

Fluorinated Silica Gels Doped with TPAP as Effective Aerobic Oxidation Catalysts in Dense Phase Carbon Dioxide

Rosaria Ciriminna,^a Sandro Campestrini,^b Mario Pagliaro^{a,*}

^a Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via Ugo La Malfa 153, 90146 Palermo, Italy

Phone: (+39)-091-680-9370; fax: (+39)-091-680-9399, e-mail: pagliaro@pa.ismn.cnr.it

^b Dipartimento di Chimica Organica, Università degli Studi, via Marzolo 1, 35131 Padova, Italy

Received: October 10, 2003; Accepted: January 17, 2004

Dedicated to the memory of Dr. David Applebaum, the eminent physician passed away, with his daughter Nava, last September in Jerusalem at the age of only 50.

Abstract: Hybrid organic-inorganic fluorinated silica glasses doped with the ruthenium species TPAP (tetra-*n*-propylammonium perruthenate) are effective catalysts for the aerial oxidation of benzyl alcohol to benzaldehyde in dense phase CO₂. Moderate silica fluorination (10%) by short-chain fluoroalkyl-containing monomers in the sol-gel polycondensation with TMOS affords highly active catalysts which at 75 °C and 220 bar selectively dehydrogenate the alcohol with oxygen as primary oxidant. Both the activity and the stability of the fluorinated materials vary with the degree of fluorination and the nature of

the fluoroalkyl residue attached to the silica polymeric network. An explanation of the behaviour of doped sol-gel oxides in supercritical carbon dioxide is proposed which is thought to be of general validity for future practical applications to heterogeneously catalysed aerobic oxidations eliminating the current need for both organic solvents and stoichiometric oxidants.

Keywords: aerobic oxidation, fluoroalkyl-containing silica, heterogeneous catalysis, ruthenium, sol-gel processes, supercritical carbon dioxide

Introduction

Catalytic heterogeneous conversions in “supercritical”^[1] carbon dioxide (scCO₂) are being carried out on an industrial scale due to numerous advantages.^[2] Besides the replacement of the volatile organic solvents (VOCs) traditionally used as reaction medium with an environmentally benign solvent,^[3] the excellent dense phase CO₂ miscibility with organics and reagents such as O₂ and H₂, along with ultralow viscosity and superior mass transport properties (absence of a gas-liquid phase boundary) permit one to conduct highly efficient continuous heterogeneous processes (those preferred by industry)^[2] in small, high-throughput flow reactors in which the CO₂ is recycled and finally completely removed from the products and from the catalyst by simply reducing the pressure, resulting in a closed-loop system or “solvent-free” reaction.^[4]

The use of supercritical carbon dioxide in place of traditional organic solvents, however, should not be regarded as a mere replacement of a solvent with another of intermediate liquid/gas properties, as the unique non-uniform distribution of solvent molecules about single solute molecules^[5] may eventually alter the reaction pathways observed in the liquid phase, while small changes in temperature or pressure may cause

dramatic changes in density, viscosity and dielectric properties making dense phase CO₂ a tunable and versatile solvent;^[6] its unique properties, for instance, permit one to achieve high concentrations of H₂ and O₂ in the same pot where they can be catalytically converted to valuable H₂O₂.^[7]

Heterogeneously catalysed oxidations in scCO₂ are particularly attractive and, yet, “largely unexplored”;^[8] an efficient aerobic alcohol oxidation process would, for example, eliminate altogether the need for potentially polluting organic solvents and stoichiometric chromium,^[9a] manganese^[9b] oxides or DMSO^[9c] employed in current industrial conversions. Moreover, no *expensive* purification steps would be required as the carbonyl reaction products would be obtained in high purity, meeting a key requirement for compounds which are widely used as precursors of drugs, vitamins, fragrances and other valuable fine chemicals. Finally, safety risks would also be mitigated due to the complete lack of flammability of CO₂.

