Heterogeneous Photooxidation of Alcohols in Water by Photocatalytic Membranes Incorporating Decatungstate

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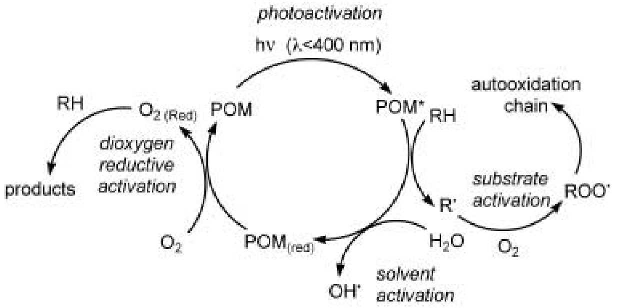
Abstract: The incorporation of decatungstate in polymeric membranes provides new heterogeneous photocatalysts for the oxidation of organic substrates performed in water under an oxygen atmosphere at 25 °C. The photooxidation of water-soluble alcohols proceeds to completion, forming the carbonyl derivative as an intermediate, and leading to degradation products with a COD loss up to 70%. Solid state characterisation techniques (SEM, IR) together with solution UV-VIS analysis and kinetic studies allowed us to identify, among diverse polymeric materials, the PDMS-based system as leaching-free under irradiation and recyclable up to >300 turnovers (4 runs) with no major loss of activity. Membrane induced discrimination of the substrate results from the oxidations of a series of alcohols, through comparison with the homogeneous reactions.

Keywords: alcohols; heterogeneous catalysis; membranes; photooxidation; polyoxometalates; tungsten

Introduction

As photocatalysts, polyoxometalates (POM) represent the homogeneous analogues of semiconductor metal oxides.[1–3] Their activity in promoting photooxygenation of various substrates under mild reaction conditions (oxygen atmospheric pressure, room temperature), is documented, both in organic solvents and in water.[1,2,4,5] This high versatility springs from the extremely rich variety of known polyanionic complexes differentiated in terms of chemical composition, structure and counterion.[6–8] With special emphasis on the development of sustainable processes and the use of solar radiation, all different types of photocatalytic oxidations performed in water with O_2 (type I: radical-initiated oxidation; type II: singlet oxygen reactions; type III: electron transfer-activation) retain a major environmental appeal, either for synthetic procedures, or for advanced oxidation processes (AOP) applied to wastewater treatment.[9–12]

The proposed mechanism for POM-based photocatalysis involves the absorption of light by the complex ground state forming a charge-transfer excited state (POM*) with strong oxidising properties (Scheme 1).[1–3,13] The POM-based photoreactant is able to undergo multi-electron reduction without structural rearrangement, leading to the well-known "blue" reduced form (heteropolyblue).[1–3,14] In the presence of aliphatic hydrocarbons, the oxidative step occurs mainly through hydrogen atom abstraction (type I photooxidation), generating in solution a reactive radical intermediate (substrate activation).[15–17] Therefore, in the catalytic cycle, dioxygen plays a multifaceted role: by intercepting the organic radicals giving rise to an autooxidation chain, and providing to the re-oxidation of the POM(red) thus closing the cycle and generating reduced oxygenating species (dioxygen activation).[18,19] Furthermore, in aqueous solution, the formation of highly reactive hydroxyl radicals OH$^\bullet$, formed through the direct reaction of water with the excited POM (solvent activation), has been proposed to enhance the photooxidation performance.[2,3,20] The existence of multiple operating activation mechanisms for the catalytic functionalisation of unreactive C−H bonds (Scheme 1) is rather unique and deserves a special attention.[2,3,20]



Scheme 1. Composite activation mechanism in the photocatalytic oxidation cycle by polyoxometalates in water.

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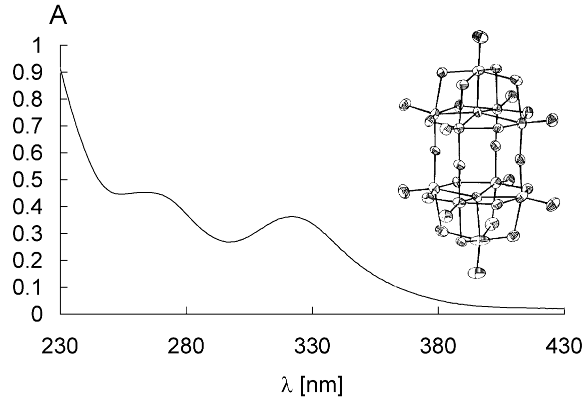


Figure 1. Structure and UV-VIS spectrum of $Na_4W_{10}O_{32}$ (0.3 mmol L^{-1}) in aqueous solution (pH = 7). Path length 1 mm.

