Aqueous Biphasic Oxidation: A Water-Soluble Polyoxometalate Catalyst for Selective Oxidation of Various Functional Groups with Hydrogen Peroxide

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Abstract: A "sandwich" type polyoxometalate, $Na_{12}[(WZn_3(H_2O)_2][(ZnW_9O_{34})_2]$, was used as an oxidation catalyst in aqueous biphasic reaction media to effect oxidation of alcohols, diols, pyridine derivatives, amines and aniline derivatives with hydrogen peroxide. The catalyst was shown by ^{183}W NMR to be stable in aqueous solutions in the presence of H_2O_2 and showed only minimal non-productive decomposition of the oxidant. Secondary alcohols were selectively oxidized to ketones, while primary alcohols tended to be oxidized to the corresponding carboxylic acids, although secondary alcohols were selectively oxidized in the presence of primary alcohols. Vicinal diols yielded carbon-carbon bond cleavage products in very high yields. Pyridine derivatives were oxidized to the respective *N*-oxides, but strongly electron-withdrawing moieties inhibited the oxidation reaction. Primary amines were oxidized to the oximes, but significantly hydrolyzed *in situ*. Aniline derivatives were oxidized to the corresponding azoxy or nitro products depending on the substitution pattern in the aromatic ring. Catalyst recovery and recycle was demonstrated.

Keywords: alcohols; biphasic reactions; homogeneous catalysis, hydrogen peroxide; oxidation; polyoxometalates,

Introduction

Despite environmental concerns, most industrial fine chemicals are still made by well-entrenched and classical stoichiometric methods leading to large amount of effluent waste, which also adds a significant economic burden due to the significant cost for treatment and/or abatement of the waste formed. Thus, for future envisioned sustainable manufacture of fine chemicals, usually prepared in liquid-phase batch processes, there is a need for the development of homogeneously catalyzed transformations. There are several requirements for the application of homogeneous catalysts including high selectivity and activity, thus requiring highly persistent compounds that operate at very high substrate to catalyst ratios.[1] Importantly, the reaction work-up should be practical including easy recovery and recycle of the catalyst.

In recent years, polyoxometalates, anionic oxoclusters based on tungsten or molybdenum, and in particular their transition metal-substituted derivatives, have received attention as promising oxidation catalysts for the selective oxidation of organic substrates by a variety of oxygen sources.[2] Most attractive oxidants from a fine chemical synthetic point are hydrogen peroxide and molecular oxygen. The oxotungstate or oxomolybdate nature of polyoxometalate compounds bodes well for activation of hydrogen peroxide by them. Indeed, originally, Ishii and his co-workers and also others used the commercially available phosphotungstate, $[PW_{12}O_{40}]^{3-}$, as catalyst for oxidation of alkenes, alcohols, diols, alkynes, amines and sulfides.[3] At practically the same time, research carried out by others showed that the catalytically active species was in fact the peroxophosphotungstate, $\{PO_4[WO(O_2)_2]_4\}^{3-}$,[4] a compound previously synthesized and characterized by Venturello et al. that had been shown to have very similar catalytic activity in various oxidation reactions with hydrogen peroxide.[5] Significantly, it should be noted that the isostructural compound $[SiW_{12}O_{40}]^{4-}$ showed almost no catalytic activity compared to $[PW_{12}O_{40}]^{3-}$, although the lacunary $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$ is quite reactive.[6]

The hydrolytic instability of the simple and lacunary Keggin type polyoxometalates, $[PW_{12}O_{40}]^{3-}$ and $[PW_{11}O_{39}]^{7-}$, in the presence of aqueous hydrogen peroxide led to the use of various hydrolytically stable transition metal-substituted "sandwich" type polyoxometalalates as catalysts for hydrogen peroxide activation. Various iron-containing polyoxometalates of dif-

