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Dynamic Catalysis in Aerobic Oxidation by Sol–Gel Living Materials**

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This work is dedicated with profound affection (and gratitude) to University of Palermo's Prof. Giuseppe Savona on the occasion of his 63rd birthday

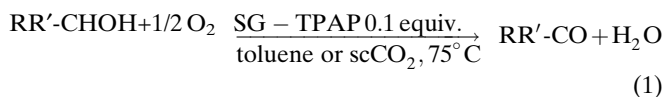
The catalytic activity of hybrid organic–inorganic silica glasses doped with the ruthenium species tetra-*n*-propylammonium perruthenate (TPAP) in the aerial oxidation of alcohols to carbonyl compounds, either in toluene or in dense-phase CO₂, substantially increases with time several months after the xerogels' preparation, yielding the most active ruthenium-based aerobic-oxidation catalysts reported thus far. The doped sol–gels are living materials, and an explanation of the observed reactivity enhancement is given, which is thought to have general validity for future applications to a wide variety of relevant heterogeneous processes.

1. Introduction

Solid catalysts for aerobic selective oxidations are considered “philosophers’ stones”,^[1] because of their importance to industry. For instance, the oxidative dehydrogenation of alcohols yielding water as the only byproduct can be achieved with solid catalysts.^[2] In recent years, intense research efforts have been devoted to searching for efficient catalysts for the oxidation of alcohols, with oxygen being the sole oxidant, and catalytic species of impressive selectivity containing Pt,^[3] Pd,^[4] Cu,^[5] W,^[6] Au,^[7] and Ru^[8] have been discovered. In general, the most active catalysts are supported Pt-group metals and Au, but their selectivity to aldehydes is usually not satisfactory. In contrast, many Ru-based catalysts (including RuO₂·*x*H₂O,^[9] RuO₂/faujasite zeolite (FAU),^[10] Ru/Al₂O₃,^[11] Ru–Al–Mg–hydroxalcalite,^[12] Ru–silicotungstate,^[13] and Ru–hydroxyapatite (Ru–HAp^[14]) provide (close to) quantitative transformation of a wide range of activated and non-activated alcohols to aldehydes, but at moderate rates.

A feasible strategy in searching for better solutions is the improvement of the activity of these Ru-based catalysts while maintaining their excellent selectivity; we recently contributed to the field with the discovery of a sol–gel-entrapped TPAP/O₂ (TPAP: tetra-*n*-propylammonium perruthenate) catalytic system for the conversion of a vast class of different alcohols to

valuable carbonyl compounds.^[15,16] The catalyst [NPr₄]⁺[RuO₄][−] is entrapped in a porous sol–gel hydrophobized matrix; the alcohol substrate and O₂ at low partial pressure are dissolved in the homogeneous phase which, upon contact with the powdered sol–gel material, spills the reactants into the pores, where the catalyst is entrapped and where the oxidative dehydrogenation takes place. Then the products are extracted according to Equation 1



where SG-TPAP is sol–gel-confined TPAP and scCO₂ is supercritical carbon dioxide

A careful choice of the sol–gel-preparation conditions is crucial for affording materials with optimal performance both in organic solvents^[15] and in scCO₂.^[16] For the latter, heterogeneously catalyzed oxidations are particularly attractive, since an efficient aerobic alcohol-oxidation process in dense-phase CO₂ would eliminate altogether the use of (potentially) polluting organic solvents and stoichiometric oxidants (chromium and manganese oxides or dimethyl sulfoxide) currently being employed by the fine-chemicals industry.

Sol–gel catalysts are increasingly being adopted by industrial and academic researchers to achieve delicate organic-chemistry syntheses that would not be feasible with traditional solution-phase chemistry or by the use of conventional surface-heterogenized materials.^[17] In light of their vast potential in catalysis, there is an urgent need for a better understanding of the structure–activity relationships dictating the chemical behavior of these materials.