Few reports concern the oxidative dehydrogenation of alcohols in carbon dioxide and, with one exception,^[10] all refer to carbon-supported noble metals (Pt, Pd).^[1,11] In each case the reported catalytic activity in scCO₂ is lower than in the liquid phase, but dense phase carbon dioxide suppresses any overoxidation of the alcohol and

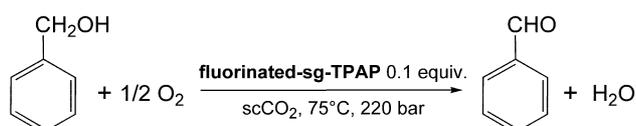
considerably improves the catalyst stability which affords carbonyls in high yields and with excellent selectivities. Invariably, increasing the hydrophobicity of the catalyst support improves the activity of the materials (i.e., teflon-coated carbon^[11a] > carbon^[1] > charcoal and ormosils^[10] > SiO₂ when the catalytic ruthenium aerobic oxidant TPAP is entrapped in sol-gel glasses).

Under the pressure and temperature conditions employed in said heterogeneous catalyses, carbon dioxide has a low dielectric constant but is a strongly fluorophilic species able to dissolve fluorinated materials with important chemical applications ranging from cleaning^[6] to catalysis;^[12] oxygen, in its turn, also has a strong affinity for fluorinated compounds being highly soluble in several fluorocarbons.^[13] We reasoned therefore that the sol-gel process is a versatile and reproducible method to prepare hydrophobic fluorinated materials with several applications^[14] and now we report that fluorinated silica sol-gels (sg) doped with [NPr₄]⁺[RuO₄]⁻ are effective catalysts for the dehydrogenation of benzyl alcohol in scCO₂ with O₂ at low pressure (Scheme 1).

The general idea is simple: The catalyst is entrapped in a porous sol-gel fluorinated matrix; the alcohol substrate and O₂ dissolved in dense phase carbon dioxide which, upon contact with the powdered hydrophobic sol-gel material, spills the reactants into the pores where the catalyst is entrapped and where the oxidative dehydrogenation takes place, and then it extracts the products. We show thus how the choice of the material precursors and sol-gel polycondensation conditions is crucial in affording effective oxidation catalysts and propose an explanation of the structure-activity relationship which is thought to be of general validity for future heterogeneously catalysed oxidations able to meet the standard required by new sustainable (or green)^[15] chemistry: *Zero Emissions*.

Results and Discussion

We prepared 2 different batches of materials (**C3F** and **C8F**, Table 1) varying the length of the fluoroalkyl chain in the silane monomer and the ratio of fluoroalkylsilane:TMOS in the sol-gel co-polycondensation using a stoichiometric amount of water (Si:H₂O = 1:4) and a high amount of co-solvent (Si:MeOH = 1:8), which was recently found to be crucial in promoting the reactivity of analogous doped ormosils in scCO₂.^[10]



Scheme 1.

Taking benzyl alcohol as model substrate under the supercritical conditions of Scheme 1, the comparison between the reactivity of TPAP encapsulated in the (most active) 10% fluoropropyl-modified sol-gel **C3F-10** and in the 50% methyl-modified gel **TPAP-Me-2**^[10] shows that a modest fluorination of the SiO₂ matrix affords, under the same reaction conditions, almost a two-fold higher catalytic activity ($k_{\text{cat.}} = 4.5 \times 10^{-3} \text{ mol}^{-1} \text{ min}^{-1}$).

The kinetics shows a unique fast stage up to complete conversion of the substrate that markedly differs from the behaviour of simple doped ormosils in scCO₂,^[10] which indicates a faster diffusion of the reactant and product molecules through the supercritical phase/solid boundary; any observed reaction rate, indeed, is controlled by the rate of the slowest reaction step which in solid-catalysed reactions of compounds in solution generally is not the rate of the inherent kinetics but rather the transport rate to and from the solid surface.

With all catalysts, the reaction proceeds to completion and no overoxidation of benzyl alcohol to benzoic acid is observed while the oxidative dehydrogenation takes place within the sol-gel cages since no ruthenium is leached from the catalyst during reaction (in reaction samples withdrawn from the sc phase with a Ru detection limit < 1 ppb). Upon reaction, the catalyst appears in fact clean and macroscopically unmodified and no post-reaction treatment was necessary to ensure retention of the activity.^[17] Results in Table 1 show that, counter to intuition, fluorination *per se* does not enhance the reactivity of the silica gels and that the materials bearing the shorter fluoropropyl chain **C3F** are generally *more* reactive than those modified with the fluoroctyl chain of batch **C8F**.