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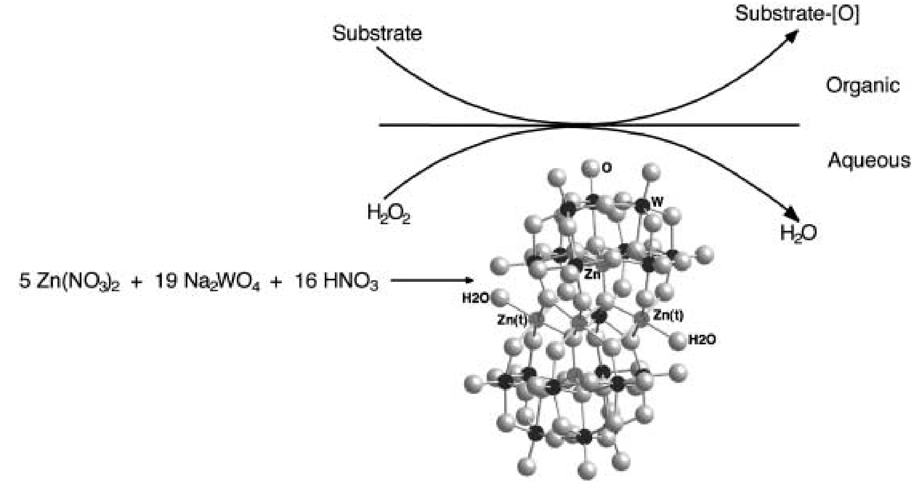
ferent structures have been investigated and reported to be hydrolytically stable and have good activity for alkene oxidation with only moderate non-productive decomposition of hydrogen peroxide.[7] A relatively new class of transition metal-substituted compounds, polyfluorooxometalates, especially $[Ni(H_2O)NaH_2W_{17}O_{55}F_6]^{9-}$, which have a quasi Wells–Dawson structure are also quite active for epoxidation of alkenes and allylic alcohols with hydrogen peroxide.[8] However, the apparently most catalytically active class of compounds are the $\{[(WZnM_2(H_2O)_2][(ZnW_9O_{34})_2]\}^{q-}$ "sandwich" type polyoxometalates.[9] Up to tens of thousands of turnovers could be attained for reactive hydrocarbon substrates. Allylic primary alcohols were oxidized selectively to the corresponding epoxides in high yields and $> 90\%$ selectivity. Secondary alcohols were oxidized to ketones and sulfides to a mixture of sulfoxides and sulfones. Finally, very recently, the efficacy of the oxidatively and solvolytically resistant sandwich-type polyoxometalates for the stereoselective epoxidation of the chiral allylic alcohols by hydrogen peroxide has been demonstrated.[10]

Besides questions of catalytic activation of oxidants by polyoxometalate catalysts, the question of polyoxometalate recovery and recycle is also important. Two broad approaches have been adopted. The first basic approach is to immobilize a catalyst with proven catalytic properties onto a solid support leading to catalytic system that may be filtered and reused. Such approaches include concepts such as simple use of catalysts as insoluble bulk material,[11] impregnation of a catalyst onto a solid and usually inert matrix,[12] attachment through covalent or ionic bonds of a polyoxometalate to a support,[13] and inclusion of the polyoxometalate catalyst in a solvent anchored supported liquid phase.[14] The second basic approach is to use biphasic liquid-liquid systems, such that at separation temperatures, which are usually ambient, the catalyst and product phases may be separated by phase separation; the catalyst phase is reused and the product is worked up in the usual manner. In general, numerous biphasic media have been discussed in the literature that include using catalysts in aqueous, fluorous, ionic liquid, supercritical fluid and other liquid phases. Surprisingly and although polyoxometalates are commonly synthesized as water-soluble alkali salts, the idea of carrying out reactions in biphasic media polyoxometalate-water/organic substrate has not been realized until recently. Thus, we have just recently communicated that the $\{[(WZn_3(H_2O)_2][(ZnW_9O_{34})_2]\}^{12-}$ polyoxometalate in water catalyzes the aqueous biphasic oxidation of alcohols with hydrogen peroxide, Scheme 1.[15]

The catalytic system was shown to be quite effective for oxidation of secondary and primary alcohols to ketones and carboxylic acids, respectively. An important additional characteristic of this catalytic system is that the catalyst, $Na_{12}[(WZn_3(H_2O)_2][(ZnW_9O_{34})_2]$ does not have to be prepared beforehand. Assembly, *in situ*, of the polyoxometalate by mixing sodium tungstate, zinc nitrate and nitric acid in water is sufficient to attain a fully catalytically active system. In this paper we present our further studies of aqueous biphasic oxidation catalyzed by $Na_{12}[(WZn_3(H_2O)_2][(ZnW_9O_{34})_2]$ with hydrogen peroxide as oxidant. Oxidation of alcohols, diols, amines, and pyridine derivatives is presented.

