FluoRuGel: a versatile catalyst for aerobic alcohol oxidation in supercritical carbon dioxide

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FluoRuGel—a hybrid fluorinated silica glass doped with TPAP (tetra-\textit{n}-propylammonium perruthenate)—is a versatile catalyst for the aerobic oxidation of different alcohols in dense phase CO\textsubscript{2} with marked stabilization and activity enhancement of perruthenate upon its confinement in the sol–gel fluorinated silica matrix. A brief competitive analysis shows large potential rewards.

Competitive advantage—and not benefits to the environment or to human health or safety—drives companies’ choices in adopting new technologies, including any “greener” options designed to replace earlier methods.\textsuperscript{1} For instance, the heterogeneously catalysed aerobic oxidation of alcohols in dense phase (or “supercritical”)\textsuperscript{3} carbon dioxide (scCO\textsubscript{2}) is highly desirable as it would eliminate the need for both potentially polluting and toxic organic solvents\textsuperscript{3} and stoichiometric Cr and Mn oxides employed in industrial oxidations.\textsuperscript{4}

Remarkably, a number of highly selective heterogeneous catalytic reactions are carried out on an industrial scale in small, high-throughput reactors in which the CO\textsubscript{2} is recycled and eventually completely removed from the products by simply reducing the pressure.\textsuperscript{5}

However, no oxidative conversions of alcohols are as yet conducted in this solvent\textsuperscript{6} despite the fact that an efficient process in scCO\textsubscript{2} would afford a variety of carbonyls of high purity\textsuperscript{7} meeting a key industry’s requirement for commercial compounds which are widely used as precursors of drugs, vitamins, fragrances and other valuable fine chemicals.

The selective oxidation of alcohols to carbonyls in scCO\textsubscript{2} remained unexplored until the early 2000s when the aerial catalytic conversion of water-insoluble alcohols in supercritical CO\textsubscript{2} in a continuous fixed bed reactor over Pt–Pd–Bi/C was reported\textsuperscript{8} to afford high yields of ketones and aromatic aldehydes, but not of primary aliphatic aldehydes, showing the same limitation in scope as noble metal-catalysed oxidation of alcohols in water.

A similar outcome was found using Pd/Al\textsubscript{2}O\textsubscript{3} catalyst,\textsuperscript{9} while higher selectivity to aldehydes was obtained using a Pt/C (teflon-coated) catalyst\textsuperscript{10} in which the fluorinated surface, spilling off water molecules, prevented overoxidation to the acid. Finally, an interesting selectivity enhancement (compared to the process in liquid solvent) was recently reported for the aerobic oxidation of cyclohexanol to cyclohexanone in scCO\textsubscript{2} over a Cu-based catalyst.\textsuperscript{11}

We recently introduced an efficient sol–gel solid catalyst (FluoRuGel) for the dehydrogenation of benzyl alcohol in scCO\textsubscript{2} with O\textsubscript{2} consisting of a fluorinated organic–inorganic silica glass doped with [NPr\textsubscript{4}]\textsuperscript{3−} [RuO\textsubscript{4}]\textsuperscript{−}.\textsuperscript{12}

The oxoruthenate catalyst is entrapped in a porous sol–gel fluorinated matrix through which dense phase carbon dioxide dissolving both O\textsubscript{2} and the alcohol substrate, upon contact with the powdered CO\textsubscript{2}-philic sol–gel material, rapidly spills the reactants into the cages where the oxidative dehydrogenation takes place, and then it extracts the benzaldehyde product (Scheme 1).

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Table 1 Oxidation of various alcohols (5 × 10⁻² mmol) with O₂ (1 bar at 25 °C) catalysed by FluoRuGel (content of TPAP: 0.5 × 10⁻² mmol per 100 mg) in scCO₂ at 75 °C and 22 MPa

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alcohol</th>
<th>k × 10⁴/mol⁻¹ min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzyl alcohol</td>
<td>49</td>
</tr>
<tr>
<td>2</td>
<td>Benzyl alcohol*</td>
<td>5.88 and 6.50*</td>
</tr>
<tr>
<td>3</td>
<td>2-Octanol</td>
<td>2.03</td>
</tr>
<tr>
<td>4</td>
<td>1-Octanol</td>
<td>5.02</td>
</tr>
<tr>
<td>5</td>
<td>1-Phenylenol</td>
<td>6.46</td>
</tr>
<tr>
<td>6</td>
<td>p-MeO-benzyl alcohol</td>
<td>9.67 e 10.45</td>
</tr>
<tr>
<td>7</td>
<td>m-Cl-benzyl alcohol</td>
<td>8.27</td>
</tr>
<tr>
<td>8</td>
<td>p-Me-benzyl alcohol</td>
<td>8.27</td>
</tr>
</tbody>
</table>

* Upon washing the catalyst with CH₂Cl₂.

