

Aerobic Oxidation of Alcohols in Carbon Dioxide with Silica-Supported Ionic Liquids Doped with Perruthenate

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Abstract: The replacement of toxic Cr^{VI} for O₂ and of chlorinated solvents for supercritical carbon dioxide (or ionic liquids) in the oxidation of alcohols remains hindered by the low selectivity and activity of the current heterogeneous catalysts. Using an integrated approach that combines sol-gel entrapped perruthenate as aerobic catalyst,

an encapsulated ionic liquid as solubility promoter, and scCO₂ as the reaction solvent, we have developed a system

capable of rapidly converting different alcohols into carbonyl compounds with complete selectivity, including substrates which are otherwise difficult to oxidise. The methodology is generally applicable and may easily be extended to other waste-free, catalytic syntheses of fine chemicals.

Keywords: heterogeneous catalysis • ionic liquids • mesoporous materials • oxidation • supercritical carbon dioxide

Introduction

The replacement of toxic heavy metals (such as Cr and Mn) still widely employed in large amounts (at least stoichiometric) in chemical oxidations in liquid-phase reactions is a major goal of current chemical research as these industrial processes normally generate 15–20 kg of hazardous waste per kilogram of desired product (or active pharmaceutical ingredient).^[1]

Similarly, the elimination of carcinogenic and bioaccumulating chlorinated (or aromatic) solvents in which these conversions are generally carried out is also highly desirable^[2] since, despite their relatively low price, solvents have a considerable life-cycle impact and the broader total costs of these typical volatile organic compounds (VOCs) are nonetheless high and constantly increasing.^[3]

The selective oxidation of the alcoholic to the carbonyl functionality in organic molecules, for instance, is one of the organic chemistry fundamental conversions. Carbonyl groups are commonly used synthons in synthetic organic chemistry precursor for the preparation of drugs, vitamins, hormones, dyes.^[4] Yet, whilst most commercial reductions are heterogeneously catalysed and employ H₂ as the reducing agent, heterogeneous aerobic catalysts using O₂ for the production of carbonyl groups are still considered “philosopher’s stone”.^[5]

New, atom-efficient heterogeneously catalysed oxidation processes in alternative reaction media are thus intensively investigated in current academy’s and industry’s research focusing on the immobilization of aerobic metal catalysts^[6] and on supercritical carbon dioxide^[7] or ionic liquids^[8] as reaction solvents.

These and other “greener” innovations, however, will eventually find applications if the advantages will surpass the costs to replace traditional processes.^[9] Enhanced selectivity compared with conventional conversions would, for instance, justify investment in alternative processes as for example with the recently commercialised heterogeneous hydrogenations in scCO₂ in small, high-throughput reactors.^[10] However, while a number of similar catalytic reactions, which afford extremely pure fine chemicals, are carried out on an industrial scale,^[10] no aerobic oxidation is yet commercially carried out in scCO₂ due to poor selectivity of traditional supported metal catalysts.

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Ionic liquids (IL) are not cheap. Preliminary investigations show evidence of toxicity at surprisingly low concentration.^[11] Hence, along with the catalyst, an efficient heterogenization of the IL is also highly desirable because a supported ionic liquid requires significantly reduced amounts of the ionic media while allowing easy separation and recyclability of both the (precious) metal catalyst *and* of the IL reaction medium.

This recently led to the concept of supported ionic liquid catalysis (Silc).^[12] For example, silica-supported ILs doped with a Rh catalytic species were used in catalytic hydrogenations^[12] and hydroformylations.^[13] The reactions proceeded with good selectivity and reaction rates up to 10 times faster than homogeneously catalysed process mostly because the active species—although the resulting material is a solid—is dissolved in the ionic liquid and acts like a homogeneous catalyst.

Similarly, solvent-free hydrogenations with Pd nanoparticles immobilized on molecular sieves by ionic liquids,^[14] and acylation reactions with silica-supported ILs doped with Al^[15] were shown to proceed with good selective activity.

However, a conventional organic solvent was used as a reaction medium in all the conversions mentioned above thus failing to meet the sustainability requirements of solvent elimination from waste-free chemical processes.

