

Solvent-free, heterogeneous photooxygenation of hydrocarbons by Hyflon[®] membranes embedding a fluoros-tagged decatungstate[†]

Mauro Carraro,^a Martino Gardan,^a Gianfranco Scorrano,^a Enrico Drioli,^b Enrica Fontananova^b and Marcella Bonchio^{*a}

Received (in Cambridge, UK) 24th July 2006, Accepted 29th August 2006

First published as an Advance Article on the web 18th September 2006

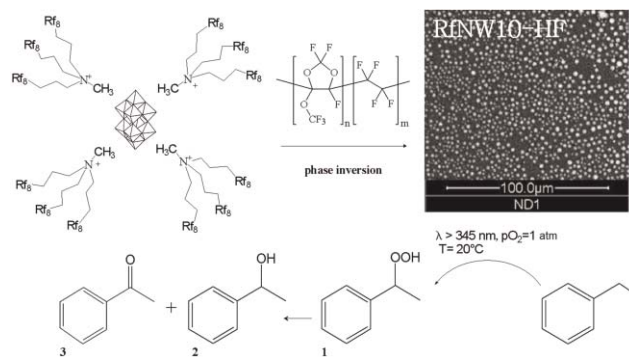
DOI: 10.1039/b610551c

Hybrid fluoropolymeric membranes with 25% loading of the fluoros-tagged (R_fN)₄W₁₀O₃₂ effect the solvent-free photooxygenation of benzylic C–H bonds with up to 6100 TONs in 4 hours.

Photocatalytic oxygenation represents a key strategy towards the development of new sustainable methods for chemical transformations.^{1,2} The combined use of photo-assisted techniques and dioxygen responds to environmental concerns to devise either “greener” synthetic protocols or advanced oxidation processes (AOPs) for pollutant mineralisation.^{3–5} As photocatalysts, soluble polyoxometalates (POMs), are considered the homogeneous counterpart of solid semiconductor metal-oxides.^{6–8} In particular, the photocatalytic properties of decatungstate, W₁₀O₃₂^{4–} have been extensively studied in organic^{9–12} and aqueous phases,^{13–16} *vis-à-vis* the most attractive perspective of solar-photoassisted applications.¹³ Indeed, irradiation of the complex CT bands ($\lambda_{\max} = 324$ nm), generates an excited charge-transfer state (W₁₀O₃₂^{4–*}) which decays in less than 30 ps to an extremely reactive radical transient (“wO”), enabling hydrogen abstraction (HA) or electron transfer (ET) oxidation pathways.¹¹ Despite the remarkable advantages of perfluorocarbon inertness, the high solubility of oxygen in these fluids and the fluorine-based effect in peroxide activation,¹⁷ POM photocatalysis in fluoros environment is unprecedented. On the other hand, due to the environmental impact of perfluorinated solvents, along with their relative high cost, innovation is moving to the concept of fluoros phase catalysis without fluoros solvents.¹⁸ We have recently reported the incorporation of decatungstate within polymeric membranes to obtain a novel class of heterogeneous photocatalysts with tunable composition and structural/surface properties.¹⁹ A proper choice and blend of both the polymeric material and of the catalyst precursor is expected to impact the functional material in terms of its hydrothermal and chemical stability, transparency to UV–Vis irradiation, the hydrophobic/hydrophilic surface character and the selective mass transport of reagents and products including dioxygen.^{19,20} In this respect, perfluoropolymers offer several advantages when compared to other polymeric materials.²¹ Besides their outstanding thermal and oxidative resistance, the peculiar nature of the C–F bond confers to these materials some unique

physical-chemical properties that have been valuably exploited in gas-separation/storage membrane technology.²¹ In particular, dioxygen preferential permeability in fluorinated membranes has been recently reported.²² Based on these considerations and building on our previous invention,¹⁹ we report herein the embedding of the fluoros-tagged decatungstate, (R_fN)₄W₁₀O₃₂ (R_fN = [CF₃(CF₂)₇(CH₂)₃CH₃N⁺]), within fluoropolymeric films, providing new photocatalytic membranes with optimized distribution of the catalyst domains and turnover frequency as high as 1500 h^{–1} in the solvent-free oxygenation of benzylic hydrocarbons. Our results include the photocatalyst characterization in fluoros media, under homogeneous or membrane environment, and the reactivity screening focussing on the impact of membrane parameters on the oxidation efficiency and selectivity.

