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Fast Catalytic Epoxidation with H_2O_2 and $[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]^{4-}$ in Ionic Liquids under Microwave Irradiation

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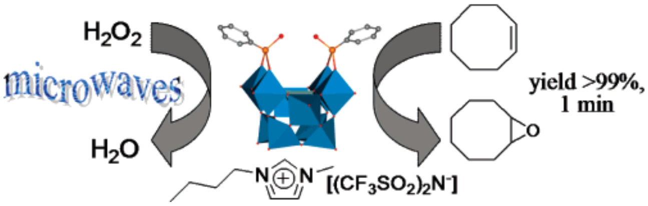

Olefin epoxidation by $[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]^{4-}$ and H_2O_2 occurs in hydrophobic ionic liquids (ILs), with yields and selectivity up to >99%. The catalytic IL phase is recyclable. Under MW irradiation the reaction occurs with up to 200 turnovers per minute. Simultaneous cooling is instrumental for quantitative H_2O_2 conversion.

The design of catalyst packages with better performance, in terms of yields, selectivities, recycling, and use of alternative solvents, is a priority task within sustainable catalysis. In particular, catalytic epoxidation with hydrogen peroxide (H_2O_2) retains a major interest. This is related to the key role of epoxides as industrial intermediates and to the use of the peroxide with the highest "atom efficiency" (47% of active oxygen), yielding H_2O as byproduct.[1] From the catalyst side, robust polyoxometalates (POMs) can promote the epoxidation of internal and terminal double bonds with outstanding catalytic performance and selectivity >99%.[2−4] Moreover, the use of hybrid polyoxotungstates has been recently proposed as a catalyst upgrade.[5,6] When compared to the nonfunctionalized precursor $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$ (**1**),[3] the phenyl phosphonate derivative $[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]^{4-}$ (**2**)[7] displays an improved thermal stability, higher turnover frequency (TOF), and a remarkably wide substrate scope, under microwave (MW)-assisted processes, in CH_3CN.[5] Further innovation toward environmental sustainability should also consider the replacement of hazardous volatile organic solvents (VOCs) by alternative reaction media, ranging from fluorinated phases[8,9] to supercritical CO_2[10] and ionic liquids (ILs),[11,12] or a combination of these.[13]

ILs media have been successfully used for metal-catalyzed oxidations with peroxides,[14−16] therefore the IL embedding of catalytically active polyanions, by a straightforward metathesis strategy, is expected to yield tailored functional phases.[17] In such perspective, we report herein the combined use of **2** and ILs for catalytic epoxidation with H_2O_2 (Scheme 1). Our results include the following: (i) the screening of ILs to optimize catalytic efficiency and recycling, (ii) catalyst speciation and recovery in the IL environment, and (iii) the advantageous use of MW,[18] which are readily absorbed by the ionic catalytic phase (IL+POM), to promote unprecedented turnover frequencies (TOF > 200 min^{-1}).[5,19] A powerful tool for more sustainable organic synthesis and catalysis is the miniaturization of chemical processes, through microreactor technology, coupled with the continuous flow processing of the reaction mixture. This aspect also has been addressed herein (vide infra).

Catalytic tests have been initially performed with *cis*-cyclooctene, as model substrate, in both hydrophilic and hydrophobic ILs containing the 1-butyl-3-methylimidazolium cation, [bmim$^+$], and different anions [BF_4^-], [$CF_3SO_3^-$], [PF_6^-], and [$(CF_3SO_2)_2N^-$] (Scheme 1).[20]

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(20) To avoid irreproducible results often obtained with commercial ILs of unknown purity, the solvents were synthesized and purified following the procedure indicated in the Supporting Information.

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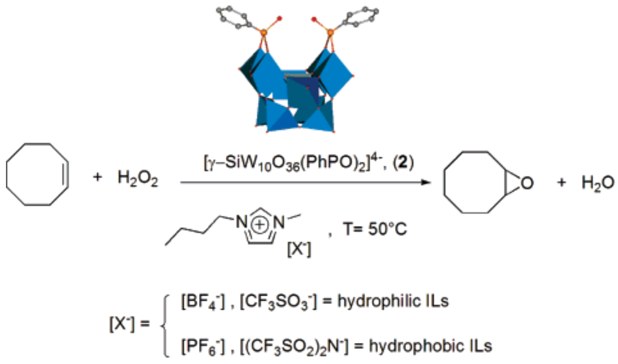
SCHEME 1. Catalytic Epoxidation of *cis*-Cyclooctene by 2 with H_2O_2 in ILs



The catalytic phase is prepared by dissolving **2** in the appropriate IL, which thereby acts as a solvating/immobilization medium for the hybrid organic−inorganic polyelectrolyte. Indeed, combined UV−vis, FT-IR, and ^{31}P NMR evidence indicates that both the polyoxotungstate framework and the organic surface domain of **2** are preserved within the IL environment (see the Supporting Information). Such spectroscopic data have been conveniently used to assess the catalyst stability under turnover regime and to rule out its washing off by extraction procedures during reaction sampling and/or recycling.