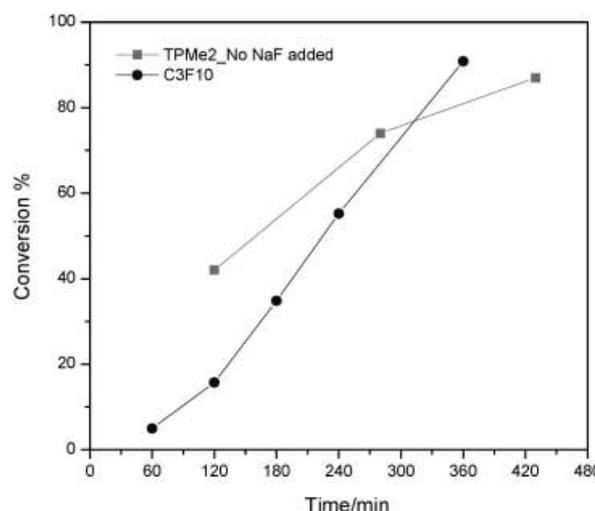


Figure 1. Aerobic oxidation of benzyl alcohol to benzaldehyde in scCO₂ over sol-gel entrapped TPAP in 10% fluoropropyl-modified sol-gel **C3F-10** (■) and 50% methyl-modified gel **TPAP-Me2** (●) silica matrices.

Table 1. Activity^[a] and textural properties of sol-gel fluorinated ormosils doped with TPAP.

Entry	Catalyst	TMS (%)	R-TMS (%) ^[b]	$k_{\text{cat}} \times 10^3$ (mol ⁻¹ min ⁻¹)	SSA (m ² g ⁻¹)	PSV (cm ³ g ⁻¹)	Loading (mmol g ⁻¹)
1	C3F-10	90	10	4.90	691	0.53	0.046
2	C3F-25	75	25	2.14	657	0.42	0.032
3	C3F-50	50	50	2.90	458	0.31	0.027
4	C8F-10	90	10	1.82	308	0.70	0.028
5	C8F-25	75	25	2.07	182	0.59	0.022
6	C8F-50	50	50	1.42	12	0.05	0.012

^[a] Reaction conditions: 0.048 mmol benzyl alcohol, 10 mol % entrapped TPAP, V = 10 mL, P = 220 bar, T = 75 °C, O₂ (1 atm.).

^[b] R = 3,3,3-trifluoropropyl-trimethoxysilane in gels denoted with **C3F** and R = 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecaoctafluoro-triethoxysilane in samples with **C8F**.

* Xerogel obtained using TBAF as condensation catalyst.

Increasing fluorination diminishes both specific surface area (SSA) and porosity (PSV, pore specific volume) and while the most active catalyst (**C3F-10**, entry 1) has the biggest pore volume and surface area it also has, surprisingly, the lowest degree of fluorination (10%); further fluorination up to 25% (**C3F-25**, entry 2) more than halves the catalytic activity which increases only slightly with further fluorination (**C3F-50**, entry 3).

On the other hand, all the modified silica gels bearing the perfluorooctyl chain (**C8F**) are *unstable* and during reaction leach a yellow fluorinated compound which is (by mass spectrometry) the hydrolysed fluorinated carbon chain itself; this effect was not diminished by the use of the condensation catalyst TBAF (tetra-*n*-butyl ammonium fluoride) in the synthesis of the 50% perfluoroalkylated gel, since the same pale yellow compound was leached from the catalyst already during the washing of the xerogel with hot CH₂Cl₂ prior to use.