The photocatalytic properties of the decatungstate anion $W_{10}O_{32}{}^{4-}$ have been extensively studied in acetonitrile solution[21–25] and applied also to photooxygenation in water.[2,24,26,27] Its UV-VIS spectrum (Figure 1) shows a maximum absorption band at 324 nm, which overlaps with the UV solar emission, so opening the potential for environmentally benign solar-photoassisted applications.[24] While it is clear that the excited charge-transfer state of decatungstate ($W_{10}O_{32}{}^{4-*}$) decays in less than 30 ps to an extremely reactive transient which is the competent photoreactant,[25] the formation of hydroxyl radicals during photoirradiation in water is still a matter of debate.[2,20,24,27] Furthermore, the solvent effect on the lifetime of the photoactive transient and on the oxidation rates of different substrates appears complicated, which hampers a direct comparison of the kinetic results obtained in different media.[23,24]

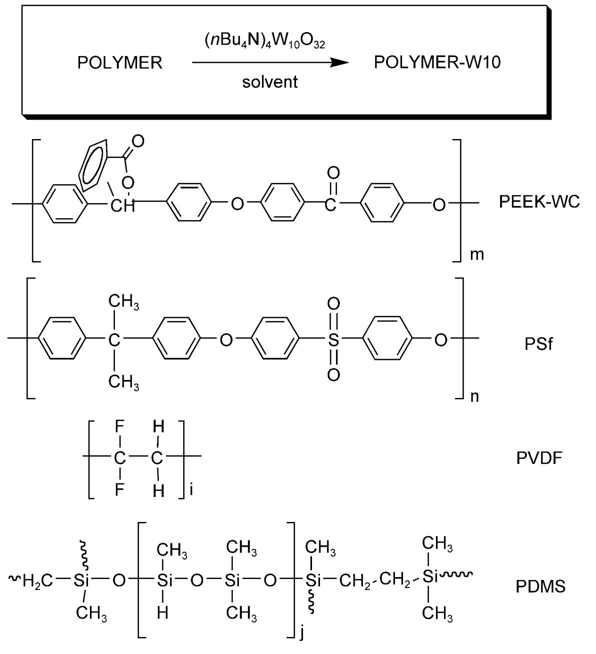
Basically, two main drawbacks dictate the method's limitation especially for practical organic synthesis: these are (i) low quantum yields, which are generally found in the range 0.1 – 0.5,[22,23] (ii) poor selectivity, due to fast over-oxidation processes leading eventually to substrate mineralisation.[2,3] Both issues can be addressed through the heterogenisation of the photocatalyst, which may allow a significant increase of the total turnover number (TON) by catalyst recycling and a selectivity tuning as a function of the substrate affinity towards the heterogeneous support.[28,29] This approach has been recently addressed experimentally by immobilising a lipophilic decatungstate salt, $(n\text{-}Bu_4N)_4W_{10}O_{32}$, on amorphous silica or a mesoporous MCM-41 type and performing the heterogeneous photooxidation in an organic dispersing medium.[28,30,31]

In the present work, we focused on aqueous photocatalysis. In water, the choice of an appropriate hydrophobic support is crucial to induce the sorption of an organic substrate in close proximity to the active site, and may be the key to discriminate among reactants based on their hydrophobic properties and affinity towards the heterogeneous catalyst so as to favour the selectivity tuning.[29] Our study reports on the preparation and characterisation of diverse photocatalytic membranes incorporating decatungstate (W10),[32] their stability under photoirradiation and their application for heterogeneous photooxidation of alcohols in water leading to high substrate conversion with an efficient catalyst recycling (total turnover number > 300). The results presented herein allow a direct comparison between the membrane-based process and homogeneous oxidations in terms of reaction rates and selectivity. A membrane induced reactivity behaviour will be evidenced.

