Sol-Gel Ormosils Doped with TEMPO as Recyclable Catalysts for the Selective Oxidation of Alcohols

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Abstract: Organically modified silicas doped with TEMPO prepared via the sol-gel method are highly recyclable catalysts of the selective Montanari-Anelli oxidation of 1-nonanol; They show a notable "positive feedback" effect of matrix alkylation on the catalyst activity which is typical of doped sol-gel materials and markedly differentiates the behaviour of these materials from that of analogous silica-supported TEMPO.

Keywords: heterogeneous catalysis; ormosils; selective oxidation; sol-gel; TEMPO.

Recently, we have independently heterogenised the stable organic nitroxyl radical TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl radical) over different silica matrices in order to obtain recyclable catalysts for alcohol oxidations showing the well-known high selectivity of homogeneous TEMPO catalyses both in the Montanari–Anelli oxidation of alcohols to carbonyl compounds[1a,1b] and in the NaOCl/Br⁻ oxidation of carbohydrates to carboxylates in water.[1c]

With similar aims, TEMPO has also been anchored to the mesoporous channels of silica MCM-41[2a] and immobilised at the surface of the oligomeric triazine Chimassorb 944 by oxidation of its amine moieties.[2b] The cyclic nitrosonium ion TEMPO⁺ is, in fact, a highly active and *versatile* selective catalytic oxidant which is readily formed *in situ* by several primary oxidants under mild conditions.[3] However, in contrast to homogeneous TEMPO that is equally applicable to the conversion of a variety of alcohols in different reaction media,[3] heterogeneous TEMPO often fails to show analogous versatility. This is unfortunate since the low product volumes of the fine chemicals industry and the new combinatorial applications of solid-phase syntheses[4] do indeed require such a high degree of versatility. Hence, for instance, while TEMPO anchored on commercial aminopropyl-silica was found to be sufficiently recyclable in the Montanari–Anelli oxidation of various alcohols,[1a] an analogously immobilised catalyst was unstable and practically inactive in the corresponding

oxidation of glucose 1-phosphate in water;[5] oligo-amine-supported TEMPO, in its turn, could neither be employed in chlorinated solvents (where it readily dissolves) nor in the presence of metals such as Ru that coordinate to the amine moieties of the polymer.[2b] Finally, hydrophilic MCM-41-grafted TEMPO could not be used above pH 8 when silica started to *dissolve* leaching the radicals in solution.[2a]

Now, we report that organically modified silica gels (ormosils) doped with TEMPO prepared under mild alkaline conditions are selective catalysts in the Montanari-Anelli oxidation of the aliphatic alcohol 1-nonanol showing a remarkable stability in their selective activity. Several different catalytic ormosils were prepared through reductive amination of 4-oxo-TEMPO with 3-aminopropyltrimethoxysilane in the presence of NaBH₃CN in methanol (see Experimental Section), followed by the sol-gel polycondensation process of suitable silicon alkoxide precursors. The N_2-BET pore volumes and surface areas (Table 1) of the resulting gels are typical of mesoporous sol-gel ormosils obtained under alkaline conditions showing a broad pore size distribution (80 – 300 Å).

Based on our most recent results with silica-supported TEMPO,[1b] in order to investigate the catalytic activity and stability of the new ormosils, we carried out the oxidation of substrate 1-nonanol in several consecutive runs (see Experimental Section) at 0 °C with a reaction time of only 15 minutes, thus expecting an incomplete conversion and – in case of absolute stability – a constant yield in all subsequent runs. The results, however, were very surprising (Figure 1).

Hence, the unmodified silica-encapsulated TEMPO (SG-TEMPO-0) lost *half* of its initial high activity upon just 1 oxidative run, its colour turning to white as a clear indication of material dissolution and leaching of the radical in the reaction mixture. However, it was sufficient to use the partly (25% of Si atoms substituted) methylated ormosil SG-TEMPO-1 to observe a remarkable stability in the activity along with an *increment* in the intermediate yields upon the first 3 runs in which the catalyst was tested that, remarkably, was also shown by the fully (100%) methylated gel SG-TEMPO-2

Table 1. Textural properties and composition of the catalytic ormosils doped with TEMPO.