Fluorophilic (R_fN)₄W₁₀O₃₂ is conveniently isolated, from the sodium salt, by cation metathesis with the fluoros ponytailed ammonium R_fN, which fosters its solubilization in hexafluoroisopropanol (HFIP) or in perfluorocarbon mixtures. This complex is embedded in Hyflon[®] (HF), a copolymer of TFE and TTD,[‡] yielding flat hybrid membranes, R_fNW₁₀–HF, by phase inversion techniques (Scheme 1).²³ Scanning electron microscopy (SEM) images of the film surface and cross-section highlight a highly dispersed, homogeneous distribution of the catalyst domains which appear as spherical particles with uniform size of approximately 2–3 μm in diameter (Scheme 1)[†]. This represents a remarkable improvement of the material morphology, in comparison with PVDF[‡] or Hyflon membranes embedding the fluoros-free (nBu₄N)₄W₁₀O₃₂.^{†19} FT-IR and UV-Vis spectra (Fig. 1)[†] confirm that the structural and spectroscopic features of the photoactive complex are preserved within the polymeric film,



Scheme 1 Embedding of (R_fN)₄W₁₀O₃₂ in Hyflon membrane, R_fNW₁₀–HF (SEM image of the surface), for the heterogeneous photooxygenation of ethylbenzene.

^aITM-CNR and Department of Chemical Sciences, University of Padova, Via Marzolo, 1, 35131, Padova, Italy

^bITM-CNR at University of Calabria, Via P. Bucci, Cubo 17C, 87030, Rende (CS), Italy

[†] Electronic supplementary information (ESI) available: Experimental section, catalyst and membrane characterization, oxygenation kinetics. See DOI: 10.1039/b610551c

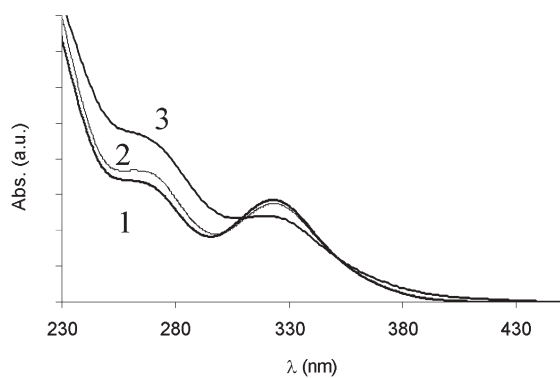


Fig. 1 UV-Vis spectra of $(R_fN)_4W_{10}O_{32}$ in HFIP (1), CH_3CN (2) (0.3 mM) and of R_fN -W10-HF with 25% catalyst loading (3).

where only a modest broadening of the CT bands ($\lambda_{max} = 324$ nm) is observed with respect to homogeneous HFIP or CH_3CN solution (Fig. 1).

Photooxygenation of ethylbenzene by $(R_fN)_4W_{10}O_{32}$ yields the autoxidation products: hydroperoxide (1), alcohol (2) and acetophenone (3) (Scheme 1 and Table 1).^{9,12}

Under homogeneous conditions, both in CH_3CN or HFIP, the oxygenation kinetic highlights the bell-shaped time profile for 1, which is initially formed and converted to 2 and 3 within the photocatalytic cycle[†]. In both media, the poor alcohol selectivity depends also on the competitive oxidation of 2 to 3 under turnover regime (entries 1 and 2 in Table 1).^{9,12} A modest increase of the hydroperoxide concentration in the fluororous phase, is likely ascribed to a more efficient O_2 trapping of the benzylic radical intermediate (entry 1, Table 1). By providing a substrate enriched liquid-phase, over-oxidation to ketone is sensibly reduced (entries 3 and 4 in Table 1). Solvent-free conditions were conveniently adopted for heterogeneous photocatalysis with hybrid membranes (entries 5–10 in Table 1). The polymeric films do not dissolve or release the photoactive component in hydrocarbon media as proved by UV-Vis, FT-IR and reactivity tests[†]. Under neat conditions, product distributions with an increased alcohol selectivity are generally observed.