By the same token, aerobic catalytic oxidation of alcohols in scCO₂ is desirable but, as mentioned above, the low selectivity of traditional carbon-supported Pd and Pt catalysts has thus far limited applicability in commercial processes.^[16] Homogeneous Ru-based oxidation catalysts,^[17] on the other hand, generally show excellent selectivity to carbonyl groups^[18] but their high costs and difficult recyclability have thus far limited the application essentially to laboratory syntheses.

We now report an integrated method for the efficient oxidation of alcohols with high selectivity in which a “green” reaction medium, a “green” extraction solvent and a “green” catalyst are used to afford a one-pot, versatile catalytic oxidation system. Besides meeting the sustainability zero-emission requirement for industrial chemical processes,^[19] the general scope of the methodology makes it an ideal candidate for practical waste-free oxidative conversions.

Materials and Methods

The following reagents were used: potassium perruthenate (KRuO₄·5H₂O) (Aldrich); 1-[3-(triethoxysilyl)propyl]imidazole (TriEOS-Pr-Im), 1-methylimidazole, 3-chloropropyltriethoxysilane, cetylpyridinium chloride as a template (>95% purity) and tetraethylorthosilicate (>99% purity, TEOS, from Aldrich); ethyl alcohol (100%, Pharmco); and NH₃ (Fisher Scientific). All other reagents were used as received, and all

aqueous solutions were prepared with deionized water (Millipore II system).

The catalysts Silc1 and Silc2 (Table 1) were prepared by ionically tethering RuO₄⁻ to the imidazolium moiety of the ordered mesoporous supported ionic liquid materials **II** and **VII** recently prepared by some of us.^[20] Compound **II** is a silica-entrapped ionic liquid obtained via grafting methyl iodide on the imidazolium containing silica xerogel obtained upon sol-gel processing of a mixture of TEOS and (EtO)₃Si(CH₂)₃-Im; while sample compound **VII** is a silica-entrapped ionic liquid prepared by co-polycondensation of TEOS and [(EtO)₃Si(CH₂)₃-Im⁺-CH₃Cl]⁻.^[20]

Table 1. Catalytic load and surface atomic composition for perruthenate-doped supported ionic liquids.

Compound	RuO ₄ ⁻ load [mmol g ⁻¹]	Ru [%] ^[a]	Si [%] ^[a]	X ⁻ [%] ^[a]
Silc1	0.41	6.82	88.26	4.92
Silc2	0.64	9.74	87.81	2.45

[a] By X-ray fluorescence, X⁻ = halide (iodide for Silc1 and chloride for Silc2).

Silc1 was prepared by mixing a suspension of **II** (100 mg; iodide content: 0.58 mmol g⁻¹) with a 20% molar excess of aqueous KRuO₄·5H₂O (14.12 mg dissolved in 5 mL H₂O) under vigorous stirring followed by sonication (10 min) in an ultrasonic bath and by further stirring for 1 h. The black catalyst thereby obtained was filtered, washed with ultrapure water (Millipore Type II, 3 × 30 mL) until washings were decoloured and eventually dried in an oven at 100 °C overnight.

Silc2 was prepared in a similar manner by treating 100 mg of **VII** (chloride content: 0.71 mmol g⁻¹) with an analogous excess of potassium perruthenate (17.4 mg dissolved in 5 mL H₂O). Table 2 presents the surface composition and catalytic load of the materials.

Table 2. Molar composition of the primary sol solutions used to prepare **II** and **VII** and textural properties of the resulting compounds.

Compounds	Organosilane	TEOS	H ₂ O	NH ₃	Cet-Py-Cl	SSA [m ² g ⁻¹]	PSV [g L ⁻¹]	Pore diam. [nm]
II	0.1 ^[a]	0.9	114	8	0.12	984	0.7	2.8
VII	0.1 ^[b]	0.9	114	8	0.12	415	–	–

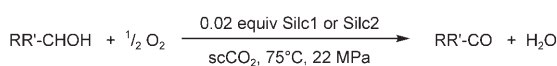
[a] [(EtO)₃Si(CH₂)₃-Im] and CetPy-Cl; [b] [(EtO)₃Si(CH₂)₃-Im⁺-CH₃Cl]⁻ and CetPy-Cl. PSV = pore specific volume; SSA = specific surface area.