Catalyst	Organosilane[a]	Si:MeOH	DF[b] [mmol/g]	S_{BET}[c] [m²/g]	V_p [mL/g]
SG-TEMPO-0	0% MTMS	1:3	0.27	217	1.24
SG-TEMPO-1	25% MTMS	1:3	0.28	213	1.19
SG-TEMPO-2	100% MTMS	1:2	0.30	267	1.25
SG-TEMPO-E	75% ETMS	1:3	0.29	160	0.74
SG-TEMPO-P	75% PTMS	1:3	0.25	75	0.38

[a] Molar percentages relative to TMOS used in each gel preparation.
[b] Degree of functionalisation based on the assumption of complete radical encapsulation during the sol-gel catalyst synthesis.
[c] Silica-supported TEMPO used for comparison (SG-TMP-O) has BET surface area $S_{BET} = 350$ m²/g.[1b]
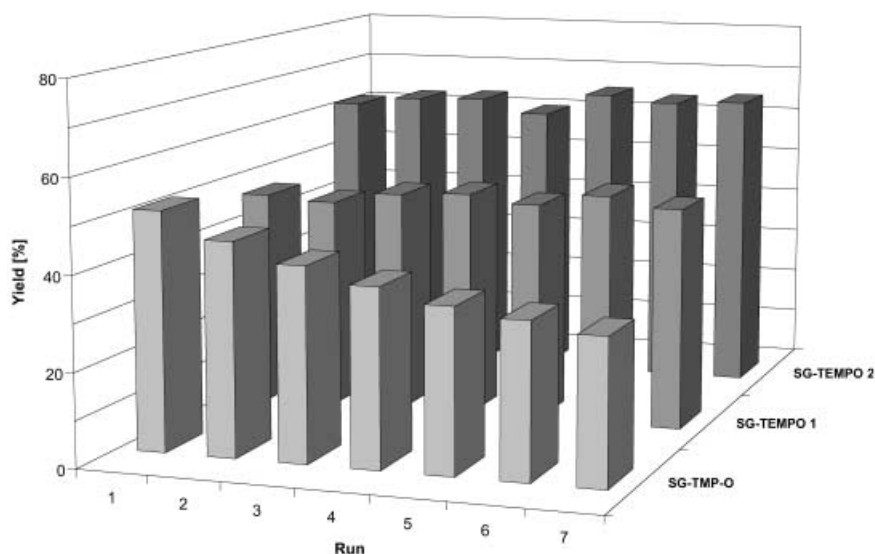

Figure 1. Yields in the Montanari–Anelli oxidation of 1-nonanol to give nonanal in the presence of silica-supported TEMPO (SG-TMP-O, front row), and of sol-gel ormosils doped with TEMPO [SG-TEMPO-1 is 25% and SG-TEMPO-2 is 100% methylated (middle and back row, respectively)].

which after 6 runs was 8% more active than the fresh catalyst and showed the same pronounced stability (Figure 1) of SG-TEMPO-1. A similar trend of incremental reaction rates was also shown by the partly (75%) propyl-modified silica SG-TEMPO-P which had an activity comparable to that of SG-TEMPO-2, while the analogous (75%) ethyl-modified gel SG-TEMPO-E was less active than SG-TEMPO-1 but, again, recyclable and stable. In each catalytic run mediated by the doped ormosils no other products besides the carbonyl were detected in the reaction mixture and there was *no* leaching of encapsulated radicals in solution as shown also by the lack of further reactivity of the reaction filtrate obtained upon separation of the catalyst from the reaction mixture shortly (7 minutes) after the beginning of the oxidation.

Silica-supported TEMPO (SG-TMP-O, 500 µmol/g radical, obtained by impregnation of commercial propyl-aminosilica with 4-oxo-TEMPO)[1a] was thus used for comparison in the same conversion of 1-nonanol to nonanal and, again,[1b] its activity measured by the intermediate yields continuously diminished upon every

reaction run. Interestingly, the transparent *microporous* silica glass doped with TEMPO prepared under acidic conditions[1c] employed in the same oxidation protocol of 1-nonanol was stable (no leaching or catalyst modification) but only modestly active (8% yield after 15 min).

To investigate the effect of reaction on the catalyst structure, EPR spectra of SG-TEMPO-2 before and after 7 consecutive oxidation runs (**a** and **b** in Figure 2, respectively) were recorded.