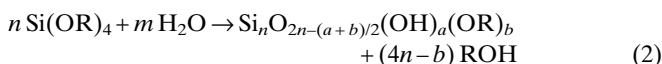
Sol–gel materials, for instance, grow by kinetic control,^[18] and not by thermodynamic control, and often resulting in “living” materials that undergo structural modifications, and thus changes in reactivity, even months after preparation. The hydrolysis and condensation reactions at the base of the sol–

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gel-oxide preparation never result in the formation of pure oxides, and—taking silica as the optimal oxide for catalytic applications^[19]—the overall hydrolytic polycondensation reaction can be written as



in which $m = 2n + (a-b)/2$.

The resulting gel is chemically unstable, since its alkoxy (OR) groups are subject to further hydrolysis by the presence of unreacted water. Consequently, the dry gel (xerogel) obtained by removal of the residual solvent is also unstable, since the remaining hydroxyl (OH) groups can further condense on exposure to moisture.^[20]

The situation is further complicated when the polycondensation is carried out with an organosilane, such as RSi(OR)_3 , in which the condensation rate is slowed down (with respect to a tetralkoxysilane) by the presence of the non-hydrolyzable organic group.^[21] We can show now how the sol–gel preparation of organically modified, perruthenate-doped hybrid gels affords aerobic-oxidation catalysts whose activity substantially increases with time (several months after preparation). We propose an explanation of the reported findings which is thought to have general validity for future applications of sol–gel-doped oxides to catalyses capable of meeting the zero-emissions standard required by sustainable (or green)^[22] chemistry.

2. Results and Discussion

To test for reactivity after 18 months, we used the same methylated xerogels obtained with a mixture of methyltrimethoxysilane (MTMS) and tetramethoxysilane (TMOS) in the sol–gel co-polycondensation.^[15] We carried out the oxidation of benzyl alcohol in scCO_2 under the reaction conditions^[16a] of Equation 1 using the most active, 75 %-methyl-modified gel, simply left to age for 18 months (AME3-18m). Now, however, the reaction proceeded almost ten times faster than with the freshly prepared gel AME3 ($k_{\text{old}} = 4.08 \times 10^{-2} \text{ mol}^{-1} \text{ min}^{-1}$ vs. $k_{\text{fresh}} = 4.9 \times 10^{-3} \text{ mol}^{-1} \text{ min}^{-1}$).

Actually, carrying out three consecutive oxidation runs with AME3-18m, the reaction was so fast that the number of points taken for each run was relatively small, because the reaction went to completion much more rapidly than expected (Fig. 1, points labeled ■). Therefore, in order to accurately monitor the reaction, the amount of catalyst was reduced by one-fifth (to 2 mol-%).

In both cases, the kinetic data are consistent, and the slight decrease in activity upon each run is solely due to inevitable catalyst loss.^[23] Hence, on using 10 mol-% perruthenate entrapped in the aged xerogel, the values of k obtained in the consecutive reaction runs (Table 1, runs 2,3) are in good agreement with each other, giving, on average, a kinetic constant $k = 4.08 \times 10^{-2}$.

Three more oxidative runs, using one-fifth of the same aged catalyst, allow more accuracy in determining the catalytic activ-

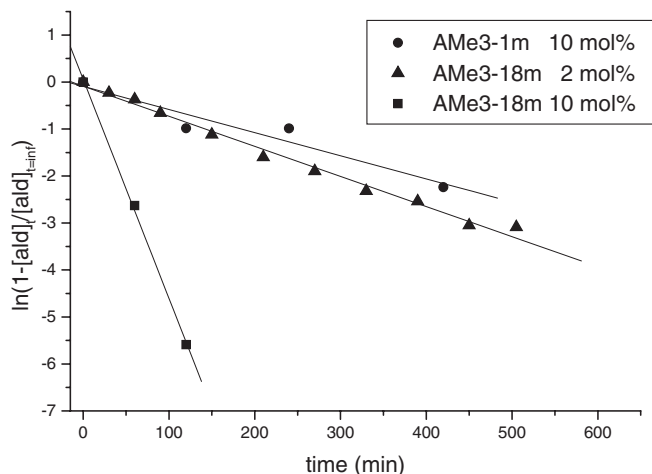


Figure 1. Aerobic oxidation of benzyl alcohol to benzaldehyde in scCO_2 over TPAP entrapped in aged (■, ▲) and fresh (●) 75 %-methyl-modified silica matrices.