Results and Discussion

Photocatalytic Membranes: Synthesis, Characterisation and Stability Studies

The lipophilic salt of decatungstate[21] $(n\text{-}Bu_4N)_4W_{10}O_{32}$ has been occluded in different polymeric membranes using a phase inversion technique[33] or a hydrosilylation reaction.[34] Four polymers, characterised by a high thermal, chemical and mechanical stability were chosen for the preparation of photocatalytic membranes: polysulfone (PSf), a modified polyether-ether ketone (PEEK-WC), polyvinylidene fluoride (PVDF) and polydimethylsiloxane (PDMS) (Scheme 2). FT-IR spectra confirm that the structure of decatungstate is still



Scheme 2. Synthesis and structural unit of polymeric membranes incorporating decatungstate.

preserved inside the hybrid films.[21] The frequencies of the W-O stretching modes are observed at $\nu = 958, 890, 803\ \mathrm{cm}^{-1}$.

The surfaces and the cross-section morphology of the membranes have been examined by scanning electron microscopy (SEM). Moreover, micrographs in backscattered electrons mode (BSE) and chemical analyses by energy dispersive X-ray spectrometry (EDX) have been used to investigate the catalyst distribution within the membranes. According to the synthetic procedure, the catalyst embedding results in the formation of asymmetric hybrid membranes, displaying a homogeneous dispersion of the catalyst on the active surface. The membrane morphology can be observed with SEM images which are shown in Figure 2 for the PVDF-W10 system. The presence of a macroporous bottom layer (Figure 2c) opposite to a more dense top layer (Figure 2b), is found for the membranes synthesised using the phase inversion technique, thus discriminating the two surface sides in terms of catalyst coverage and access. In all photooxidation experiments, illumination of these catalytic membranes was set from the top layer.

The stability of the different photocatalytic membranes was studied in water under photooxidation conditions to assess the occurrence of a self-induced degradation. This process is of primary importance since it controls the membrane resistance; it is related to the number, accessibility and reactivity of the different sites of attack on the polymers, which may react through different photooxidation mechanisms (hydrogen-atom-transfer or charge-transfer) and, by forming radical initiators, may contribute to the substrate oxidation process.[35] The membrane resistance was evaluated by means of total organic carbon (TOC) release determination, UV-VIS analyses of the immersion solution, inspection of the FT-IR spectra and SEM images of the membranes surface, before and after irradiation. TOC released in solution from the heterogeneous photocatalyst after 2 h irradiation provides a direct indication of the oxidative damage of the polymer material. Data reported in Figure 3 show that membranes with aromatic residues are the most affected (PSf-W10, PEEK-WC-W10,) while a minor TOC release can be determined for PVDF- and PDMS-based systems.

PSf-W10 is the least stable membrane and the SEM images of its surface clearly reveal the self-induced degradation of the membrane. No damages are observed in the SEM micrographs of the other catalytic membranes submitted to the same stability test. The extensive degradation of the PSf-W10 membrane, under photocatalysis condition, causes the release of the decatungstate in solution. This is evident from inspection of the UV-VIS spectral change of the aqueous solution during irradiation, showing the progressive increase of the absorbance at $\lambda_{max} = 324$ nm and therefore the accumulation of the homogeneous photocatalyst over time (Figure 4). The loss of the polyoxotungstate component is also confirmed by FT-IR analysis of the recovered membrane.