The spectra show that the distance between the outer lines (related to the coupling constant of the interaction of the unpaired electron with the spin of ^{14}N nucleus)[6] increases slightly, while the lesser increment (20%) of the line widths (related to the isotropic rotation correlation times)[6] indicates an analogous increase of the viscosity sensed by the spin label within the sol-gel cage, likely to be due to water adsorption within the cages (resulting in more hydrogen bonding between silanols and water) upon its prolonged use in the CH_2Cl_2-H_2O reaction medium (see below for a consistent interpretation of the FTIR spectra). The reduction in
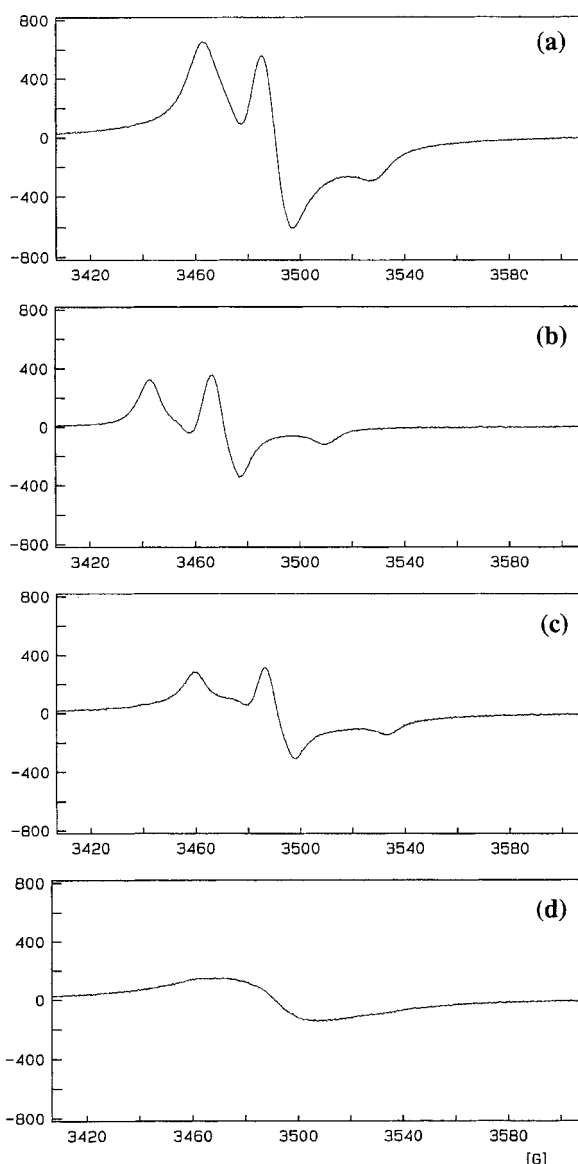
Figure 2. EPR spectra of sol-gel ormosil doped with SG-TEMPO-2 prior to (**a**) and after (**b**) 7 consecutive reaction runs in the Montanari-Anelli oxidation of 1-nonanol. The spectra of sol-gel (**c**) and commercial (**d**) aminopropyl-silicas doped with TEMPO are also shown.

intensity of the resonance peak in the used catalyst to about 1/2 of its original value might, in turn, be due to the partial conversion of TEMPO radicals to nitrosonium ions TEMPO$^+$ that are rapidly formed upon addition of aqueous NaOCl (in 20% excess) to the reaction mixture containing the catalyst (when the slightly orange powder suddenly changes its colour from pale to bright orange), and that after several consecutive reactions are left attached as oxoammonium ions.

Evidence for lack of degradation of the ormosil structure in the buffered alkaline reaction environment (pH 9.1) was obtained by FTIR analysis of the catalyst prior and after 7 oxidative runs (Figure 3).

The overlapping bands at 2930 and 2871 cm^{-1} in the spectra in Figure 3 are assigned to the asymmetrical and symmetrical vibration of CH$_2$ groups in the propyl chains[2a] carrying the bound nitroxyl radicals and clearly indicate that these groups are unmodified prior to and after reaction; the broad signals overlapping in the 1085 – 1100 cm^{-1} region are, in turn, due to the Si-O-Si asymmetric stretching[7] and show that the silica gel polymeric backbone is unaffected by the prolonged use in the reaction system. Interestingly, the only notable difference in the FTIR spectra in Figure 3 is shown by the enhancement of the signal at 1635 cm^{-1} (which is due to H-O-H bending)[7] and by the related enhancement of the broad signal in the 3000 – 3600 cm^{-1} region due to the stretching vibrations of the H-bonded silanols with water,[7] thus confirming the uptake of water molecules in the sol-gel cages during the reaction (in accord with the results of the EPR experiments given above).

Finally, the difference in the EPR spectra of silica-encapsulated and silica-supported TEMPO shows how different the sol-gel encapsulation of dopant molecules is as compared to adsorption at an external surface: the silica-supported TEMPO gives a broad low signal (Figure 2, **d**) reflecting extensive intermolecular spin interactions among the radicals anchored at the surface, while the triplet (Figure 2, **a**) shown by the encapsulated radicals reflects the isolation of the radicals within the sol-gel cages. Incidentally, it may also be noted that the 100% methylated gel SG-TEMPO-2 yields a 3-times more intense peak (Figure 2, **a**) compared to the same amount of TEMPO encapsulated in unmodified SiO$_2$ (Figure 2, **c**), thus indicating a pronounced protection of the radicals against quenching that is probably related to a lesser degree of free radical formation[8] during the sol-gel synthesis of the ormosils as compared to the synthesis of silica using TMOS alone.