Table 1. Aerobic catalytic activity [a] in scCO_2 of the methylated ormosil doped with TPAP after 18 months (AME3-18m), compared with the fresh xerogel AME3.

Catalyst	Reaction run	$k \times 10^3 [\text{mol}^{-1} \text{ min}^{-1}]$
AME3-18m, 10 mol-%	1	46.58
	2	41.27
	3	34.50
	average	40.78
AME3-18m, 2 mol-%	4	9.85
	5	6.41
	6	7.67
	normalized average	39.90
AME3, 10 mol-%	7	4.92

[a] Reaction conditions: 0.048 mmol benzyl alcohol, 10 or 2 mol-% entrapped TPAP, $V = 10 \text{ mL}$, $P = 22 \text{ MPa}$, $T = 75 \text{ }^\circ\text{C}$, O_2 (1 atm.).

ity (Table 1, runs 4–6), with straight lines nicely fitting the experimental points (Fig. 1); clearly, the constants thereby calculated are lower (since less catalyst is being used), but simple normalization yields, on average, $k = 3.99 \times 10^{-2}$, close to the former value found employing 10 mol-% perruthenate. Eventually, run 7 in Table 1 shows that the reaction rate observed with the freshly prepared catalyst, AME3, ($k = 4.92 \times 10^{-3}$)^[16a] is at least eight times lower than the value measured with the same xerogel 18 months later.

These results suggest two relevant conclusions: i) the reaction is remarkably reproducible, i.e., catalytic ormosils in scCO_2 are recyclable at length, which is often not the case for heterogeneous reactions; and, ii) the oxidation kinetics is first-order in ruthenium, considering that even with a substrate/catalyst ratio of 25:1 the oxidation kinetics is still perfectly first-order (Fig. 1, points labeled ▲).

It is also relevant to this report that upon each reaction run the catalyst appeared clean and macroscopically unmodified, and no post-reaction treatment was necessary to ensure retention of the activity. The reaction proceeded to completion and no overoxidation of benzaldehyde to acid was observed. The

oxidative dehydrogenation took place within the sol–gel cages, since no ruthenium was leached from the catalyst during the reaction (in reaction samples withdrawn from the supercritical phase with a Ru detection limit < 1 ppb).

We thus checked whether this pronounced enhancement in activity in the aged xerogel was evident also when employing the catalyst in toluene, where the effect of the textural properties on the material's activity is less pronounced than in a supercritical fluid.^[15] To our delight, comparably large activity increases were observed.

Hence, the same catalyst, AMe3, which enabled a 62 % conversion of benzyl alcohol after five minutes, was able to convert 93 % of the added benzyl alcohol after being aged for eight months (AMe3-8m) in the same reaction time (Table 2, entry 1).

Table 2. Aerobic catalytic activity [a] in toluene of the methylated ormosil doped with TPAP after eight months (AMe3-8m) compared to the fresh xerogel AMe3.

Entry	Catalyst [10 mol-%]	Conversion [%]	Time [min]	TOF [b]
1	AMe3	62	5	31
2	AMe3-8m	93	5	90
3	AMe3-4m* [c]	90	30	18
4	AMe3-8m* [c]	99	5	120

[a] Reaction conditions: 0.2 mmol benzyl alcohol, 10 mol-% entrapped TPAP, toluene, 4 mL, $T = 75^\circ\text{C}$, O_2 (1 atm). [b] $\text{TOF} = [\text{mol}(\text{alcohol})/\text{mol}(\text{Ru})]\text{h}^{-1}$. [c] These xerogels were prepared after aging the intermediate alcogels in a closed vessel for two days instead of one day.