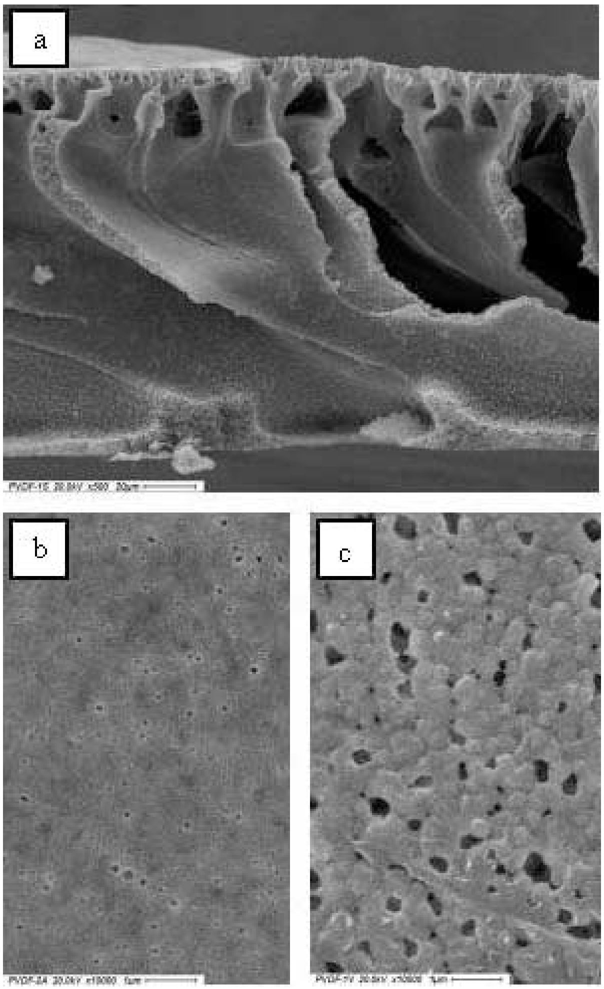


Figure 2. SEM images of the PVDF-W10 membrane: (a) cross-section; (b) top layer; (c) bottom layer.

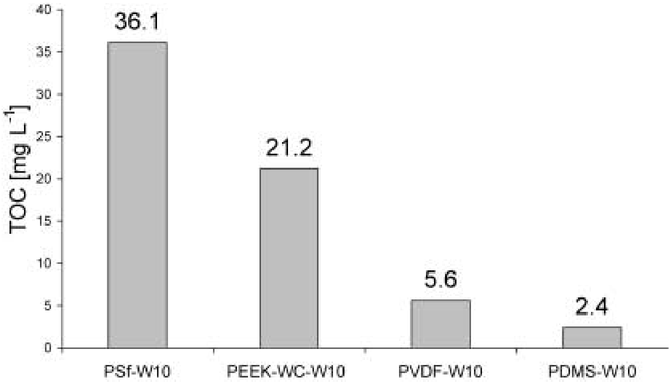


Figure 3. Total organic carbon release upon irradiation of the photocatalytic membranes (2 h) under air, at 25 °C.

In contrast, analogous experiments performed on the PVDF-W10 and PDMS-W10 membranes indicate that they are stable under irradiation, so these systems

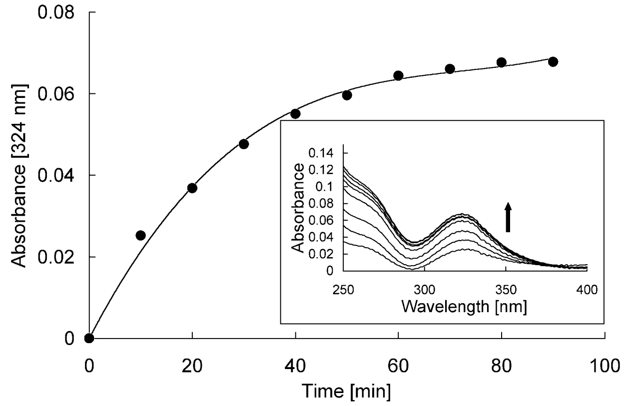


Figure 4. Time evolution of decatungstate release in solution as monitored from the absorbance increase at 324 nm upon irradiation of the PSf-W10 photocatalyst. Inset: UV-VIS spectral change of the water solution over time.

represent the best choice for photocatalytic applications and reactivity studies.

Photocatalytic Oxidations in Water

The activity of the heterogeneous photocatalysts has been assessed in the oxidation of *n*-pentanol chosen as model substrate. The photooxidation experiments have been performed in batch (see Experimental Section) and the results, collected in Table 1 and Figure 5, allow us to compare the activity of the photocatalyst embedded in the two different membranes: PVDF-W10 and PDMS-W10 with respect to homogeneous conditions (W10). To this aim, the membrane retail was cut to provide an equal irradiation surface and the closest amount of total catalyst loading, while the homogeneous reaction was set up according to this latter parameter. It is, however, difficult to compare the diverse reaction systems in terms of turnover numbers as the actual content of decatungstate on the photoactive surface is elusive as is the possible reactivity of the photocatalyst within the membrane deeper layers. For this reason, the system reactivity will be discussed in terms of substrate conversion and/or oxidation rates which provide a direct tool to analyse the photocatalyst behaviour. In all cases, the alcohol oxidation occurs following a degradation pathway in which the aldehyde forms as an intermediate (chemical oxygen demand loss >70%). This reactivity behaviour is known for photooxidations promoted by POMs in water, and may be related to an efficient flow of hydroxyl radicals generated from the solvent (Scheme 1).[2,20,24,27,36]