These results indicate that in the heterogeneous Montanari–Anelli alcohol oxidation mediated by sol-gel ormosils a *cooperative* mechanism may be in action through which the more alcohol (and aldehyde) molecules are adsorbed (and formed) within the inner cage surface, the faster is the diffusion of the reactant and product molecules through the porous network. Notably, an analogous explanation was recently proposed to explain the results of the adsorption properties of similar sol-gel doped ormosils,[9] and was based on the observation that these materials are chemical *sponges* with chromatographic properties, i.e., they adsorb and concentrate the reagents at the cage surfaces where reactions take place while the adsorbed molecules promote further diffusion of incoming reactants.

Indeed, besides the diffusional limitations imposed by the narrow pore network, the chemical behaviour of sol-gel doped ormosils is affected by other fundamental factors, and namely – as in the case of analogous ormosils-mediated esterifications[10a] and oxidations[10b] in the liquid-phase – by the *hydrophobicity*[11a] and
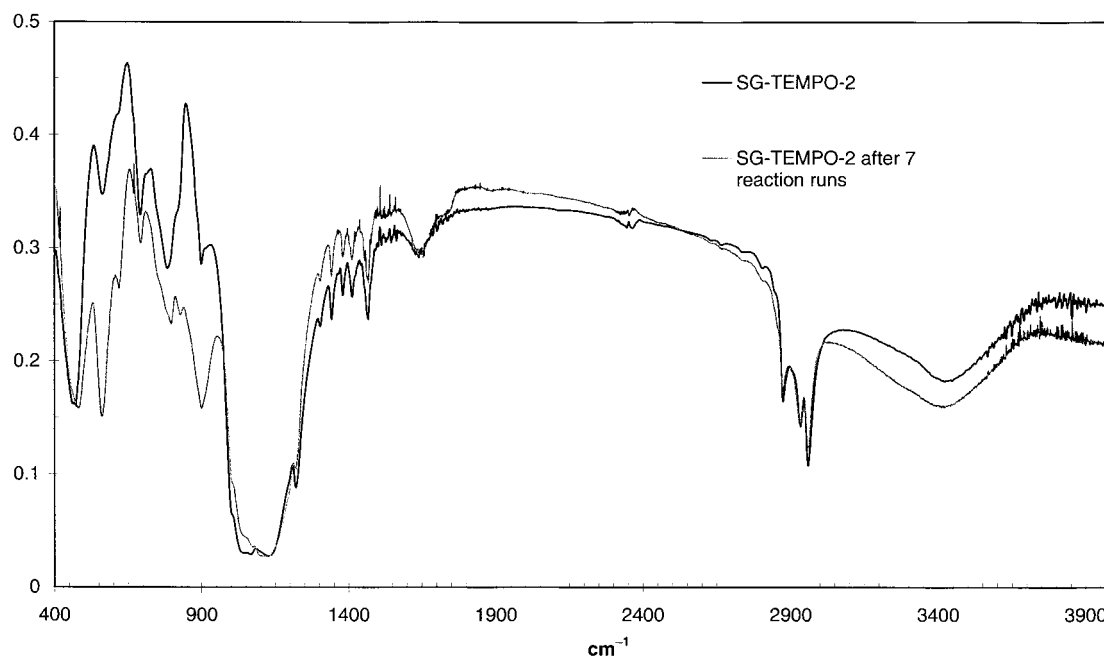
Figure 3. FTIR spectra of the solgel ormosil doped with SG-TEMPO-2 prior to (solid line) and after (broken) 7 consecutive reaction runs in the Montanari–Anelli oxidation of 1-nonanol.

flexibility[11b] of the sol-gel cages that are both known to be crucially affected by the employment of substituted silanes R'Si(OR)$_3$ in the sol-gel polycondensation. It is the enhanced hydrophobicity of the silica sol-gel cages doped with TEMPO *and* organically modified by the presence of the alkyl groups that promotes the diffusion of the hydrophobic alcohol and aldehyde molecules within the porous network, and also largely diminishes the amount of hindering intra-cage hydrogen bonds between Si-OH groups and silanols and water (confirmed one EPR by the lack of spurious peaks in Figure 2, **a** compared to **c**), which, in turn, largely enhances the freedom of the encapsulated TEMPO by providing the needed flexibility.