Furthermore, when the 75 %-methylated silica xerogel is prepared, allowing the intermediate alcogel to age in a closed vessel for two days rather than for one day, the effect of the aging of the resulting xerogel on the activity is even more pronounced: the four-month-old 75 %-methyl-modified gel (AMe3-4m*, Table 2, entry 3), which gave a 90 % benzaldehyde yield after 30 min, upon four extra months of aging becomes so highly active (AMe3-8m*) that it is capable of converting the same amount of benzyl alcohol in only 5 min ($\text{TOF} ([\text{mol}(\text{alcohol})/\text{mol}(\text{Ru})]\text{h}^{-1}) = 120$, entry 4, Table 2), becoming the most active Ru-based aerobic-oxidation catalyst reported thus far.^[24]

To the best of our knowledge, these results are the first reported evidence of the relevance to catalysis of the structural modification in xerogels upon drying, and give a crucial insight into the behavior of the entrapped dopant in the sol–gel matrix.

The enhanced reactivity of the 75 %-methylated and doped gel AMe3 with time may be ascribed to the transfer of the active perruthenate ion pair from the aggregates at the surface of the ormosil sol–gel cages, where it is partly buried and inaccessible for catalysis, to the newly accessible pores of the xerogel, which form upon further hydrolysis and con-

densation of the unreacted –Si(OR) groups. Indeed, the surface Ru/Si atomic molar ratio, determined from elemental analysis of the xerogel surface (Fig. 2), in fresh and old xerogels shows (Table 3) that the simple aging of the ormosil at room temperature considerably lowers the surface Ru/Si atomic molar ratio. This fact indicates the more effective dispersion and caging of the Ru active sites at the inner surface of the freshly prepared catalyst.

The cornucopia of chemical applications of sol–gel materials are indeed due to the unique phenomenon of the caging of the dopant molecules into the micropores of the resulting highly porous oxides (several hundreds of meters squared per gram compared to 1–2 m^2g^{-1} of external surface),^[25] and in catalysis, such entrapment of the dopant molecules (Fig. 3) affords catalysts with enhanced selectivity in a variety of conversions compared to reactions in homogeneous phase.^[17] This concept—activity enhancement by catalytic-site isolation—was recently shown to have a general validity in heterogeneous catalysis.^[26]

What happens during in the synthesis of organically modified sol–gel materials^[27] is that, at the early stages of the sol–gel process, pseudomicellar aggregates rapidly form in which the R–Si(OH)₃ monomers generated in solution tend to arrange themselves with the polar –Si(OH)₃ groups at the forefront of the growing sol–gel material and the hydrophobic non-polymerizable –R residue orientating away from the interfacial, strongly hydrogen-bonding solvent (water/methanol). Thus, the hydrophobic organometallic catalyst is partly entrapped within the micellar core. On the other hand, the second, opposite expectation is that more of these residues, R, are expected to be found on the pore walls than in the bulk, because the trialkoxy tails will polymerize with each other (and with the tetraalkoxy monomer), tending to direct the alkyl heads away from the polymerizing microenvironment.

In the present case, in which a Si/H₂O/MeOH = 1:8:1 molar ratio was used in the preparation of the catalysts of the AMe3 series, the former process is favored by the low amount of co-solvent and the second process by the high amount of H₂O. In addition, the aging of the alcogel in a closed vessel prevents methanol evaporation, further slowing down the rate and extension of the hydrolysis of the –Si(OR) groups and also the condensation (that in the case of ormosil synthesis takes place only via elimination of water,^[28] and not by alcohol formation).

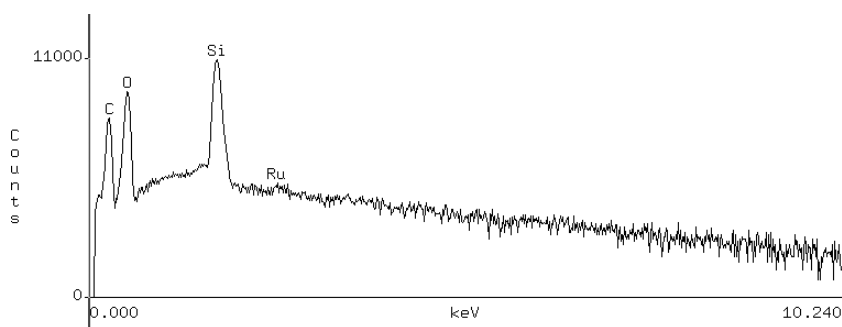


Figure 2. Representative electron-probe microanalysis of the gel AMe3-8m taken with an accelerating voltage of 15 keV and take-off angle of 40°.