Washing the catalyst with DCM, as we originally attempted for recovering the product, results in rapid evolution of gaseous Cl₂ bubbles with the significant reduction in the catalyst's original activity mentioned above (from 49 to 6 × 10⁻⁴ mol⁻¹ min⁻¹). This shows first evidence that the sol–gel encapsulation of TPAP ion pairs indeed changes the reactivity of the entrapped dopant as TPAP alone readily dissolves in DCM which in fact is used as optimal solvent for perruthenate-mediated oxidations.

We recently investigated this surprising outcome and found that rapid oxidation of DCM to Cl₂ does indeed take place; with a similar deactivation occurring also with a variety of other solvents, but deactivation occurred at the lowest pace with unreactive solvents such as n-hexane. On the other hand, the use of dense phase CO₂ as the sole reaction and recovery solvent considerably improves catalyst stability and this, along with the sol–gel entrainment of the oxoruthenate, ensures stabilization of the material's reactivity. Ru-based oxidation catalysts generally lose their activity due to aggregation of the intermediate ruthenate species, a phenomenon that is intrinsically prevented here by the encapsulation of perruthenate in the inner porosity of the sol–gel organosilica matrix.

We are currently investigating the nature (and the mechanism) of the entrainment of perruthenate in sol–gel glasses. XPS analysis of a similar ORMOSIL (organically modified silicate) doped with 1.7 wt% TPAP, for instance, is not capable of detecting the entrapped ruthenium even after two minutes' sputtering of the surface with Ar⁺ ions accelerated at 4 keV to remove contaminants, showing how deep the encapsulation of Ru is in these catalysts.

FluoRuGel consists of an agglomerate of organosilica particles whose regular surface geometry, upon large magnification, retains its morphology also on the nanometre scale (Fig. 2) which is that experienced by the approaching reactant molecules dissolved in scCO₂ (where the only diffusional barrier is that between the “supercritical” phase and the solid).

In all cases, in fact, the oxidative dehydrogenation takes place within the sol–gel cages since no TPAP is leached from the catalyst during the reaction (in reaction samples withdrawn from the sc phase with a Ru detection limit <1 ppb).

Surprisingly, comparison between the reactivity of TPAP and TPAP encapsulated in FluoRuGel shows a different kinetic behaviour (Fig. 3).

While both homogeneous TPAP and also ORMOSIL-entrapped TPAP show typical perruthenate-mediated oxidation kinetics consisting of a fast initial stage up to 40–50% conversion, followed by a slower oxidation stage mediated by less reactive RuO₂, the reaction mediated by FluoRuGel shows an initial induction stage followed by a faster linear stage up to complete conversion of the substrate.

This points to improved catalysis by TPAP entrapped in the fluoroalkyl-modified silica matrix, i.e. a different chemistry of the entrapped dopant obtained by changing the properties of the entrapping silica sol–gel cage, similar to what happens when dopant molecules are co-entrapped in silica with a surfactant that modifies the sol–cage properties.

We make the hypothesis that the partly positive carbon in highly dipolar –CF₃ groups that concentrate at the cage surface further attracts the entrapped RuO₄⁻ (Fig. 4) synergistically adding to the effect of the large N(CH₂CH₂CH₃)₄⁺ cation whose use in combination with perruthenate was introduced to mitigate...
the strong oxidation power of RuO$_4^-$ alone and thus promote selectivity.

Eventually, this results in mutually isolated RuO$_4^-$ anions entrapped in the inner porosity of the fluorinated gel where they mediate the oxidative dehydrogenation of the alcohol substrate according to a bi-electronic reaction mechanism that involves formation of the alcoholate, but without formation of inactive RuO$_2$. In general, Ru-based aerobic catalysts are highly selective and afford good yields of carboxyls but, in liquid-phase, they also show considerably lower activity compared to less selective carbon-supported Pt and Pd. This is not the case in scCO$_2$. Hence, while Pt/C, Pt–Pd–Bi/C and Pd/Al$_2$O$_3$ afford the desired carbonyl in good yields with catalytic activity in the order of $10 \times 10^{-5}$ mol$^{-1}$ min$^{-1}$ (kinetic constant), FluoRuGel is generally 100 times faster (Table 1) while retaining the pronounced selectivity typical of Ru catalysts even upon prolonged reaction time.

