

Solvent-free, heterogeneous photooxygenation of hydrocarbons by Hyflon® membranes embedding a fluororous-tagged decatungstate: the importance of being fluororous.

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Experimental section

1. General methods

Commercially available reagents and solvents were used as received without further purification. $\text{Na}_4\text{W}_{10}\text{O}_{32}$ ¹ and $[\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{CH}_2]_3\text{CH}_3\text{N}^+ \text{CH}_3\text{OSO}_3^-$ salt were prepared following literature procedures.² Hyflon AD60x and Galden HT 55 were kindly supplied by Solvay Solexis. FT-IR spectra were recorded with a Nicolet 5700-Thermo Electron Corporation instrument, UV-Vis spectra were recorded with a Lambda 45 Perkin Elmer instrument, subtracting polymers absorption; Scanning electron microscopy (SEM) images were obtained using a Cambridge Instruments Stereoscan 360 and a Quanta 200F FEI Philips. In photooxidation experiments, continuous irradiation was performed with a light source housing (Oriel instruments) equipped with a 500W Hg-Xe arc lamp, power supply (200-500 W), F/1.5 UV grade fused silica condenser to collect the radiations from the emitting source, a 5 cm path length liquid (water) filter with fused silica windows to absorb IR radiations, a secondary focusing lens to maximize the incident light on the membrane, and a cut off filter ($\lambda > 345$) to prevent extensive photolysis of organic substrates. GLC analyses were performed on a HP instrument equipped with a flame ionization detector (FID) using a 30 m (0.25 mm i.d., 0.25 μm film thickness) capillary column.

2. Photocatalyst preparation

The fluorophilic salt of decatungstate $(\text{R}_f\text{N})_4\text{W}_{10}\text{O}_{32}$ has been isolated by introducing 4.3 equivalents of $[\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{CH}_2]_3\text{CH}_3\text{N}^+ \text{CH}_3\text{OSO}_3^-$ (0.882 mmol) in a solution of 2,2,2-trifluoroethanol and water (3:1) containing $\text{Na}_4\text{W}_{10}\text{O}_{32}$ (0.205 mmol). The resulting complex was recovered by filtration, dried under vacuum and recrystallized from HFIP/water. Yield 70%. FT-IR analyses (KBr, $\nu < 1300 \text{ cm}^{-1}$): 1237(s), 1202(s), 1149(s), 1134(w), 1117(w), 961(m), 895(w),

810(m), 705(w), 659(w) cm^{-1} . Elemental analysis, calculated: C 20.4; N 0.70; found: C 21.0; N 0.66.

2. Homogeneous Photooxidation procedure

The photocatalytic experiments were carried out in a quartz cell hosted in a thermostatted holder. The reaction solution (2 ml of HFIP or CH_3CN) containing the substrate (0.02 M) and the W_{10} photocatalyst (0.3 mM) were placed in the cell, under magnetic stirring, and dioxygen was supplied through a small Teflon tube connected with a tank. Reaction aliquots (25 μl) were diluted with a dichloromethane solution (500 μl) containing C_{12} as internal standard. The reaction was monitored over time by quantitative GLC-analysis. Peroxide content was determined using the triphenylphosphine quencher method.³ In figure S1 the oxidation kinetic recorded for the HFIP solution is reported. Carboxylic acids, revealed by silylation with BSTFA before GLC-MS analysis, and dimers accounted for 40% of total oxidation products at high percentages of substrate conversion.

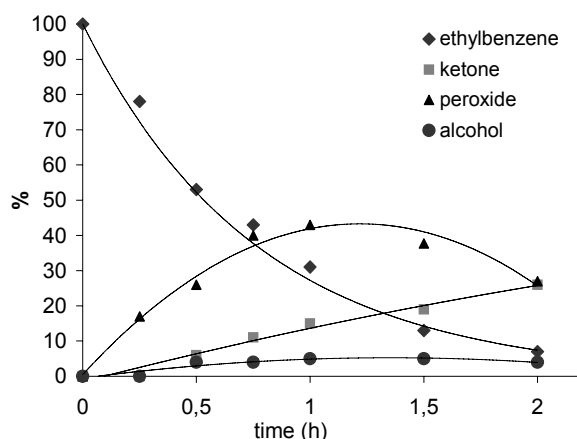


Figure S1. Oxidation of ethylbenzene in hexafluoro *iso*-propanol. See conditions in Table 1, entry 2.