The catalytic oxidations of four representative alcohols were performed in a stainless steel 10 mL reaction vessel at a final total pressure of 22.0 MPa and at 75 °C, in the presence of O₂ (1.0 × 10⁵ Pa at 25 °C) and Silc1 (1.77 mg) or Silc2 (1.44 mg) as catalyst. The molar ratios of the components of reaction mixtures (perruthenate/alcohol/oxygen 1:50:350) were chosen after a detailed kinetic study of aerobic oxidation over sol-gel entrapped ORMOSIL.^[21] Progress of reaction was monitored by GLC analysis of supercritical phase samples taken at appropriate times to determine the concentration of carbonyl formed (internal standard method). In each reaction, the sole product observed was the carbonyl.

Results and Discussion

Under the experimental conditions outlined in Scheme 1, the oxidative conversion of structurally different alcohols mediated by Silc2 proceeds to completion and *no* overoxidation of aldehydes to acids is observed (Table 3).

Upon each reaction run the catalyst appeared clean and macroscopically unmodified with the oxidative dehydrogen-



R, R' = H, alkyl, benzyl

Scheme 1.

Table 3. Aerobic catalytic activity in dense phase CO₂ of perruthenate-doped supported ionic liquid Silc2 compared with TPAP encapsulated in 75% methyl-modified ORMOSIL.^[a] The performance of Silc1 (entry 1) is shown for comparison.

Substrate	Catalyst/2% mol RuO ₄ ⁻	k _{cat} × 10 ² [min ⁻¹]
benzyl alcohol	Silc1	0.046
benzyl alcohol	Silc2	2.87
1-phenylethanol	Silc2	0.274
1-octanol	Silc2	0.105
2-octanol	Silc2	0.062

[a] Reaction conditions: 4.83 × 10⁻² mmol alcohol, 2% entrapped perruthenate (content of RuO₄⁻ per g of xerogel: 0.58 mmol in Silc1 and 0.71 mmol in Silc2), O₂ (1.0 × 10⁵ Pa at 25°C), CO₂ (10 mL, 22.0 MPa); T = 75°C.

ation reaction taking place within the sol-gel cages since no ruthenium leached from the catalyst during the reaction (in reaction samples taken from the sc phase, with a Ru-detection limit < 1 ppb).

The corresponding rate constants (k_{cat}) were obtained from integrated pseudo-first-order plots, that is, ln(1 - [aldehyde]_t / [aldehyde]_{t=∞}) versus time, which are linear up to 80–90% completion of the reaction as reported in Figure 1; the graphic also shows the kinetics of the aerobic benzyl alcohol oxidation mediated by 2% mol perruthenate entrapped in Silc1 and Silc2 compared with that of the most active ORMOSIL-entrapped perruthenate oxidation catalyst recently reported by some of us.^[22]

The straight lines nicely fit the experimental points to perfect first-order oxidation kinetics for ruthenium and clearly show that Silc2 is >60 times more active than the Silc1 ob-

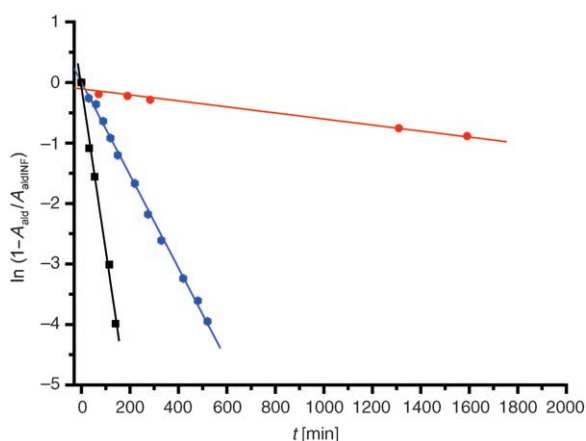


Figure 1. Aerobic oxidation of benzyl alcohol to benzaldehyde in scCO₂ over TPAP entrapped in aged 75% methyl-modified silica matrix (2% mol AME3-18 m, blue) and in silica-supported ionic liquids with 2% mol RuO₄⁻ Silc1 (red) and Silc2 (black).

tained by grafting of methyl iodide (k_{Silc2} = 2.87 × 10⁻² min⁻¹ versus k_{Silc1} = 4.6 × 10⁻⁴ min⁻¹).