The reaction setup has been designed to foster the continuous feeding of the IL-immobilized catalyst, through a neat-hydrocarbon phase layered in the system. The hydrocarbon reservoir provides a stationary concentration of the olefin within the IL catalytic phase, thus fostering maximum rates at substrate-saturation conditions.[21] Quantitative GC analysis, performed under turnover conditions, indicates that the limiting olefin amount in the IL-phase is 1.5 M. Epoxidation occurs upon addition of aqueous H_2O_2 under vigorous stirring.[22] Both the supply of the peroxidic reagent and its evolution under catalysis result in H_2O accumulation in the system, which varies in the range 11−45% calculated with respect to the IL medium (Table 1). The optimization of the catalytic performance has been evaluated in selected ILs with increasing hydrophobicity (Table 1). According to the water content determined after high vacuum drying at 70 °C for 4−30 h, IL hydrophobicity is reported to increase in the order $[bmim^+][BF_4^-] \approx [bmim^+][CF_3SO_3^-] < [bmim^+][PF_6^-] < [bmim^+][(CF_3SO_2)_2N^-]$.[23]

TABLE 1. Catalytic Epoxidation of *cis*-Cyclooctene by 2 with Aqueous H_2O_2 in ILs at 50 °C[a]

entry	IL	H_2O,[b] %	time, min	epoxide yield,[c] %	TOF,[d] min^{-1}
1	$[bmim^+][BF_4^-]$	23	300	62	0.6
2	$[bmim^+][CF_3SO_3^-]$	23	240	81	0.7
3	$[bmim^+][PF_6^-]$	23	180	>99	0.8
4		11	90	>99	3.5
5		45	90	17	0.1
6	$[bmim^+][(CF_3SO_2)_2N^-]$	23	120	92	1.2
7		11	45	>99	5.7
8[e]		11	1	>99	210
9[e,f]		22	2	94	100
10[g]		11	2	10	6.3

[a] Reactions performed in the presence of a layered hydrocarbon phase, *cis*-cyclooctene (3.0 mmol); H_2O_2 (0.60 mmol), provided by aqueous solutions with concentrations in the range 7−24 M; **2** (4.80 μmol); 200 μL of IL. [b] Total amount of water (v/v %) introduced and formed during turnovers. [c] Calculated with respect to H_2O_2. [d] Turnover frequency calculated as epoxide (mol)/**2** (mol) per minute, and determined at <60% conversion. [e] MW irradiation at $W = 10$ W, under stirring and simultaneous cooling with compressed air at 40 psi; $T_{bulk} = 80$ °C. [f] Entry 8 recharged with H_2O_2 (0.60 mmol). [g] Microflow reaction at 0.017 mL/min (see the Supporting Information).

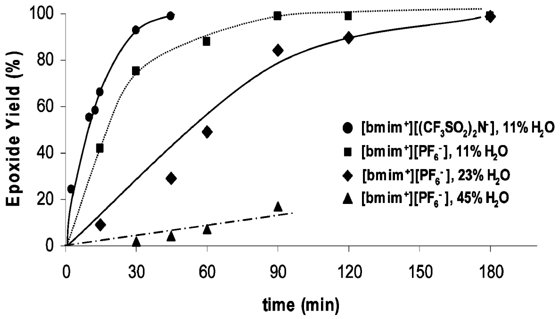


FIGURE 1. Kinetics of *cis*-cyclooctene epoxidation by **2** with aqueous H_2O_2 in hydrophobic ILs, at 50 °C.