Activity is now highest with the 25% fluorinated silica gel (**C8F-25**) and lowest using the most hydrophobic gel (**C8F-50**). However, the latter material shows a certain activity despite the *apparently* low porosity^[18] due to the employment of fluoride as catalyst of the sol-gel process which, enhancing strongly the rate of the condensation by multiple F⁻ coordination to the silane Si centres, accelerates condensation and largely reduces the size of the cages in the final xerogel.^[19]

These results offer the first insight in the behaviour of sol-gel fluorinated oxides in aerobic oxidation catalysis and provide new valuable information. The enhanced reactivity of the short-chained 10% fluoroalkylated doped gel **C3F-10** may be ascribed to the negligible viscosity of the supercritical CO₂ and enhanced diffusivity of the dissolved substrate and product molecules through the vast accessible porosity (0.53 cm³ g⁻¹) of the gel that facilitates the transfer of molecules to and from the internal catalyst surface.^[20]

Partial *burying* of the hydrophobic TPAP ion pair in the bulk of the resulting silica xerogel, inaccessible for catalysis, is prevented by the high amount of methanol used in the material's sol-gel synthesis which disrupts

the micellar aggregates typical of the early stages of the sol-gel process in which the slowly generated R-Si(OH)₃ monomers tend to arrange themselves with the polar -Si(OH)₃ groups at the forefront of the growing sol-gel material with the hydrophobic non-polymerisable R residue orientating away from the interfacially strongly hydrogen-bonding solvent (water/methanol).^[21]

This hypothesis would explain the higher reactivities of catalysts of batch **C3-F** with lower fluorination. In this case, indeed, the shorter fluoroalkyl chain favours the hydrolysis and slows down the condensation, so that rapid aggregation of the early sol particles is prevented and TFPTMS can fully hydrolyse to CF₃CH₂CH₂-Si(OH)₃ and this copolymerises with the Si(OH)₄ monomers obtained by the parallel (and faster) hydrolysis of TMOS. An open porous network is formed in which most of the TPAP molecules dissolved in the original sol are encapsulated at the *surface* of the resulting silica cages, where they are accessible for catalysis resulting in gels that are generally more active than those of batch **C8-F** in which such encapsulation is more difficult due to the high difference in the rate of hydrolysis between TMS and the octylfluoro-derivatised alkoxide. On the other hand, the cages are heavily fluorinated (Figure 2) despite the low fluoroalkyl:TMS ratio since the terminal fluoroalkyl groups mostly concentrate at the surface of the cages favouring the diffusion of fluorophilic CO₂.^[22]

The predominant role of the textural properties in controlling the material's reactivity in compressed carbon dioxide is consistent with the appreciable reactivity observed with TPAP encapsulated in unmodified SiO₂, which in toluene was practically inactive^[23] and in scCO₂ showed pronounced catalytic activity.^[10] The pore-size distribution obtained by N₂-adsorption reveals clearly that **C3F-10** is a microporous glass with type I adsorption isotherm^[24] having the largest porosity in the **C3-F** series (Figure 3).

The SEM photographs of the catalysts (Figure 4) show the smooth, compact surface geometry of the low fluorinated materials **C3F-10** and **C8F-25**, while high

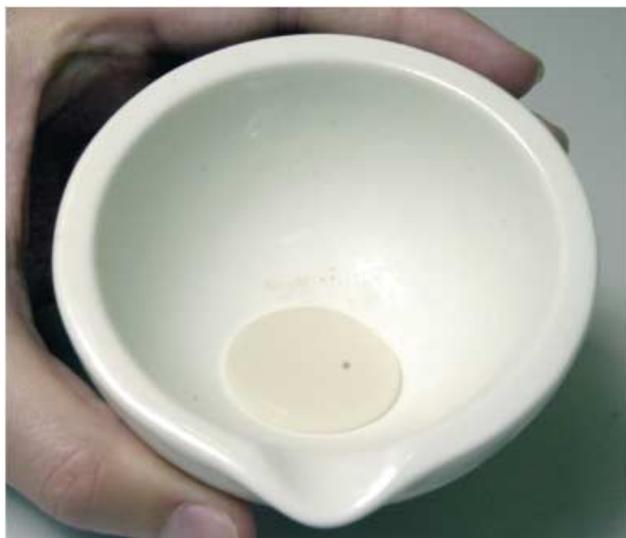


Figure 2. A typical TPAP-doped fluorinated silica gel is made of silica particles that when rinsed with water upon powdering in a mortar clearly reveal their hydrophobic character.