Interestingly, the continuous decrease of the activity of TEMPO anchored to commercial aminopropyl-silica was recently proposed[1b] to be due to intramolecular quenching of the radicals anchored in proximity at the material surface. In fact, surface derivatisation of a material's surface requires the formation of a new covalent bond through a slow heterogeneous reaction that leaves the anchored molecules unprotected at the material's pore surface, while the homogeneous sol-gel encapsulation process disperses and protects the dopant species *within* nano- or mesoporous modified silica cages, allowing the use of doped gels with higher catalytic loads without loss in material activity.

In conclusion, we have found that the coupling of sol-gel and TEMPO-mediated oxidation processes affords the synthesis of doped materials that are recyclable heterogeneous catalysts for the oxidation of the aliphatic alcohol 1-nonanol with bleach, rapidly affording high yields of 1-nonanal with the known selectivity of homogeneous TEMPO and no loss of chemical activity upon consecutive reactions. Considering the versatility of both technologies,[3,12] the method is thought to be of utility for the selective oxidation of other alcoholic substrates, while the results of the present work are intended to provide further guidelines for the development of versatile heterogeneous catalysts for selective oxidations.

Experimental Section

Preparation of SG-TEMPO Catalysts

All the chemicals employed were obtained from Sigma Aldrich and used without further purification. The radical species 4-oxo-TEMPO (1 g, 7 mmol) was added to a solution of 3-aminopropyltrimethoxysilane (5 mL, 28 mmol) containing NaBH$_3$CN (0.220 g, 4 mmol) dissolved in methanol (18 mL). The reaction solution was stirred for 40 h and then the unreacted cyanoborohydride destroyed by the addition of 7 M HCl (1 mL).

The precursor mixture thereby obtained was equally divided into 7 portions and each vessel charged with different amounts (in subsequent order) of MeOH, alkyltrimethoxysilane, TMOS and H$_2$O to yield gels with the chosen total molar ratios Si:H$_2$O:MeOH = 1:8:2 (or 3, as specified in Table 1). Sodium fluoride was added as condensation catalyst in the ratio Si:F = 1:0.017 for the preparation of the gel obtained from methyltrimethoxysilane (MTMS) alone (ETMS and PTMS are ethyl- and propyltrimethhoxysilane, respectively). Hence, for example, the gel SG-TEMPO-2 with Si:H$_2$O = 1:2 was ob-

tained by charging one vessel of the precursor mixture mentioned above with MeOH (1 mL), MTMS (5.82 mL) and H_2O (5.35 mL). The resulting sol was stirred using a Vortex shaker prior to the addition of aqueous 1 M NaF (0.750 mL) under fast stirring that resulted in fast gelation. Likewise, all the other sols gelled rapidly yielding elastic alcogels that were left sealed to age for 20 h at room temperature prior to be opened and densified at 60 °C for 3 days during which the gels further shrank to about half of the initial volume reaching constant weight. The resulting xerogels isolated as pale orange-coloured powders, were washed with boiling CH_2Cl_2 (3 × 20 mL, 50 °C) under reflux, dried and used as such in the oxidations.

General Oxidation Procedure with SG-TEMPO-2 as Catalyst

The oxidations were performed in a glass tube with a cooling mantle equipped at the bottom with a ceramic filter plate that allowed easy separation of the catalyst upon reaction. In a typical experiment the catalyst (30.0 mg, 8 μmol radical) was added to the tube followed by a CH_2Cl_2 solution (2.0 mL) of the alcohol (0.4 M) with the internal standard dodecane (0.12 M), and 0.16 mL of aqueous KBr (0.5 M). After cooling the mixture to 0 °C, 2.7 mL of aqueous NaOCl diluted to a concentration of 0.37 M and buffered by NaHCO$_3$ to pH 9.1 were added and the resulting mixture shaken vigorously for 15 min. After filtration, the organic phase was separated, dried over MgSO$_4$ and the product analysed by GC (ultra-2-column, HP). The filtered sol-gel catalyst was washed 5 times with H_2O, MeOH and CH_2Cl_2 (2 mL each), air-dried and reused as such in 7 consecutive oxidation runs after which the catalyst was used for the EPR measurements carried out at 296 K on a Bruker spectrometer working at medium frequency (50 kHz) and low amplitude (0.101 G) modulation. The BET measurements were performed on a Carlo Erba Sorptomatic 1900, and a Bruker Vector 22 spectrometer was used for the FTIR analyses obtained from samples dispersed in KBr.

Acknowledgements

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