The impact of the fluororous-tagged decatungstate on the material performance, is highlighted in Fig. 2, comparing the turnover efficiency of three diverse membranes, with equal photocatalyst

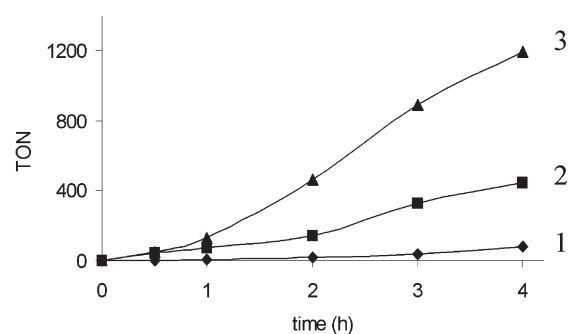


Fig. 2 Time dependence of total turnover number for ethylbenzene photooxygenation by TBAW₁₀-PVDF (1), TBAW₁₀-HF (2) R_fNW_{10} -HF (3) (entries 5–7 in Table 1).

content, but increasing fluororous character. While catalysis by TBAW₁₀-PVDF is negligible (entry 5),[§] the Hyflon systems, TBAW₁₀-HF and R_fNW_{10} -HF, show a remarkable activity with peak performance depending on the fluororous content of the photocatalyst counterion (Fig. 2 and entries 6,7 in Table 1). This observation is likely ascribed to the optimized dispersion of the fluorophilic catalyst within the perfluorinated polymeric film, fostering an enhanced on-membrane reactivity also with respect to the homogeneous solution (compare entries 4 and 7 in Table 1).

The turnover dependence on the R_fNW_{10} -HF film thickness was studied with membranes at 25% loading and section in the range 7–94 μm (entries 7–9 in Table 1). Although a steady increase in the total oxidation products is observed as a function of the overall photocatalyst content, the reverse correlation between turnover efficiency (TOF) and the membrane thickness, indicates a preferential activity of the surface layers with respect to the material bulk (Fig. 3). Indeed, a low hydrocarbon penetration is generally expected for Hyflon-based materials, thus fostering surface catalysis.²² On the other hand, the mechanical properties of the thinner Hyflon membranes can be improved by using a secondary PTFE support, without affecting the catalytic efficiency (entry 10 in Table 1).²⁴

The scope of the heterogeneous photooxidation has been addressed in Table 2. Noteworthy, tetraline and indane photooxygenation proceeds with $TON > 6000$ and remarkable alcohol selectivity, thus providing a convenient alternative to other radical-centered oxygenation systems.^{12,25} Furthermore, the on-membrane

Table 1 Photocatalytic oxygenation of ethylbenzene by homogeneous or membrane embedded decatungstate^a

	Photocatalyst (thickness)	Solvent	Cat., ^b μmol	Products, ^c mM (% 1:2:3)	TON ^d
1 ^e	(nBu ₄ N) ₄ W ₁₀ O ₃₂	CH ₃ CN	0.60	20 (30 : 3 : 67)	50
2 ^e	(R _f N) ₄ W ₁₀ O ₃₂	HFIP	0.60	19 (47 : 7 : 46)	47
3 ^f	(nBu ₄ N) ₄ W ₁₀ O ₃₂	CH ₃ CN	0.20	64 (36 : 32 : 32)	351
4 ^f	(R _f N) ₄ W ₁₀ O ₃₂	HFIP	0.18	95 (56 : 23 : 21)	581
5	TBAW ₁₀ -PVDF (185 μm)	Neat	0.32	23 (45 : 23 : 32)	78
6	TBAW ₁₀ -HF (76 μm) ^g	Neat	0.20	81 (14 : 66 : 20)	443
7	R_fNW_{10} -HF (50 μm)	Neat	0.18	196 (25 : 41 : 34)	1198
8	R_fNW_{10} -HF (7 μm)	Neat	0.03	94 (16 : 46 : 38)	3447
9	R_fNW_{10} -HF (94 μm)	Neat	0.70	270 (15 : 48 : 37)	424
10	R_fNW_{10} -HF/TF (124 μm) ^h	Neat	0.05	99 (13 : 49 : 38)	2055

^a Reaction conditions: ethylbenzene, 1.1 ml; pO_2 1 atm; $\lambda > 345$ nm; $T = 20$ °C; 4 h irradiation time. ^b Photocatalyst content provided as homogeneous complex or membrane embedded with 20–25% loading. ^c Total oxidation products and % distribution determined by GC-MS and GLC analyses. ^d Turnover number calculated as products (mol)/catalyst (mol). ^e Ethylbenzene, 0.02 M, $t = 2$ h; carboxylic acids and dimeric products were also observed. ^f Pseudo-neat conditions by addition of 20 μl of solvent. ^g Porous membrane. ^h R_fNW_{10} -HF supported on PTFE. Support thickness 117 μm , coating thickness 7 μm , catalyst loading 5.9 wt%.