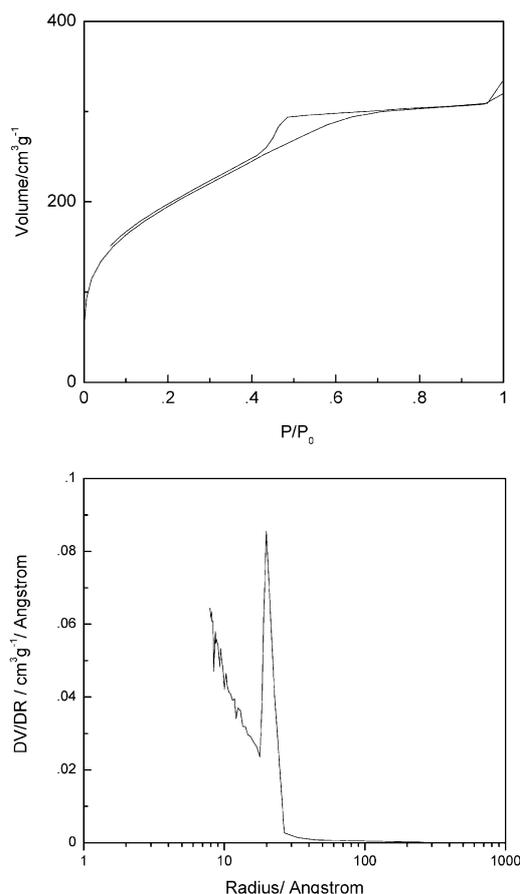


Figure 3. N_2 adsorption isotherm at -193°C of the TPAP-doped fluorinated silica xerogel **C3F-10** (a) and its pore-size distribution (b).

fluorination (in **C8F-50**) results in a globular non-uniform surface. Such surface geometries are those experienced by the approaching reactant molecules and the crucial effect of a material's geometry on determining a material reactivity^[25] should, in principle, be even more relevant in $sc\text{CO}_2$ where the only diffusional barrier is that between the sc phase and the solid.^[20]

Accordingly, and considering that this geometry is tunable by adjusting the parameters of the sol-gel polycondensation,^[26] large improvements in the catalytic performance of such fluorinated materials are expected by development research for which an industrial partnership is currently being sought.^[27]

Conclusion

Short-chain hybrid organic-inorganic fluorinated silica gels doped with TPAP are leach-proof catalysts suitable for the selective aerobic conversion of benzyl alcohol to benzaldehyde in dense phase CO_2 . The best performing catalysts require a modest degree of fluorination of the silanes which ensures both a high surface hydrophobicity and an open microporous network in which the catalytic oxidant is accessible to the reactants. Preliminary results with other substrates clearly confirm^[23] the generality of these catalysts which are applicable to the conversion of a vast range of different alcohols to valuable carbonyl compounds.

As doped sol-gel oxides, the materials are highly versatile^[28] and will easily be adapted to continuous heterogeneous oxidations in dense phase carbon dioxide^[29] with relevant practical advantages which, considering the commercial and synthetic relevance of alcohols selective oxidations,^[30] will lead to commercial oxidation processes devoid of any volatile organic solvents and by-products besides water resulting from the oxidative dehydrogenation.

Experimental Section

Catalysts Preparation

Several fluorinated xerogels were prepared by sol-gel processing a fluoroalkyl-containing monomer (3,3,3-trifluoropropyltrimethoxysilane, TFPTMOS purchased from Fluka; or 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecaoctafluoroethoxytriethoxysilane, TDO FTEOS purchased from ABCR, Karlsruhe) with tetramethyl orthosilicate (TMS) in the presence of TPAP dissolved in methanol, and keeping constant the Si:MeOH:H₂O molar ratio at 1:8:4. Other chemicals including benzyl alcohol, *n*-decane, TMS and TPAP were purchased from Sigma Aldrich and were used without further purification. Ultrapure water (Millipore Type 1) was used in all the preparations.