The kinetic traces, determined by following the substrate conversion over time (Figure 5), highlight the superior velocity of the homogeneous photocatalyst, nevertheless both membrane-based systems show a good performance (cf. entries 1, 2, and 8 in Table 1). Control experiments on the reaction mixture and on the recovered membrane (UV-VIS, FT-IR) allow excluding the occurrence of a competing homogeneous pathway in these heterogeneous photooxidations.

The loss of activity found for the supported photocatalyst may result from different factors: (i) a reduced

Table 1. Photooxidation of *n*-pentanol with membranes incorporating decatungstate (PVDF-W10 and PDMS-W10) and under homogeneous conditions (W10).

Entry[a]	Catalyst	Loading [%]	μmoles	T [°C]	t [h]	Run[b]	Conv.[c] [%]	R_0[d]	TON[e]
1	W10		0.6	25	1	/	97	82	65
2	PVDF-W10	25	0.6	25	4	I	100	13	67
3				25	4	II	61	5	41
4				25	4	III	39	4	26
5	PVDF-W10	25	0.6	40	2	I	87	17	57
6				40	2	II	70	11	47
7	PVDF-W10	25	0.6	50	2	I	99[f]	23	27
8	PDMS-W10	6.3	0.6	25	4	I	94	25	62
9				25	4	II	87	16	58
10	PDMS-W10	9	2	25	4	I	98	31	20
11				25	4	II	92	21	18
12	PDMS-W10	4.4	0.35	25	4	I	88	7	100
13				25	4	II	67	8	77
14				25	4	III	74	7	84
15				25	4	IV	52	7	59

[a] In all reactions: *n*-pentanol (0.04 mmol), H_2O (2 mL, pH = 7) pO_2 = 1 atm, $\lambda > 345$ nm.
[b] Recycling experiments (see text).
[c] Substrate conversion determined by quantitative GLC analysis.
[d] Initial rate units: 10^{-5} mol L^{-1} min^{-1}.
[e] Total turnover number (TON) = moles of substrate converted per mole of catalyst.
[f] Traces of W10 released in solution were observed.

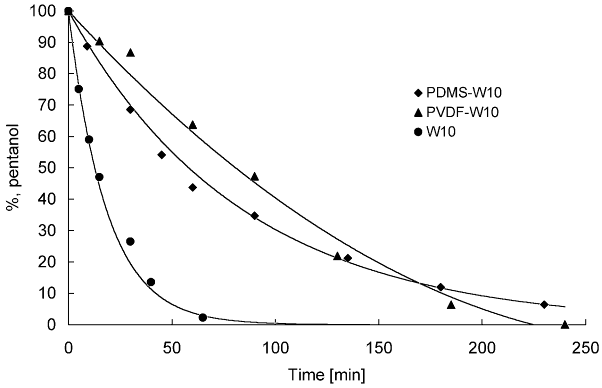


Figure 5. % conversion of *n*-pentanol (0.02 mol dm^{-3}) during photooxidation with homogeneous W10 (0.6 μmol) and heterogeneous PDMS-W10 (6.3% loading, 0.6 μmol) or PVDF-W10 (25% loading, 0.6 μmol). $pO_2 = 1$ atm, $\lambda >$ 345 nm, at 25 °C.

effective concentration of decatungstate on the membrane surface (ii) a limiting rate of supply of reagents to the active sites (mass transport limitation) (iii) slow oxidation of the reduced catalyst embedded in the membrane (iv) formation of aggregates quenching the photocatalytic activity.[31] These aspects will be addressed by studying the effect of the membrane loading on reaction rates (*vide infra*).