3. Membrane preparation

Flat sheet membranes were prepared by mixing a solution of Hyflon in a Galden (2.4 wt%) with a HFIP solution containing $(\text{R}_f\text{N})_4\text{W}_{10}\text{O}_{32}$ (6.8 wt%) in appropriate ratio in order to provide the desired catalyst loading in the membrane. The solutions were cast on an inert support or on a PTFE porous support (pore diameter 0.22 μm) and removed after membrane formation.⁴ Phase inversion techniques induced by solvent evaporation at $25\pm 1^\circ\text{C}$ was applied to prepare the catalytic membranes.^{5,6}

4. Membrane analysis

Characterization of PFAW10-HF membranes was performed by FT-IR, UV-vis and SEM spectroscopies also in back scattered electrons mode (BSE). The improved catalyst dispersion in the R_fNW_{10} -HF membrane is evident from SEM micrographs in Figure S2.

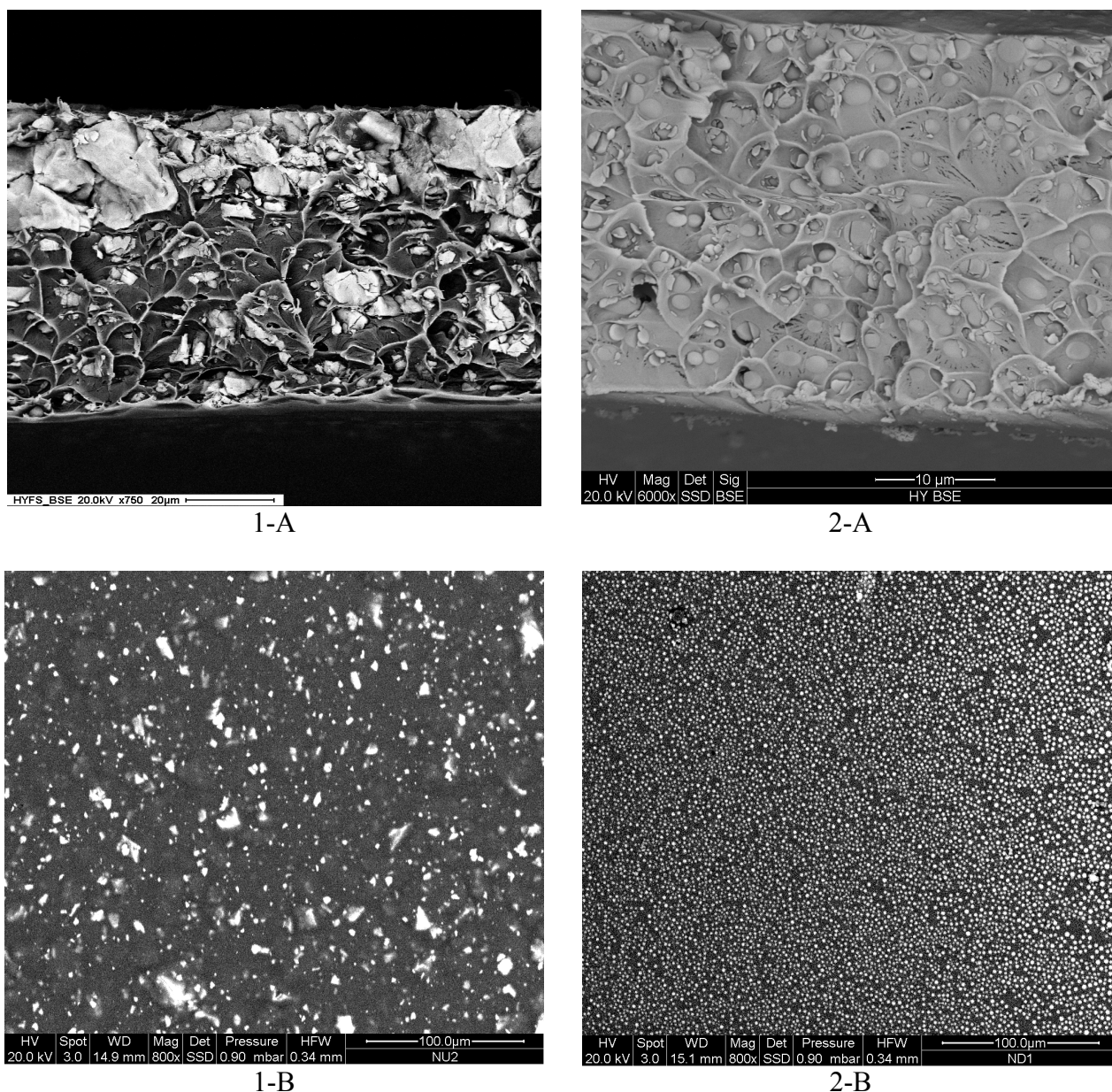


Figure S2 . Cross section (A) and surface (B) BSE images of TBAW₁₀-HF (1) and of R_fNW₁₀-HF (2) membranes.

5. Heterogeneous Photooxidation procedure

The photocatalytic experiments were carried out in a photoreactor composed of a quartz window and a rubber ring to host the membrane retail, that was placed on the internal wall of the cell opposite to the light source (8.5 cm distance from the focusing lens), to collect all the focalized radiation. The hydrocarbon (1.1 ml) was placed in the cell, under magnetic stirring, and oxygen was

supplied through a small Teflon tube connected with a tank. Reaction aliquots (25 μl) were diluted with a dichloromethane solution (500 μl) containing C_{12} as internal standard. The reaction was monitored over time by quantitative GLC-analysis. Peroxide content was determined using the triphenylphosphine