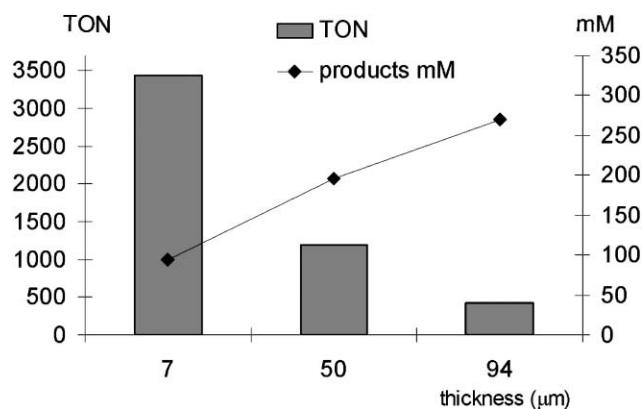


Fig. 3 Total turnover number (TON) and products (mM) of ethylbenzene heterogeneous photooxygenation as a function of the membrane thickness (7–94 μm).

Table 2 Photocatalytic oxygenation of benzylic hydrocarbons by R_fNW_{10} -HF membrane.^a

Substrate	Products (% distribution) ^b	mM ^c (TON)
Tetralin	1-Tetralin hydroperoxide (14)	167 ^d (6124)
	1-Tetralol (58)	
	1-Tetralone (6)	
Indane	1-Indane hydroperoxide (31)	165 ^d (6051)
	1-Indanol (48)	
	1-Indanone (10)	
Cumene	Cumene hydroperoxide (47)	91 (3337)
	Cumyl alcohol (53)	
2-Ethyl-naphthalene	1-(2-Naphthyl)-ethane-1-hydroperoxide (21)	30 (1100)
	1-(2-Naphthyl)-ethan-1-ol (26)	
	1-(2-Naphthyl)-ethan-1-one (53)	

^a Reaction conditions: substrate 1.1 ml; $pO_2 = 1$ atm, $\lambda > 345$ nm, $T = 20$ °C, 4 h irradiation time, R_fNW_{10} -HF (7 μm, 25% catalyst loading). ^b % distribution determined by GC-MS and GLC analyses. ^c mM concentration of total oxidation products and turnover number calculated as products (mol)/catalyst (mol). ^d 10–20% of dimerization products were also observed.

catalyzed accumulation of the alkyl hydroperoxide might be exploited in coupled tandem catalysis routines as oxygen transfer reagent.²⁶

In summary, the application of membrane technology in catalysis offers the combination of advanced molecular separation and selective transport properties, with reactivity on heterogeneous support. In our protocol, the solvent-free use of dioxygen under mild temperature and pressure conditions, for multi-turnover hydrocarbon oxygenation represents an encouraging step forward in sustainable catalysis.

We thank Dr John C. Jansen for helpful discussion and Solvay Solexis for polymer supply. We acknowledge the financial support in the frame of FIRB CAMERE-RBNE03JCR5 and Center of Excellence CEMIF.CAL -CLAB01TYEF.

Notes and references

‡ TF: polytetrafluoroethylene; PVDF: polyvinylidene difluoride; HF: Hyflon; TFE: tetrafluoroethylene; TTD: 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxide; HFIP: hexafluoroisopropanol.

§ The uncatalyzed photooxygenation gives similar results.