Table 3. The external surface Ru/Si molar ratio of 75 %-methylated ormosil AMe3 prior to and after several months of aging.

Catalyst	Ru/Si atomic molar ratio ($\times 10^3$) [a]
AMe3	4.22
AMe3-8m	2.41
AMe3-4m* [b]	4.81
AMe3-8m* [b]	2.70

[a] Determined by electron-probe microanalysis. [b] These xerogels were prepared after aging the intermediate alcogels in a closed vessel for two days instead of one day.

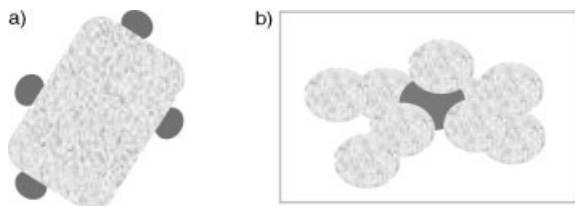


Figure 3. Schematic illustration (a) of a traditional impregnated catalyst, in which metal nanoparticles (dark gray) are supported on at the external surface of an oxide (light gray), and a catalytic nanoarchitecture in which the dopant nanoparticles are protected by the sol–gel oxide cages (b).

We assume that aging of the ormosil xerogel, involving further hydrolysis of the unreacted Si(OCH₃) groups and condensation of the Si(OH), which enhances the crosslinking, causes a better dispersion of the active perruthenate from the aggregates formed in bigger pores to the newly formed inner microporosity. The aggregates indeed dissolve in methanol formed in the microenvironment of the cages, ensuring transfer and dispersion of TPAP; this explains both the enhancement of reactivity in aged xerogel and the lower external Ru/Si ratio in the aged materials.

According to this hypothesis, aging of the alcogel is detrimental to catalysis, since it is known to cause dissolution of the smaller particles in the silica network formed early in the reaction and reprecipitation of silica onto larger particles. This results in a net decrease of the interfacial area and an increase of the average pore size,^[29] where dopant aggregation is favored.

Interestingly, furthermore, the question of dopant aggregation in the sol-cages emerged in the early studies of sol–gel-doped materials, when it was assumed that single-molecule caging was occurring,^[30] while it was later established, studying the entrapment of the ruthenium complex Ru(bpy)₃²⁺ in a silica matrix, that some dopant aggregation was actually occurring.^[31]

3. Conclusions

The catalytic activity of hybrid organic–inorganic silica glasses doped with the ruthenium species TPAP in the aerial oxidation of alcohols to carbonyl compounds either in toluene or in dense-phase CO₂^[32] substantially increases with time sev-

eral months after the xerogels' preparation, yielding the most active ruthenium-based aerobic catalysts reported thus far.

Doped sol–gel oxides are indeed living materials, and an explanation of the observed reactivity enhancement is given that is thought of general validity for future applications of doped sol–gel materials to a wide variety of relevant chemical processes.

4. Experimental

Both catalyst preparation [15], use in toluene [15], and in scCO₂ [16] have been described elsewhere. The content of carbonyl products was determined by gas-chromatography (GC) analysis using a Shimadzu chromatograph equipped with a Supelcowax 10 capillary column (30 m, 0.25 mm in diameter) using the internal-standard method. The rate constants, k_{cat} , 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 $\ln(1 - [\text{ald.}]/[\text{ald.}]_{t=\infty}) = -k_{\text{cat}}[\text{O}_2]t$. The N₂-BET (BET: Brunauer–Emmett–Teller) textural values were obtained with a Carlo Erba Instruments Sorptomatic 1900 powder analyzer, and ruthenium contents were measured by inductively coupled plasma mass spectrometry (ICP-MS) on a HP 4500 spectrometer. The surface Ru/Si molar ratio was determined from elemental analysis of the surface, carried out with a JEOL JXA-8600 electron-probe microanalyzer equipped with a NORAN Vantage automation system. This method gave the ratio between the external surface-bonded ruthenium and surface-Si atoms to a depth of 1 μm .

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