C3F batch. A typical 10% fluoropropyl-doped silica gel C3F-10 was synthesised by adding TMS (2.68 mL) and TFPTMOS (0.39 mL) to a solution of TPAP (24.5 mg) in

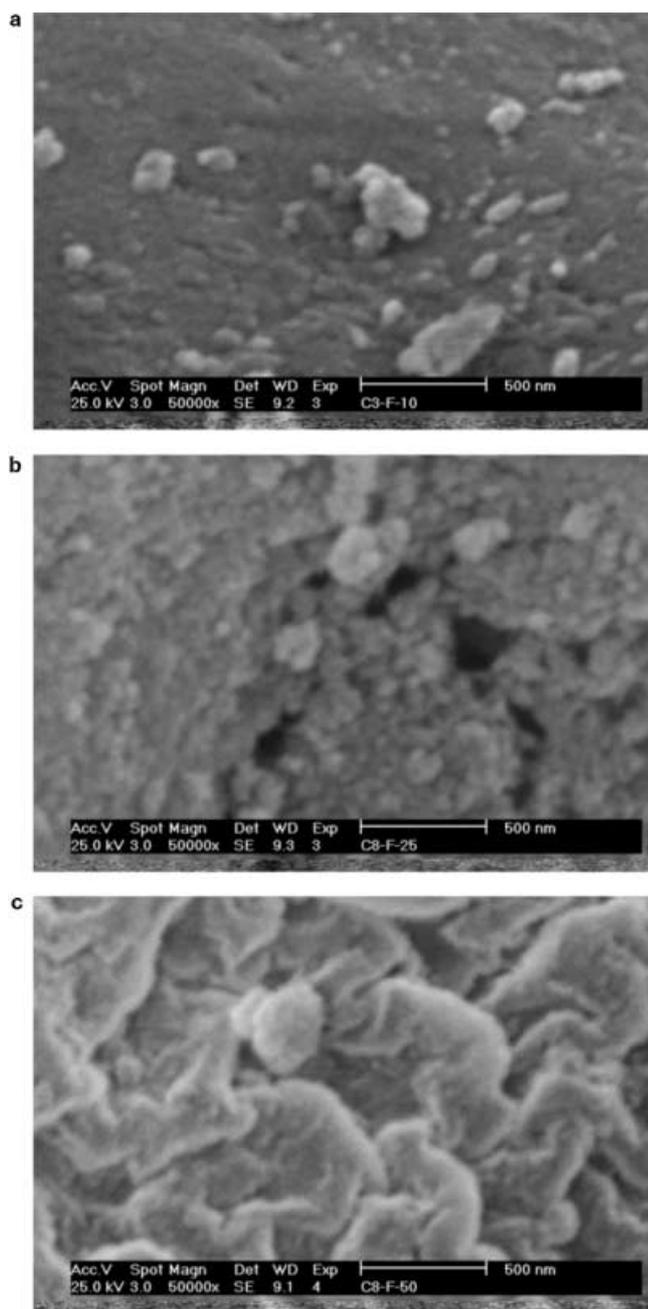


Figure 4. TPAP-doped fluorinated silica gels (here are shown 50,000 \times micrographs) show a smooth, compact geometry surface at lower fluorinations (**C3F-10** and **C8F-25**; **a** and **b**, respectively) while the 50% fluoroalkyl-modified gel **C8F-50** shows a globular non uniform surface (**c**).

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 \times 2, 40 °C) and dried at 50 °C prior to use.

C8F batch. A typical 25% perfluorooctyl-doped silica gel C8F-25 was synthesised as mentioned above by mixing TMOS (2.63 mL) and TDOFTES (1.12 mL) along with a solution of TPAP (21.3 mg) in MeOH (5.67 mL), followed by the addition of H₂O (1.42 mL). The resulting alcogel was treated as described above for C3F-25 yielding a grey powder with a typical 0.022 mmol/g catalytic load.