In general, the catalytic stability of all the catalytic materials mentioned above considerably improves in dense phase carbon dioxide with a concomitant enhanced activity with increasing lipophilicity of the catalyst support (i.e. Pt/teflon-coated carbon > Pt/carbon > Pt/charcoal > Pt/SiO$_2$ and ORMOSIL > SiO$_2$). Only FluoRuGel, however, shows similar good activity in the oxidation of primary and secondary aliphatic alcohols such as 1- and 2-octanol (Table 1) whereas, for comparison, Pt/SiO$_2$ employed in scCO$_2$ is not capable of aerobically converting more than 20% of the secondary alcohol substrates. FluoRuGel in fact is a mesoporous glass whose vast accessible porosity (0.53 cm$^3$ g$^{-1}$) narrowly distributed around 20 Å allows facile access of widely different alcohol molecules to the confined catalytic species.

Fig. 2 FluoRuGel (shown here are SEM 100, 10 000 and 50 000x photographs) shows a regular, compact surface (bottom) which is experienced by the approaching reactant molecules.
Experimental

Catalyst preparation

FluoRuGel was prepared by sol–gel processing the fluoro-alkyl containing monomer 3,3,3-trifluoropropyl-trimethoxysilane (TFPTMOS purchased from Fluka) with tetramethyloxysilicate (TMOS) in the presence of TPAP dissolved in methanol keeping the Si–MeOH–H₂O molar ratio at 1 : 8 : 4, i.e. using a stoichiometric amount of water (Si : H₂O = 1 : 4) and a high amount of co-solvent (Si–MeOH = 1 : 8), that was recently found to be crucial in promoting reactivity of analogous doped ORMOSILs in scCO₂.11 Other chemicals including benzyl alcohol, n-decane, TMOS and TPAP were purchased from Sigma Aldrich and were used without further purification. Ultra pure water (Millipore Type 1) was used in all the preparations.

FluoRuGel, a 10% fluoro-propyl doped silica gel, was thus synthesised by adding TMOS (~2.68 mL) and TFPTMOS (~0.39 mL) to a solution of TPAP (~24.5 mg) in MeOH (~6.45 mL) cooled in an ice bath, followed by the addition of H₂O (~1.44 mL). The mixture was stirred for 30 min when it gelled yielding a black alcogel which was sealed and left to age at room temperature for 24 h prior to drying at 50 °C (5 days). The grey xerogel thus obtained was powdered, washed under reflux (CH₂Cl₂ × 2, 40 °C) and dried to 50 °C prior to use.

Oxidation procedure

A typical oxidation was carried out in the 10 mL modified Carlo Erba SFC 3000 reactor described elsewhere13 at 75 °C and 22 MPa. Benzyl alcohol (~5 µL, 0.5 mmol) and 0.1 equiv. of FluoRuGel (~156 mg) were added to the reaction vessel with n-decane (~5 µL, 1 mmol) as internal standard. After flowing the oxygen (1 bar), the reaction vessel was sealed, placed into a thermostated oven and liquid CO₂ was pumped into the autoclave using a cryogenic pump to bring the reactor pressure to 22 MPa. The reaction mixture was kept stirring at 400 rpm by means of an alternating magnetic field stirrer for the desired reaction time and reaction samples were withdrawn through a 6-way valve connected to a restrictor (kept at 90 °C) prior to GC analysis. When reaction was complete, the heating was stopped and the system was allowed to cool to ambient temperature. The reactor was then opened and the CO₂ gradually vented off in n-hexane allowing the total pressure inside the reactor to reach the atmospheric value, after which the product was extracted with a further amount of n-hexane and the catalyst recovered, dried and reused as such in a subsequent reaction run.

Analyses and reaction rates

The carbonyl products’ 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 rate constants kcat were assessed from the aldehyde formed integrating the pseudo first-order plots obtained from a quadratic equation in which one reactant (O₂ in this case) is in large excess, that is

\[ k_{cat} = \frac{1}{t} \ln\left(\frac{[O_2]}{[O_2, t=0]}\right) \]

The N₂–BET textural values were obtained with a Carlo Erba Instruments Sorptomatic 1900 powder analyzer, and ruthenium contents measured by ICP-MS on a HP 4500 spectrometer.
Acknowledgements

This article is dedicated to the memory of Mr Giovanni Locorotondo, whose humanity shown daily for many years at Palermo’s CNR will not be forgotten. Thanks to the University of Padova’s Massimo Carraro for the kinetic measurements and to Assotec (Milan) and Dr Oreste Piccolo (Scsop, Lecco) for assistance in technology transfer.

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