The actual performance of the heterogeneous photocatalyst has been also evaluated on the basis of the system recycling. A set of experiments was carried out for both PVDF-W10 and PDMS-W10 in order to examine their activity along 2–4 oxidation runs. After each run the membrane was recovered, and treated according to washing cycles to remove sorbed products. Data in Table 1 show a poor recycling performance for PVDF-W10 (entries 2–4). The heterogeneous catalyst looses activity in progressive runs, and such a reactivity drop emerges from determination of the initial reaction rates which become almost halved in every reaction cycle (cf. entries 2–4 in Table 1). The FT-IR spectrum of the catalytic membrane recovered after each run still shows the typical bands of the embedded decatungstate, so leaching can be neglected. The decrease in the activity could be attributed to the incomplete extraction of residual products causing the accumulation of retained solutes on the membrane surface (membrane fouling). Since sorption is an equilibrium process, this could prevent an efficient supply of fresh reagents. This hypothesis finds support from the analysis of the UV-VIS spectra registered for a DMSO solution of the membrane before irradiation and recovered after two reaction cycles which show an increase of absorbance in the region expected for oxidation products (270–320 nm). Indeed, the photocatalyst recycling is substantially improved at higher temperature, as shown by the experiments run at 40 °C (entries 5 and 6). A further temperature increase up to 50 °C leads to a partial leaching of the decatungstate, which has been revealed in solution by UV-VIS spectroscopy after two hours of irradiation (entry 7).

The PDMS-W10 photocatalyst appears to be the most stable and effective in multiple reaction runs (entries 8–15). For this system the amount of decatungstate loaded in the membrane was varied to verify its effect on oxidation rates and total turnover number (TON). Preliminary results point to a saturation behaviour where an activity plateau is reached for a loading of 6%. A likely possibility is the attainment of an optimal surface dispersion of the active decatungstate so leading both to a maximum photoactivity and to a better substrate supply.

The reaction scope has been investigated considering the photooxidation of several alcohols soluble in water (Table 2). To address the role of the polymeric support in tuning the system reactivity, the same reactions were also performed under homogeneous conditions. The performance of both heterogeneous photocatalysts (PDMS-W10 and PVDF-W10) with respect to the homogeneous reaction (W10) can be evaluated in terms of initial reaction rates and product selectivity. This latter parameter refers to the formation of the carbonyl product, that accumulates in solution up to a substrate conversion in the range 10–30% and then undergoes a consecutive oxidation.

Inspection of data reported in Table 2 show that, in all cases, the homogeneous oxidation is faster. The interesting observation is that the structure-reactivity behaviour may indeed be induced by the nature of the polymeric membrane. A convenient analysis of the diverse results is provided by the graph in Figure 6. The line trend highlights the substrate dependence of the reaction rates found for the homogeneous photocatalyst. This trend in not reproduced by either heterogeneous systems (bar graph). In particular, in the case of PDMS-W10, a membrane with a dense structure, a strong enhancement of the oxidation rate is registered for *n*-pentanol, i.e., the alicyclic alcohol bearing a hydrophobic linear alkyl chain. In contrast, the reaction rates determined for the PVDF-W10 system, a porous membrane, show a rather flat response towards substrate structure, as expected according to the different transport mechanisms foreseen for dense and porous membranes.[33] However, considering the series of aliphatic cyclic alcohols a preferential reactivity towards the higher C_7 form is registered, which again stands in contrast with the homogeneous reference. These observations point to a specific substrate recognition exerted by the heterogeneous matrix; the preferential interaction with the polymeric membrane (mutual affinity) promotes the oxidation favouring the sorption equilibria and leading to an enrichment of the substrate concentration on the catalytic surface, close to the photoactive sites.[34] A membrane-induced substrate discrimination is also consistent with the different

Table 2. Photooxidation of alcohols in water by the heterogeneous PDMS-W10, PVDF-W10 and with the homogeneous $Na_4W_{10}O_{32}$ (W10).

Substrate[a]	Catalyst[b]	t [h]	Conv.[c] [%]	R_0[d]	TON[e]	Select. [%][f] (Conv. [%])
cis-1,2-cyclohexandiol (CyD)	W10	1	100	41	67	52 (15)
	PVDF-W10	4	75	7	50	51 (16)
	PDMS-W10	4	36	7	24	80 (14)
cycloheptanol (c-C7)	W10	1	94	97	64	7 (24)
	PVDF-W10	4	100	17	67	21 (28)
	PDMS-W10	4	36	5	24	9 (26)
cyclohexanol (c-C6)	W10	1	100	163	67	14 (33)
	PVDF-W10	4	76	8	51	17 (34)
	PDMS-W10	4	36	5	24	7 (36)
cyclopentanol (c-C5)	W10	1	100	34	67	22 (26)
	PVDF-W10	4	91	9	60	15 (28)
	PDMS-W10	4	35	2	23	16 (24)
n-pentanol (n-C5)	W10	1	97	82	65	<2 (13)
	PVDF-W10	4	100	13	67	<2 (13)
	PDMS-W10	4	94	25	62	<2 (12)
benzyl alcohol (Bz)	W10	1	92	51	61	67 (9)
	PVDF-W10	4	81	15	54	96 (10)
	PDMS-W10	4	70	11	46	74 (9)