quencher method. At the end of irradiation, the membrane was separated from the reaction mixture, washed with hexanes and ethyl benzene and dried under vacuum. FT-IR analysis was used to assess the membrane integrity after catalysis (Figure S 3). In the FT-IR spectrum of the used membrane, the presence of an absorption band at 1700 cm^{-1} might be ascribed to retention of oxidization products which could affect the catalytic membrane efficiency in successive runs. A drop in efficiency of about 20-25 % was indeed observed upon membrane recycling. A better recycle of the membrane can be expected with the use of photocatalytic membrane reactors operating with continuous flow.

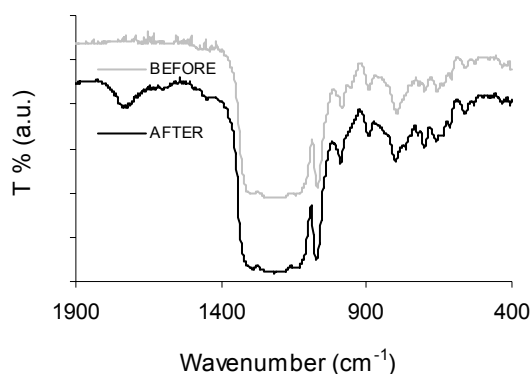


Figure S 3. FT-IR spectra of hybrid membranes. W-O stretching modes are observed at $\nu = 970\text{-}800\text{ cm}^{-1}$.

Catalyst leaching was excluded by Uv-Vis analysis of the homogeneous solution and by control experiments in which the catalytic membrane was removed during ethylbenzene irradiation. By monitoring the product evolution over time, a steady reaction quenching is observed, confirming the removal of the heterogeneous photocatalytic initiator of the autoxidation chain (Figure S 4).

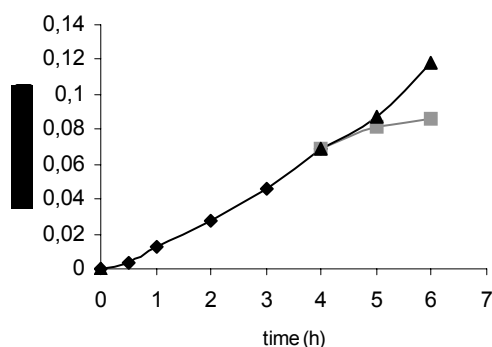


Figure S 4. Product evolution over time observed during irradiation in the presence or after removal of the catalytic membrane after 4 hours irradiation.

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- ⁵ *Basic Principles of Membrane Technology*, ed. M. Mulder, Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996.
- ⁶ M. Bonchio, M. Carraro, G. Scorrano, E. Fontananova, E. Drioli, *Adv. Synth. Catal.*, 2003, **345**, 1119-1126.