Oxidation Procedure

The reaction conditions were chosen to ensure complete solubility of the alcohol and of the aldehyde (Scheme 1) in the homogeneous supercritical phase and a typical oxidation was carried out in the modified Carlo Erba SFC 3000 reactor described elsewhere^[16] at 75 °C and 220 bar where scCO₂ exhibits a density of 0.67 g/mL. Benzyl alcohol (5 μ L, 0.5 mmol) and 0.1 equiv. of catalyst C3F-25 (156 mg) were added to the reaction vessel with *n*-decane (5 μ L, 1 mmol) as internal standard. Hence, after purging the oxygen (1 bar), the reaction vessel was sealed, placed into a thermostatted oven and liquid CO₂ was pumped into the autoclave using a cryogenic pump to bring the reactor pressure at 220 bar. The reaction mixture was kept under 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) and trapped in dichloromethane prior to GC analysis. When the 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 CH₂Cl₂ allowing the total pressure inside the reactor to reach the atmospheric value, after which the product was extracted with a further amount of CH₂Cl₂ 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 rates constant 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 $\ln(1 - [\text{ald.}]_t/[\text{ald.}]_{t=\infty}) = -k_{\text{cat}}[\text{O}_2]t$. 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

We thank Dr. Giuseppe Marci, University of Palermo, for the SEM photographs.

References and Notes

- [1] As recently remarked by R. Gläser, R. Jos, J. Willardt, *Topics in Catal.* **2003**, *22*, 31, a critical point can only be

