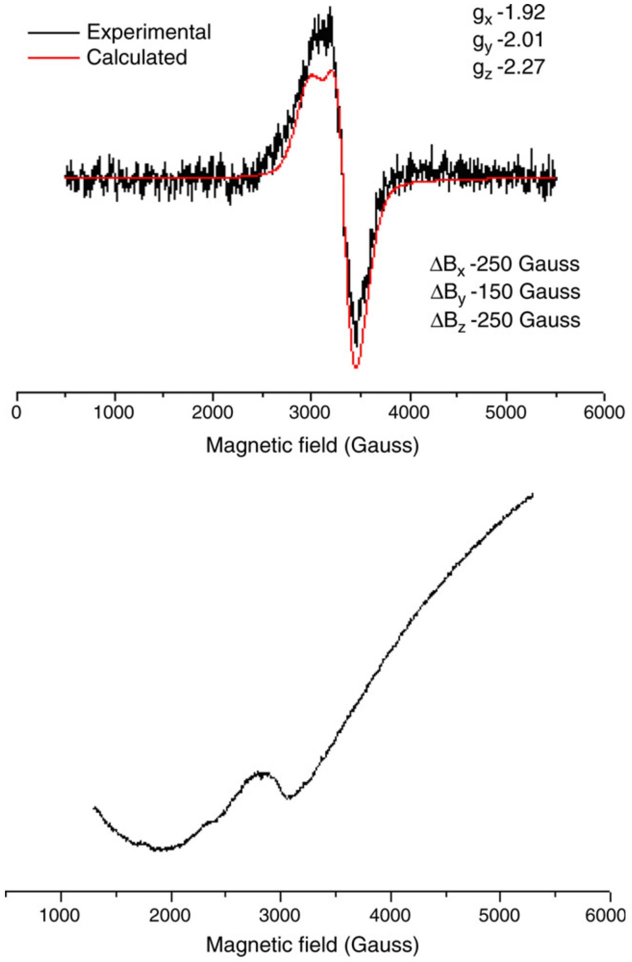

Fig. 3. EPR spectra at 110 K for catalyst Me3A-TPAP prior to use (*top*, including simulation) and after two recycles (*bottom*) washing with DCM between the runs.

Results of Table 2 show that inorganic carbonate (entry 2) exhibits a negligible effect on the maximum TON but a significative *detrimental* effect on the reaction rate. Conversely, NMM (entry 5) determines a significative improvement in the maximum TON whereas the reaction rate decreases by about one third. TBAOH (entry 3) promotes an increment in both TON and reaction rate. Interestingly, however, by simply changing the nature of hydroxyl counter-cation (entry 4) the effect on TON becomes negligible again but the reaction rate decreases to 0.11 h^{-1}.

Table 2
Maximum turnover number (TON) and turnover frequency (TOF) for the oxidation of benzyl alcohol (2.5×10^{-1} mmol) with oxygen (1.0×10^5 Pa at 25 °C) catalyzed by 10 mg of TPAP-Me3A co-doped with base (content of perruthenate: 0.5×10^{-2} mmol per 100 mg of ORMOSIL), in $scCO_2$ at 22.0 MPa and 75 °C

Entry	Embedded base (5×10^{-5} mol/g)	TON (mol/mol)	TOF h^{-1}
1	—	59	0.59
2	K_2CO_3	48	0.14
3	TBAOH	214	0.75
4	TMAOH	56	0.11
5	NMM	125	0.19

Obviously these outcomes do not fit a simple basicity order thus suggesting that the effects exercised by the particular base employed are manifold and arise from the profound influence of the basic conditions in the sol–gel polycondensation (including, in the case of TPAP, a contribute represented by Hofmann elimination, which in the case of TFF cannot take place). Indeed, we observed that the gelation times in the preparation of the various catalysts reported in Table 2 cover a wide range. Base catalyzed sol–gel polycondensation of silicon alkoxides occurs primarily through the addition of monomers to the more highly condensed particles rather than by particle aggregation which results in mesoporous, highly branched silica clusters.[24] Moreover, the effect of the base is higher for the purely inorganic TEOS than for alkyl-modified alkoxysilane.

Under less basic conditions such as those arising from addition of organic base, these structural effects are largely reduced. On the other hand, large organic cations such as tetrabutylammonium of TBAOH function as condensation templates, which might explain the enhanced performance of the gel obtained employing the latter base in the polycondensation. Overall, the final xerogels will be characterized by a different internal structure, which in its turn will impart different efficiency by dictating accessibility to external reactants. However, the efficiency of all these Ru-based catalysts in terms of maximum turnover numbers remains substantially unchanged in the worst case, but significantly increases in some others, thus corroborating the idea that perruthenate survives longer in a basic microenvironment.[25]

In conclusion, the catalytic activity of hybrid silica glasses doped with perruthenate in the aerial oxidation of benzyl alcohol in $scCO_2$ increases in terms of TONs by co-entrapment of a base in the sol–gel cages entrapping the perruthenate anions. Inorganic and organic bases were studied with the best result observed with TBAOH. Moreover, the reusability of the heterogeneous catalyst increases by replacing tetra-*n*-propylammonium with tetraphenylphosphonium cation. Clearly, there is much room for improvement to achieve catalytic activities in $scCO_2$ comparable to those obtainable with heterogeneous Au and Pd catalysts in organic solvents,[26] and we are currently investigating new approaches modifying the structures of the ORMOSIL matrices. However, even though the efficiency of aerobic commercial metal catalysts is far higher in terms of TOF, the said Pd-based materials are highly selective in the oxidation of aromatic alcohols, such as benzyl alcohol, at temperatures 88–120 °C.[27] Moderate activity is the main limitation of Ru-based catalysts[13] but there are several commercial processes in which enhanced selectivity for substrates with several oxidizable groups is required and that, accordingly, use TPAP-based catalysis. Indeed, in the oxidation of benzyl alcohol discussed in this report there is only one product, namely, benzaldehyde, obtained with 100% selectivity. Industry, in which catalytic productions of fine chemicals over heterogeneous catalysts in $scCO_2$ are already carried out,[28] demands selective catalysts of enhanced stability and these findings contribute further elements of evidence that the route to the development of more sustainable oxidation processes for the production of carbonyls in compressed carbon dioxide may soon be based on sol–gel entrapped Ru nanohybrids.

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M.P. dedicates this article to his unforgettable Maestra Angela Lo Nigro, in the grateful memory of the splendid 1974–1979 years at the Garden School.

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