[a] In all reactions: substrate (0.04 mmol), H_2O (2 mL, pH = 7), $pO_2 = 1$ atm, $\lambda > 345$ nm, 25 °C. Substrate abbreviation as indicated in brackets.

[b] W10 (0.6 μmol), PDMS-W10 (6.3% loading, 0.6 μmol); PVDF-W10 (25% loading, 0.6 μmol).

[c] Substrate conversion determined by quantitative GLC analysis.

[d] Initial rate units: 10^{-5} mol L^{-1} min^{-1}.

[e] Total turnover number (TON) = moles of substrate converted per mole of catalyst.

[f] Highest selectivities observed for the carbonyl product, calculated with respect to the converted substrate indicated in brackets.

selectivities, determined at similar alcohol conversion, for the three systems under examination (Table 2). In general, the membrane-assisted process favours the accumulation of the carbonyl derivative, although acceptable chemoselectivities are indeed registered only at low conversion. The reason for this is likely found in the multiple activation mechanism featured by the photooxidation leading to a very efficient oxidative attack which can be hardly controlled by differential sorption equilibria.

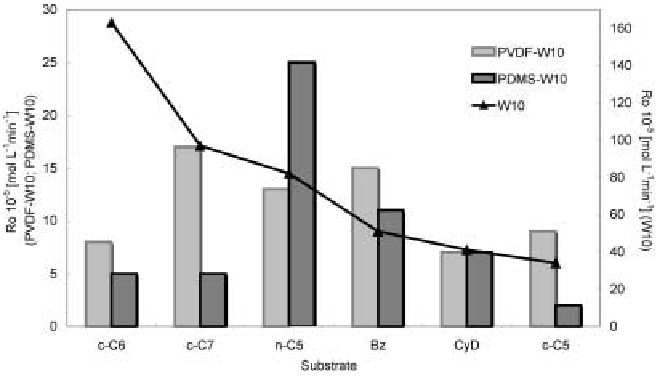


Figure 6. Structure-reactivity trend observed in the photooxidation of alcohols in water by heterogeneous PDMS-W10, PVDF-W10 and homogeneous $Na_4W_{10}O_{32}$ (W10). See Table 2 for reaction conditions.

Conclusion

Novel heterogeneous photooxidation catalysts, performing in water with oxygen, have been synthesised by embedding the photoactive decatungstate within polymeric membranes. The characterisation of the photocatalytic membranes before/after irradiation and spectroscopic studies realised under turnover conditions allowed us to: (i) identify two systems, namely PVDF-W10 and PDMS-W10, where the POM structure and reactivity is preserved; (ii) exclude the occurrence of competing homogeneous pathways; (iii) verify the stability of the embedded photocatalyst during recycling. The heterogeneous photooxidation of water-soluble alcohols proceeds to completion in 2–4 hours, yielding the carbonyl derivative, with appreciable chemoselectivity, only at low substrate conversion. However, the key observation is provided by a membrane-induced structure-reactivity trend that may be exploited to achieve selective processes. Further research work will be focused to a better understanding of the membrane-based substrate recognition in order to improve the synthetic potential of the method.