- defined for a single-component fluid and the term “supercritical” in heterogeneous catalysis refers to a dense multi-component, but single, reaction phase.
- [2] By the British fine chemicals manufacturer Thomas Swan & Co. Ltd; see also: A. M. Rouhi, *Chem. Eng. News* **2003**, 81 (28), 37.
- [3] a) A. D. Curzons, D. J. C. Constable, D. N. Mortimer, V. L. Cunningham, *Green Chem.* **2001**, 3, 1; and both academia, b) : S. R. Oakes, A. A. Clifford, M. C. Rayner, *J. Chem. Soc. Perkin Trans. 1* **2001**, 917, and industry are increasingly interested in dense phase CO₂ as reaction medium c) : M. McCoy, *Chem. Eng. News* **1999**, 77 (24), 11; d) M. Freemantle, *Chem. Eng. News* **2001**, 79 (1), 21; e) *Chem. Eng. News* **2001**, 79 (22), 30.
- [4] a) N. J. Meehan, A. J. Sandee, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, M. Poliakoff, *Chem. Commun.* **2000**, 1497; b) M. G. Hitzler, M. Poliakoff, *Chem. Commun.* **1997**, 1667.
- [5] C. Eckert, *Nature* **1996**, 383, 313; and both this and the molecular phenomena taking place on solid surfaces in supercritical fluids await fuller understanding (personal correspondence with Prof. Roger Gläser).
- [6] J. M. DeSimone, *Science* **2002**, 297, 799.
- [7] D. Hâncu, E. J. Beckman, *Green Chem.* **2001**, 3, 80.
- [8] W. Leitner, *Appl. Organom. Chem.* **2000**, 14, 809.
- [9] a) E. J. Corey, G. Schmidt, *Tetrahedron Lett.* **1979**, 399; b) M. Hirano, S. Yakabe, H. Chikamori, J. Clark, T. Morimoto, *J. Chem. Research* **1998**, 308; c) A. J. Mancuso, D. Swern, *Synthesis* **1981**, 165.
- [10] R. Ciriminna, S. Campestrini, M. Pagliaro, *Adv. Synth. Catal.* **2003**, 345, 1261.
- [11] a) A. Steele, J. Zhu, S. C. E. Tsang, *Catalysis Lett.* **2001**, 73, 9; b) G. Jenzer, D. M. Sueur, T. Mallat, A. Baiker, *Chem. Commun.* **2000**, 2247.
- [12] The fluorophilic character of CO₂ is exploited in catalysis by fluorination of the ligands: a) P. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1999**, 99, 475; by fluorine modification of the encapsulating material: b) V. Chechik, R. M. Crooks, *J. Am. Chem. Soc.* **2000**, 122, 1243; or by employing fluorinated surfactants: c) J. Zhu, A. Robertson, S. C. E. Tsang, *Chem. Commun.* **2002**, 2044.
- [13] Recent experimental and theoretical results on the high solubility of O₂ in perfluorocarbons are available in: M. F. Dias, J. A. P. Coutinho, I. M. Marrucho, <http://symp15.nist.gov/pdf/p193.pdf>, *Fifteenth Symposium on Thermophysical Properties*, Boulder, CO, USA, June 22–27, **2003**.
- [14] For example, recently fluorinated silica gels have been introduced as effective organic pollutants adsorbers: a) L. W. Hrubesh, P. R. Coronado, J. H. Satcher, Jr., *J. Non-Cryst. Solids* **2001**, 285, 328; as low dielectric constant semiconductors: b) B. P. Gorman, R. A. Orozco-Teran, J. A. Roepsch, H. Dong, R. F. Reidy, D. W. Mueller, *App. Phys. Lett.* **2001**, 79, 410; and as super water repellent coatings: c) K. Satoh, H. Nakazumi, M. Morita, *J. Sol-Gel Sci. Technol.* **2003**, 27, 327.
- [15] P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford (UK), **1998**.
- [16] S. Campestrini, U. Tonellato, *Adv. Synth. Catal.* **2001**, 343, 819.
- [17] Such stability is consistent with both the high solubilities of organics in supercritical carbon dioxide (preventing catalyst deactivation by the adsorbed species acting as cage blocking agents), and with the stability towards leaching of sol-gel encapsulated metal “onium” ion pairs. See, for instance: J. Blum, D. Avnir, H. Schumann, *Chemtech* **1999**, 29, 32.
- [18] Nitrogen adsorption at –195 °C cannot be used for the measurement of the porosity of ultramicroporous sol-gel materials as explained in Y. Plevaya, J. Samuel, M. Ottolenghi, D. Avnir *J. Sol-Gel Sci. Technol.* **1995**, 5, 65; the addition of TBAF during the sol-gel synthesis, in fact, has a dramatic effect on the textural properties yielding a nanoporous xerogel whose porosity can be measured with CO₂ at 0 °C.
- [19] I. C. Tilgner, P. Fischer, F. M. Bohnen, H. Rehage, W. F. Maier, *Microporous Mater.* **1995**, 5, 77.
- [20] A. Baiker, *Chem. Rev.* **1999**, 99, 453.
- [21] H. Frenkel-Mullerad, D. Avnir, *Chem. Mater.* **2000**, 12, 3754.
- [22] B. Ameduri, B. Boutevin, J. J. E. Moreau, H. Moutaabbid, M. Wong Chi Man, *J. Fluorine Chem.* **2000**, 104, 185; a thorough structural characterisation is underway in our laboratories and preliminary quantitative IR data confirm indeed the non-homogeneous distribution of the fluoroalkyl groups.
- [23] a) R. Ciriminna, M. Pagliaro, *Chem. Eur. J.* **2003**, 9, 5067; b) M. Pagliaro, R. Ciriminna, *Tetrahedron Lett.* **2001**, 42, 4511.
- [24] G. Leofanti, M. Padovan, G. Tozzola, B. Venturelli, *Catal. Today* **1998**, 41, 207.
- [25] A. Sery-Levy, D. Avnir, *Surf. Sci.* **1991**, 248, 258.
- [26] a) D. Avnir, *Acc. Chem. Res.* **1995**, 28, 328; b) D. Avnir, J. Blum, O. Lev, in: *The Encyclopedia of Materials: Science and Technology*, (Eds.: K. H. J. Buschow, M. C. Flemings, E. J. Kramer, R. W. Cahn, B. Ilschner, S. Mahajan), Elsevier, Amsterdam, **2001**; pp. 8040–8049.
- [27] R. Ciriminna, M. Pagliaro, *Italian Patent Application* **2003**, RM2003 A 000502.
- [28] Commercial doped ormosils, for instance, have already reached a “2nd generation” level of performance: M. T. Reetz, P. Tielmann, W. Wiesenhofer, W. Konen, A. Zonta, *Adv. Synth. Catal.* **2003**, 345, 717.
- [29] The rate of heterogeneously catalysed continuous conversions depends mainly on temperature and reactants concentration which can be controlled independently to optimise conditions adjusting also the flow rate in order to tune the selectivity. See Refs.^[2,5] for details.
- [30] R. A. Sheldon, I. W. C. E. Arends, G.-J. ten Brink, A. Dijkstra, *Acc. Chem. Res.* **2002**, 35, 774.