For comparison (Table 3), this value is almost four times higher than that of our most active Ru-based oxidation catalyst,^[22] that is, a 75% methyl-modified ORMOSIL which has a kinetic constant of 0.798 × 10⁻² upon eighteen months of catalyst aging under the same reaction conditions.

These results address the problem posed by the low activity of many Ru-based catalysts which usually provide (close to) quantitative transformation of a wide range of activated and non-activated alcohols to aldehydes, but at moderate rates.^[18] Hence, the catalysts herein described retain the excellent selectivity to aldehydes (or ketone) which in the case of supported Pt-group metals^[16] and gold^[23] is usually *not* satisfying.

The linear plots in Figure 1 suggest that RuO₄⁻ anions are entrapped in very similar microenvironments, that is, that the active perruthenate species are homogeneously immobilized at the xerogel's huge surface, as nonlinear kinetic plots typically arise from using low amounts of catalyst (as in the present case, ~1 mg); this indicates that the dopant molecules "report" simultaneously from more than one microenvironment exhibiting different chemical properties.

The large difference in activity between the post-functionalised silica Silc1 and the xerogel obtained by co-polycondensation Silc2, suggest either that the accessibility of perruthenate in the latter compound is largely superior or that the affinity of iodide for the imidazolium cation is higher than of chloride. Such a difference was indeed immediately evident during the preparation of the catalyst.

Hence, while addition of aqueous KRuO₄ to **VII** resulted in immediate decoloring of the black-green solution, the color of aqueous perruthenate was partly retained when **II** was ion-exchanged with a perruthenate solution of the same concentration. Limited accessibility of the imidazolium moieties in the latter material, on the other hand, may be ruled out as grafting with CH₃I indeed resulted in complete consumption of the alkylating agent.^[20]

Finally, large affinity of the soft (in the Pearson's notation) I⁻ anion for the similarly soft Im⁺ cation could be confirmed by elemental analysis of Silc1 which showed that some 30% of the original iodide contents is retained upon impregnation with RuO₄⁻ compared with less than 10% in the case of the material bearing chloride anions (Table 2).

Mechanism and generality of scope: The general concept of *supercritical* Silc is represented in Figure 2.

The alcohol substrate and O₂ at low partial pressure are dissolved in the homogeneous scCO₂ phase which, upon contact with the powdered sol-gel entrapped catalyst, spills the reactants into the pores where the oxidative dehydrogenation takes place. It then extracts the products, in analogy to the extraction of reaction products from insoluble-in-scCO₂ ILs in olefins epoxidation.^[24]

Furthermore, the RuO₄⁻ immobilization at an imidazolium-modified surface which acts as a potent solubilizing agent accelerates substrate/product dissolution and thus the

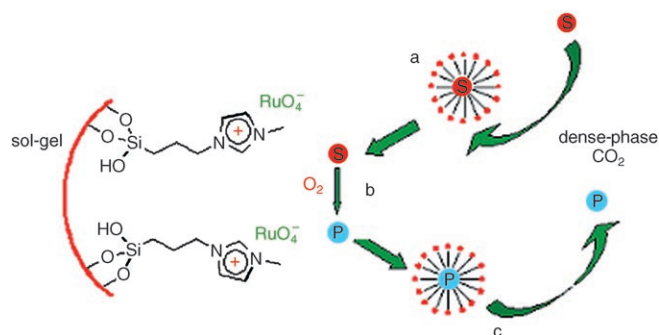


Figure 2. Illustration of the transport, reaction, and adsorption/desorption steps of the sc-silic process. The dense phase CO_2 dissolving the substrate a) spills its content into the catalyst tethered to the ionic liquid moiety where b) the catalytic process takes place. Then, c) the highly diffusible dense phase CO_2 carries the product back into solution.

reaction rate. As a result, as shown by the smooth oxidation of the less reactive primary aliphatic alcohol 1-octanol (entry 4 in Table 3), a versatile active catalyst is obtained that can be used for the fast conversion of different substrates.

Figure 2 depicts the main difference between a surface-heterogenized and a sol-gel entrapped ionic liquid doped with a metal catalyst. Whereas in the first case the support limits its function to being the physical carrier of the catalyst and promoting reactants solubility,^[12–14] in the co-encapsulated catalyst/ionic-liquid material the surface of the entrapping matrix also takes active part in the chemical reaction occurring at the interface by dictating the accessibility of the active center to the external reactants. Moreover, scCO_2 assists in water removal (thus preventing aldehyde hydration and overoxidation) through its well known ability of drying solid matrices.