Experimental Section

General Remarks

Commercially available reagents and solvents were used as received without further purification. MilliQ-deionised water was used as solvent. $(n\text{-Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ was prepared following a literature procedure.[21] PSf was supplied from Amaco under the trade name Udel®. PEEK-WC was from the Chanchung Institute of Applied Chemistry, Academia Sinica. PVDF was from Elf Atochem, under the trade name Kinar 460®. PDMS was synthesised from a two-component system: prepolymer (General Electric, RTV 615 A) and a cross-linker (General Electric, RTV 615 B). FT-IR spectra were recorded with a Perkin Elmer 1600 or a 430 JASCO instrument; UV-VIS spectra were recorded with a Perkin Elmer Lambda 16 or EZ201 spectrophotometer, using 1 mm path length quartz cells; Scanning electron microscopy (SEM) images were obtained using a Cambridge Instruments Stereoscan 360. The casting knife was supplied by Braive Instruments. EDX microanalyses were performed on an analyses system by Philips EDAX. In the stability studies a membrane retail (0.04 g) was irradiated with a 500 W medium-pressure mercury lamp, (Helios Italquarz, Milan), emitting in the field of 300–400 nm. The membrane was immersed in water (70 mL) under magnetic stirring, at atmospheric pressure and irradiated for 2 h with the light source, placed at a distance of 17 cm. TOC analyses were carried out using a Cuvette test LCK 380 Dr Lange. In the photooxidation experiments, continuous irradiation was performed with a light source housing (Oriel instruments) equipped with a 500W Hg-Xe arc lamp, (200–500 W) power supply, 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, and a secondary focusing lens to maximise the incident light on the membrane. GLC analyses were performed on a Shimadzu GC-2010 instrument equipped with a flame ionisation detector (FID) using a 30 m (0.25 mm i.d., 0.25 μm film thickness) EC™-1000 capillary column. Chemical oxygen demand (COD) analyses were performed with the standard kit IDRIMETER by Carlo Erba.

Preparation of Membranes Incorporating Decatungstate

Flat sheet PSf-based membranes (PSf-W10) were prepared following the phase inversion process obtained by immersion precipitation technique.[33] The membranes were prepared using 1-methyl-2-pyrrolidinone (NMP) as solvent and distilled water as non-solvent. A solution (15.0 wt %) of PSf was prepared by dissolving the polymer in NMP (80.0 wt %) by magnetic stirring at room temperature, then decatungstate (5.0 wt %) was added and the resulting solution was left under stirring for additional 24 h. The solution was cast on a glass plate by setting the knife gap at 250 μm and after 1 min of exposure in air, the cast film was immersed for 2 h in a coagulation bath containing deionised water at 20 °C. Then, the membranes were removed from the coagulation bath and dried in a oven at 60 °C under vacuum for 24 h. PVDF- (PVDF-W10) and PEEK-WC- (PEEK-WC-W10) based membranes were prepared following the same methodology, but using dimethylacetammide (DMA) for PVDF and dimethylformamide (DMF) for PEEK-WC, as solvents. PDMS-based catalytic membranes were prepared from a two-component system consisting of a vinyl terminated prepolymer with high molecular weight (GE, RTV 615 A) and a cross-linker (GE, RTV 615 B) containing several hydride groups on shorter polydimethylsiloxane chains.[34] The membranes were cured *via* a Pt-catalysed hydrosilylation reaction to form a densely cross-linked polymer network. A solution (25.0 wt %) of PDMS prepolymer and cross-linker, in a ratio 10:1, prepared using dichloromethane as solvent, was stirred for 2 h at room temperature. The catalyst (insoluble in DCM) was then added with loading from 4.3 to 9% relative to PDMS. The suspension was left under magnetic stirring for additional 24 h, and then it was cast on a petri disk and kept overnight at room temperature. Finally, the mixture was cured under vacuum at 150 °C for 1 h.

Photooxidation Procedure

The photocatalytic experiments were carried out in a batch set-up employing a quartz cell hosted in a thermostatted holder and a single piece of membrane (size: 1.1 × 1.6 cm) and was placed on the one internal wall of the cell opposite to the light source (8.5 cm distance from the focusing lens), to collect all the focused radiation. The reaction solution (H_2O, 2 mL) containing the substrate (0.04 mmol) 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 extracted with a dichloromethane solution (500 μL) containing biphenyl (0.9 mmol L^{-1}) as internal standard, and dried over anhydrous $MgSO_4$. The reaction was monitored over time by quantitative GLC-analysis. At the end of irradiation, the membrane was separated from the reaction mixture, washed with water, exposed to oxygen atmosphere to complete the oxidation of the reduced heteropolyblue complex and then left overnight in water. Before recycling, the membrane was dried under vacuum. Experiments were performed in duplicate to assess the reproducibility of the kinetic determinations providing initial rates with average error in the range 5–10%.

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