Inspection of data in Table 1 reveals that selective epoxidation and quantitative conversion of H_2O_2 (epoxide yields up to >99%) is achieved in the hydrophobic ILs, namely $[bmim^+][PF_6^-]$ and $[bmim^+][(CF_3SO_2)_2N^-]$. Instead, slower to sluggish reactions occur in the hydrophilic media, $[bmim^+][CF_3SO_3^-]$ and $[bmim^+][BF_4^-]$. The extent of water content in ILs is an often-overlooked parameter for the optimization of the catalytic protocol. This instance has been further addressed by evaluating the impact of water addition/accumulation on the epoxidation kinetics and on the resulting turnover frequency (TOF) (Table 1 and Figure 1). Faster epoxidation profiles are obtained by using the more concentrated H_2O_2 in hydrophobic $[bmim^+][(CF_3SO_2)_2N^-]$ and $[bmim^+][PF_6^-]$ (● and ■ in Figure 1), yielding respectively a maximum TOF of 5.7 and 3.5 turnovers per minute (entries 7and 4 in Table 1).[24] Addition of more diluted H_2O_2 solutions in $[bmim^+][PF_6^-]$ results in a remarkable abatement of the oxidation rate with TOF values decreasing below unity (◆ and ▲ in Figure 1 and entries 3 and 5 in Table 1).

The delivery of water is expected to impact the mass-transfer processes within the substrate/ILs/water multiphase system. Moreover, the reactivity of POMs is known to be driven by protonation equilibria and ion-pair association, which can be strongly affected by the medium composition under turnover regime.[4,25] Consequently, a direct, on-site, recharge with additional portions of aqueous H_2O_2 fails to restore the pristine catalytic efficiency, leading to lower TOF values (recharge of reactions 2, 3, and 6 in Table 1, TOF < 0.5 min^{-1}) and overall epoxide yields <60%.[26]

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[21] Under stoichiometric conditions (olefin = 40 μmol, H_2O_2 = 40 μmol, **2** = 0.32 μmol, in 200 μL of $[bmim^+][(CF_3SO_2)_2N^-]$ at $T = 50$ °C) slower reaction rates were generally observed, leading to cyclooctene epoxide (99%) after 18 h and to 1,2-epoxyoctane (51%) after 66 h (compare with data in Table 2).

[22] Aqueous H_2O_2 is soluble in all hydrophilic ILs, while a highly dispersed emulsion is formed within hydrophobic ILs.

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[24] Under the particular condition explored, anydrous H_2O_2 in the form of urea complex (UHP) was not fully soluble in the IL-phase.

[25] Protonation equilibria and the extent of ion-pair association are known to influence POMs reactivity and their physical-chemical properties. (a) Musaev, D. G.; Morokuma, K.; Geletii, Y. V.; Hill, C. L. *Inorg. Chem.* **2004**, *43*, 7702−7708. (b) Grigoriev, V. A.; Cheng, D.; Hill, C. L.; Weinstock, I. A. *J. Am. Chem. Soc.* **2001**, *123*, 5292−5307.

Nevertheless, a good recycling performance has been obtained after extraction of the spent catalytic phase (IL+POM) with hexane and water followed by vacuum anhydrification over P_2O_5. With this treatment the epoxide is recovered with quantitative yield, in at least four consecutive runs (total TON = 500). FT-IR and quantitative UV−vis analysis of the recovered catalytic phase confirm that both the POM structure and its loading are preserved upon extraction and recycling (see the Supporting Information). As a corollary, *cis*-cyclooctene epoxidation by the nonhybrid precursor (**1**) has been screened in $[bmim^+][PF_6^-]$, $[bmim^+][(CF_3SO_2)_2N^-]$, and $[bmim^+][CF_3SO_3^-]$. In these reactions, the epoxide is obtained only in moderate yields (44−74%), while the exhausted catalyst precipitates out of the solution. FT-IR analysis indicates a major structural rearrangement of the lacunary POM.[27] Therefore, further optimization of the reaction protocol and of the substrate scope has been performed only with **2**, which exhibits a superior stability.[5] A noteworthy implementation of the system has been achieved under MW irradiation (entries 8 and 9 in Table 1).[5,8,19] Indeed, the polyelectrolytic nature of the catalytic phase (POM+IL) guarantees negligible vapor pressure, as well as fast and selective MW-induced heating by ionic conduction mechanism, even at low power (4−10 W). In our study, continuous MW irradiation has been applied with simultaneous cooling (T_{bulk} < 80 °C). Here, the reaction vessel is cooled from the outside by compressed air or by a cooling fluid, allowing a higher level of microwave power to be directly administered to the reaction mixture, while preventing bulk overheating.[28] Due to the fast and efficient response of ILs to MW induced dielectric heating, a careful optimization of both the supplied MW power and the cooling flow is crucial to promote selective epoxidation versus the unproductive decomposition of H_2O_2. Under the conditions explored, quantitative epoxidation occurs in 1 min, incrementing the TOF value by ca. 35 times (entries 7 and 8 in Table 1).[29] Considering the experimental setup, the epoxide productivity amounts to ca. 7500 mol/h per mol of catalyst. Moreover, the in situ recharge with H_2O_2 provides a second epoxidation run with a reduced, but still remarkable TOF of 100 min^{-1} (entries 8 and 9 in Table 1). The fast turnover regime achieved under MW irradiation is amenable to flow type operations and microfluidic technology, responding to process intensification issues.[30] In this respect, the application of microreactors for multiphase systems is expected to provide a high surface-to-volume ratio, short diffusion distances, improved mass transfer, fast and efficient heat dissipation, and control. This latter aspect is of particular importance dealing with the potentially harmful peroxide run-over. Interestingly, epoxidation performed in a PTFE microchannel tube (300 μm × 400 mm) under flow conditions occurs with similar TOFs (entries 7 and 10 in Table 1).