- 1 K. Szaciłowski, W. Macyk, A. Drzewiecka-Matuszek, M. Brindell and G. Stochel, *Chem. Rev.*, 2005, **105**, 2647–2694.
- 2 (a) A. G. Griesbeck and A. Bartoschek, *Chem. Commun.*, 2002, 1594–1595; (b) M. Bonchio, T. Carofiglio, M. Carraro, R. Fornasier and U. Tonellato, *Org. Lett.*, 2002, **4**, 4635–4637.
- 3 B. Meunier and A. Sorokin, *Acc. Chem. Res.*, 1997, **30**, 470–476.
- 4 O. Legrini, E. Oliveros and A. M. Braun, *Chem. Rev.*, 1993, **93**, 671–698.
- 5 Y. G. Adewuyi, *Environ. Sci. Technol.*, 2005, **39**, 8557–8570.
- 6 (a) *Heteropoly and Isopoly Oxometalates*, ed. M. T. Pope, Springer-Verlag, New York, 1983; (b) *Polyoxometalate Chemistry. From Topology Via Self-assembly to Applications*, ed. M. T. Pope and A. Müller, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2002.
- 7 (a) A. Hiskia, A. Mylonas and E. Papaconstantinou, *Chem. Soc. Rev.*, 2001, **30**, 62–69; (b) A. Mylonas, A. Hiskia, E. Androulaki, D. Dimotikali and E. Papaconstantinou, *Phys. Chem. Chem. Phys.*, 1999, **1**, 437–440.
- 8 (a) A. Maldotti, A. Molinari and R. Amadelli, *Chem. Rev.*, 2002, **102**, 3811–3836; (b) M. Bonchio, M. Carraro, G. Scorrano and A. Bagno, *Adv. Synth. Catal.*, 2004, **346**, 648–654.
- 9 D. Attanasio, L. Suber and K. Thorslund, *Inorg. Chem.*, 1991, **30**, 590–592.
- 10 (a) D. C. Duncan, T. L. Netzel and C. L. Hill, *Inorg. Chem.*, 1995, **34**, 4640–4646; (b) C. L. Hill, *Synlett*, 1995, 127–132; (c) C. L. Hill and Z. Zheng, *Chem. Commun.*, 1998, 2467–2468.
- 11 (a) C. Tanielian, K. Duffy and A. Jones, *J. Phys. Chem. B*, 1997, **101**, 4276–4282; (b) C. Tanielian, *Coord. Chem. Rev.*, 1998, **178–180**, 1165–1181; (c) C. Tanielian, R. Seghrouchni and C. Schweitzer, *J. Phys. Chem. A*, 2003, **107**, 1102–1111 and references therein.
- 12 (a) I. N. Lykakis and M. Orfanopoulos, *Tetrahedron Lett.*, 2004, **45**, 7645–7649; (b) I. N. Lykakis, C. Tanielian and M. Orfanopoulos, *Org. Lett.*, 2003, **5**, 2875–2878.
- 13 I. Texier, J. A. Delaire and C. Giannotti, *Phys. Chem. Chem. Phys.*, 2000, **2**, 1205–1212.
- 14 Y. Nosaka, T. Takei and N. Fujii, *J. Photochem. Photobiol., A*, 1995, **92**, 173–179.
- 15 R. R. Ozer and J. L. Ferry, *J. Phys. Chem. B*, 2000, **104**, 9444–9448.
- 16 M. Bonchio, M. Carraro, V. Conte and G. Scorrano, *Eur. J. Org. Chem.*, 2005, 4897–4903.
- 17 (a) K. Neimann and R. Neumann, *Org. Lett.*, 2000, **2**, 2861–2863; (b) S. P. de Visser, J. Kaneti, R. Neumann and S. Shaik, *J. Org. Chem.*, 2003, **68**, 2903–2912; (c) A. Berkessel and J. A. Adrio, *Adv. Synth. Catal.*, 2004, **346**, 275–280; (d) M. Vazylyev, D. Sloboda-Rozner, A. Haimov, G. Maayan and R. Neumann, *Top. Catal.*, 2005, **34**, 93–99 and references therein.
- 18 (a) M. Wende and J. A. Gladysz, *J. Am. Chem. Soc.*, 2003, **125**, 5861–5872; (b) L. V. Dinh and J. A. Gladysz, *Angew. Chem., Int. Ed.*, 2005, **44**, 4095–4097.
- 19 M. Bonchio, M. Carraro, G. Scorrano, E. Fontananova and E. Drioli, *Adv. Synth. Catal.*, 2003, **345**, 1119–1126.
- 20 I. F. Vankelecom, *Chem. Rev.*, 2002, **102**, 3779–3810.
- 21 (a) V. Arcella, P. Colaianna, P. Maccone, A. Sanguineti, A. Gordano, G. Clarizia and E. Drioli, *J. Membr. Sci.*, 1999, **163**, 203–209; (b) V. Arcella, C. Troglia and A. Ghielmi, *Ind. Eng. Chem. Res.*, 2005, **44**, 7646–7651.
- 22 (a) J. C. Jansen, F. Tasselli, E. Tocci and E. Drioli, *Desalination*, 2006, **192**, 207–213; (b) R. S. Prabhakar, B. D. Freeman and I. Roman, *Macromolecules*, 2004, **37**, 7688–769.
- 23 *Basic Principles of Membrane Technology*, ed. M. Mulder, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1996.
- 24 A. Gordano, V. Arcella and E. Drioli, *Desalination*, 2004, **163**, 127–136.
- 25 G. Yang, Q. Zhang, H. Miao, X. Tong and J. Xu, *Org. Lett.*, 2005, **7**, 263–266.
- 26 (a) R. Neumann and M. Dahan, *J. Chem. Soc., Chem. Commun.*, 1995, 171–172; (b) J. C. Wasilke, S. J. Obrey, R. T. Baker and G. C. Bazan, *Chem. Rev.*, 2005, **105**, 1001–1020; (c) J. M. Lee, Y. Na, H. Han and S. Chang, *Chem. Soc. Rev.*, 2004, **33**, 302–312.