Sol-gel entrapment of perruthenate in ORMOSIL matrices, in fact, often affords catalysts with enhanced activity and selectivity compared to the homogeneous reaction.^[21] Similarly to what happens with all the variety of chemical applications of doped sol-gel materials^[25] (including catalysis)^[26] this phenomenon is due to the unique phenomenon of sol-gel encapsulation of the dopant molecules within the inner surface offered by these highly porous oxides compared to few m^2g^{-1} of external surface. A concept – activity enhancement by catalytic site isolation – that in heterogeneous catalysis was recently shown to have general validity.^[27]

Furthermore, in a detailed kinetic study^[21] we have recently shown that TPAP inactivation is caused by i) self-aggregation of the oxoruthenate species formed during reaction, and ii) by the solvent employed to carry out the reaction. Remarkably, therefore, both these factors do not play a role in our system as a results of the sol-gel encapsulation of the Ru active centers (Figure 3) which prevents aggregation of the intermediate ruthenate species,^[28] and to the use of chemically inert carbon dioxide acting as superior reaction medium.

Hence, at the end of the reaction, the CO_2 is easily vented off by simple pressure release, leaving the solid catalyst

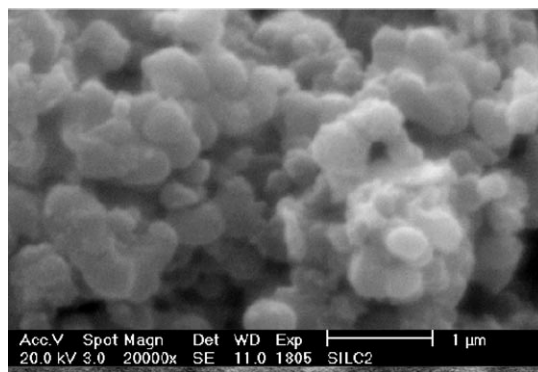


Figure 3. Sol-gel confinement of TPAP ensures mutual isolation of the Ru active centers, thus preventing catalyst deactivation due to association of ruthenate of intermediate oxidation state.

physically and chemically unmodified and thereby ensuring stability of the catalyst.^[29] In the course of the present study, inevitable loss of material between consecutive runs allowed recovery and recycling of the catalyst Silc2 for three runs, with minor (< 3%) loss in the measured activity, after which it became impossible to recover a sufficient amount of catalyst due to the above-mentioned loss.^[30]

Conclusion

A general concept of supported ionic liquid catalysis in supercritical phase (sc-Silc) has been introduced and successfully applied to the aerobic selective oxidation of alcohols. The methodology synergically combines the advantages of ionic liquids as a solvent promoter, dense-phase carbon dioxide as reaction (and extraction) solvent, and immobilized metal catalyst for easy product separation and catalyst recycling.

Hence, the hybrid mesostructured silica gel co-encapsulating the ionic liquid imidazolium and the aerobic catalyst perruthenate (best prepared by co-polycondensation of TEOS and imidazolium-modified organosilane) is a highly active and selective catalyst in oxidative dehydrogenation of alcohols in dense phase CO_2 .

Its activity is substantially higher compared with ORMOSIL-entrapped perruthenate (amongst the most active ruthenium-based aerobic catalysts reported thus far), while reciprocal isolation of the entrapped Ru centers prevents catalyst degradation and renders these silica gels ideal candidates for practical use in commercial alcohols oxidation. The catalyst is selective, stable and—being a sol-gel doped ceramic—it may easily be obtained with higher catalytic loads and in any desired shape.^[31] No traditional organic solvent has to be employed to extract the product out of the IL, and the same leach-proof entrapped IL has broad application. The method is general and further applications to other relevant catalytic processes are easily envisaged.

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M.P. dedicates this article to Professor Ernesto Anzon: teacher of sport, physics and humanity. The authors thank to University of Palermo's Giuseppe Marci for the SEM pictures and Filippo Saiano for the ICP-MS analyses. Support from the CNR/CNRS bilateral agreement program is gratefully acknowledged.

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