TABLE 2. Catalytic Epoxidation by 2 with Aqueous H_2O_2 in $[bmim^+][(CF_3SO_2)_2N^-]$ at 50 °C[a] and under MW Irradiation (Results in Parentheses)[b]

entry	olefin	time, h	epoxide yield,[c] %
1	cyclohexene	4 (0.25)	>99
2	*E*-2-octene	15 (0.75)	>99
3	1-octene	40 (3)	75 (54)
4	1-hexene	40 (2)	85 (99)
5	*Z*-2-hexene	15 (0.5)	77 (97)
6	*E*-2-hexene	15 (1)	89 (99)
7	*Z*-stilbene	15 (0.5[d])	89 (44)

[a] In all reactions: olefin (0.20 mmol), H_2O_2 (40 μmol) provided by 24 M aqueous solution; **2** (0.32 μmol); 200 μL of $[bmim^+][(CF_3SO_2)_2N^-]$; T = 50 °C. [b] Reactions performed in the presence of a layered hydrocarbon phase (2.0 mmol); H_2O_2 (40 μmol), provided by 24 M aqueous solution; **2** (3.2 μmol); 200 μL of $[bmim^+][(CF_3SO_2)_2N^-]$. MW irradiation at 5 W, under stirring and simultaneous cooling; T_{bulk} = 57−65 °C (see the Supporting Information for details). [c] Calculated with respect to H_2O_2. [d] MW irradiation at 4 W; T_{bulk} = 58−73 °C.

The substrate scope is addressed in Table 2, including the MW-assisted optimized protocol (results in parentheses).[31] In these reactions the amount of water is maintained below 1%, to prevent the epoxide conversion to diol and to its overoxidation products.

The epoxidation of both internal and terminal olefins was shown to proceed with up to 99% yield and selectivity. A further point concerns the steric constrains of stereospecific oxygen transfer to *Z*- and *E*-alkenes. Competitive epoxidation of diastereomeric 2-hexenes shows a reactivity ratio *Z*/*E* of 6 (at 50 °C) and 5 (under MW irradiation) at conversion of H_2O_2 <30%. Such *Z* preference is similar to that reported for other tungstate-based catalysts.[5,32]

In conclusion, the combined use of POMs, ionic liquids and MW irradiation represents an innovative strategy for the immobilization, recycling, and activation of the catalytic phase within a solvent-free reaction setup. Further experiments will be aimed at optimizing the reaction performance and its water-tolerance with the use of tailor-made, water-proof, IL phases which might be instrumental for catalytic oxidation with H_2O_2.

Experimental Section

Caution: The uncontrolled heating of large amount of peroxides must be avoided. Care must be taken to avoid possible explosion.

The synthesis of ILs used in this work was performed in a two-step procedure by quaternization of the alkyl-substituted imidazole with an alkyl-bromide followed by metathesis exchange with a suitable anion.[33−35] The resulting ILs were characterized by ^1H NMR, ^{13}C NMR, and FT-IR and their identity was confirmed by comparison with literature data.[36,37]

Microwave experiments were performed with use of a monomode microwave apparatus operating at 2.45 GHz with continuous

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(26) At long reaction time, H_2O_2 decomposition becomes a competing process.

(27) Evolution of **1** to dimeric complexes has been reported to occur in nonaqueous environment. Yoshida, A.; Yoshimura, M.; Uehara, K.; Hikichi, S.; Mizuno, N. *Angew. Chem., Int. Ed.* **2006**, *45*, 1956−1960.

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(31) Under MW irradiation, T_{bulk} depends both on the substrate nature and on its concentration. With less reactive substrates, at high temperature, decomposition of H_2O_2 competes with catalytic epoxidation, so both the presence of a layered substrate phase and a higher catalyst loading are instrumental for higher epoxide yields.

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irradiation power. $(Bu_4N)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ (**1**)[3a] and the hybrid complex $(Bu_4N)_3K[\gamma\text{-}SiW_{10}O_{36}(PhPO)_2]$ (**2**)[7,38] were prepared following literature procedures. They were characterized by FT-IR and ^{183}W NMR and their identities were confirmed by comparison with literature data. Solution characterization of **2** in CH_3CN and in $[bmim^+][(CF_3SO_2)_2N^-]$ was also performed by UV−vis, ESI-MS, ^{1}H NMR, and ^{31}P NMR.

1: FT-IR (KBr, $1200 < \nu < 600$, cm^{-1}) 998, 958, 920, 902, 877, 783, 745, 691. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.26 (2H, s), 6.61 (2H, s), 3.19 (32H, m), 1.56 (32H, m), 1.32 (32H, m), 0.91 (48H, m); ^{183}W NMR (16.67 MHz, DMSO/DMSO-d_6) δ −94.7 (2W), −98.1 (2W), −115.6 (2W), −118.1 (2W), −193.8 (2W).

2: UV−vis ($[bmim^+][(CF_3SO_2)_2N^-]$) λ 244 nm ($\log \epsilon_{244} = 4.56$); FT-IR (KBr, $1200 < \nu < 600$, cm^{-1}): 1196, 1137, 1049, 1008, 970, 943, 911, 884, 834, 796, 785, 752, 699; ESI-MS (−) (CH_3CN/H_2O) *m/z* 896.9, $[HSiW_{10}O_{36}(PhPO)_2]^{3-}$; ^{1}H NMR (300 MHz, CD_3CN) δ 7.95−7.88 (m, 4H), 7.55−7.49 (m, 6H), 3.11 (m, 24H), 1.61 (m, 24H), 1.37 (m, 24H), 0.97 (t, $J = 7.3$ Hz, 36H); ^{31}P{^{1}H} NMR (121.5 MHz, CD_3CN) δ 14.9; ^{31}P{^{1}H} NMR (121.5 MHz, $[bmim^+][(CF_3SO_2)_2N^-]$) δ 15.7; ^{183}W NMR (16.67 MHz, CH_3CN/CD_3CN) δ −106.6 (2W), −114.4 (4W), −154.9 (4W, d, $J = 10.9$ Hz).

Catalytic Epoxidation of *cis*-Cyclooctene by 2 with H_2O_2 in ILs. The catalyst (4.8 μmol) was dissolved in the IL phase (200 μL) upon sonication. *cis*-Cyclooctene (3.0 mmol) was added and the biphasic system was placed in a oil bath at 50 °C. H_2O_2 (0.60 mmol, 7−24 M aqueous solution) was added under vigorous stirring. The reaction was sampled by quantitative GC analysis after dilution in CH_2Cl_2 containing dodecane, as internal standard, and the Ph_3P quencher. The catalytic phase was extracted with hexane (5×0.5 mL), washed with H_2O (0.5 mL), dried under vacuum over P_2O_5 at 70 °C for 4 h, and then recycled in three more consecutive runs with no loss of catalytic activity. Microwave experiments were performed with continuous irradiation power at 10 W, under simultaneous cooling ($T_{bulk} < 80$ °C).

General Procedure for Catalytic Epoxidation of Internal and Terminal Alkenes by 2 with H_2O_2 in $[bmim^+][(CF_3SO_2)_2N^-]$ at 50 °C. The catalyst (0.32 μmol) was dissolved under sonication in the IL (200 μL). The alkene (0.2 mmol) and H_2O_2 (40 μmol, 24 M aqueous solution) were added and the mixture was stirred vigorously in a oil bath at 50 °C. At the end of the reaction the mixture was diluted in CH_2Cl_2 containing dodecane as internal standard and monitored by quantitative GC analysis.

General Procedure for Catalytic Epoxidation of Internal and Terminal Alkenes by 2 with H_2O_2 in $[bmim^+][(CF_3SO_2)_2N^-]$ under MW Irradiation. The catalyst (3.2 μmol) was dissolved under sonication in the IL (200 μL). The alkene (2.0 mmol) and H_2O_2 (40 μmol, 24 M aqueous solution) were added. The reaction vessel was placed in the single-mode cavity of the instrument and irradiated with power at 4 or 5 W, thus reaching a $T_{bulk} = 57-65$ °C, under simultaneous cooling by a stream of compressed air (pressure = 60 psi). At the end of the reaction, the mixture was diluted in CH_2Cl_2 containing dodecane as internal standard and monitored by quantitative GC analysis.

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Supporting Information Available: Additional experimental procedures and spectral and chromatographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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