Results and Discussion

Oxidative transformations catalyzed by polyoxometalates with hydrogen peroxide have almost invariably been carried out using hydrophobic quaternary ammonium salts of these polyanions.[3] Often in organic solutions, effective catalysts of the "sandwich" structure



Scheme 1. Generalized picture for the aqueous biphasic oxidation of organic substrates with H_2O_2 catalyzed by $Na_{12}[(WZn_3(H_2O)_2][(ZnW_9O_{34})_2]$.

have been shown to be stable under reaction conditions with relatively minor non-productive decomposition (dismutation) of hydrogen peroxide *via* a Haber–Weiss type reaction mechanism. The use of water-soluble sandwich-type polyoxometalates in biphasic aqueous media first requires an examination of the stability of the polyoxometalate in aqueous hydrogen peroxide and a measurement of the degree of hydrogen peroxide dismutation. In Figure 1 (*top*) is presented the ^{183}W NMR spectrum of the Na$_{12}$[(WZn$_3$(H$_2$O)$_2$][(ZnW$_9$O$_{34}$)$_2$] catalyst used in this research. The Na$_{12}$[(WZn$_3$(H$_2$O)$_2$][(ZnW$_9$O$_{34}$)$_2$] compound shows 10 peaks at δ (ppm) = 22.6 (1), – 16.5 (2), – 41.6 (2), – 84.2 (2), – 89.4 (2), – 93.8 (2), – 153.9 (2), – 187.3 (2), – 226.6 (2) and – 304.7 (2). The ^{183}W NMR spectrum has been previously discussed in detail and is indicative of 10 unique W absorptions with one peak for a tungsten atom in the "belt" of the polyoxometalate and nine additional peaks for the tungsten atoms of the ZnW$_9$O$_{34}$ fragments.[16] Upon addition of 2000 equivalents of H$_2$O$_2$, the ^{183}W NMR spectrum of the Na$_{12}$[(WZn$_3$($_2$O)$_2$][(ZnW$_9$O$_{34}$)$_2$] solution, Figure 1 (*bottom*), similarly shows 10 peaks at somewhat slightly different chemical shifts: δ (ppm) = 22.7, – 28.2, – 45.6, – 93.4, – 94.3. – 96.8, – 158.4, – 192.6, – 231.3 and – 299.4. In addition, two peaks appear at – 655.4 and – 697.3 ppm.

The results would seem to indicate that the general symmetry (10 peaks in the + 25 to – 300 ppm region) and therefore the general structure of the Na$_{12}$[(WZn$_3$(H$_2$O)$_2$][(ZnW$_9$O$_{34}$)$_2$] polyoxometalate is retained upon addition of the hydrogen peroxide. The appearance of two additional distinct peaks at *ca.* – 700 ppm indicates the formation of two distinct monoperoxo tungsten species;[17] in each species the peroxo unit can be assumed to be attached to any of the nine tungsten atoms of each of the ZnW$_9$O$_{34}$ fragments with a peroxo unit at the belt tungsten position probably deemed less likely due to reduced accessibility. The integration of the ^{183}W peaks is inexact, thus the comparative contribution of each peak, e.g., tungsten-oxo or tungsten-peroxo is very approximate and we interpret the ^{183}W NMR as indicating a mixture of two {[(WZn$_3$(H$_2$O)$_2$][(ZnW$_9$O$_{34}$)$_2$]}$^{12-}$ polyoxometalate-peroxo species. Important also is the fact that there is no evidence for decomposition of the polyoxometalate. For example, dissociation of a tungsten center from the polyoxometalate in the presence of a very large excess of hydrogen peroxide would lead to a signature peroxo species with its unique absorption in the ^{183}W NMR spectrum. Thus, addition of H$_2$O$_2$ to Na$_2$WO$_4$ (δ = 0 ppm) gave a peak at δ = – 1242 ppm (0.76 M Na$_2$WO$_4$, 5 M H$_2$O$_2$). No such peak, however, was observed in the spectrum of Na$_{12}$[(WZn$_3$(H$_2$O)$_2$][(ZnW$_9$O$_{34}$)$_2$] with H$_2$O$_2$. As is known from the literature, the zinc atoms in the terminal positions, Zn(t) in Scheme 1, can be metathetically exchanged with other transition metals.[16] The transition metal substitution may have a significant effect on the rate of dismutation of hydrogen peroxide and thus on the yield of aqueous biphasic oxidation of organic substrates. We, thus, examined the decomposition of H$_2$O$_2$ in the presence of various transition metal substituted polyoxometalates, Figure 2.

The calculated initial rates of hydrogen peroxide decomposition under the reaction conditions given in Figure 2 are 1.61×10^{-4}, 3.35×10^{-4}, 1.61×10^{-3}, 1.96×10^{-3}, 1.25×10^{-2} mmol min^{-1} µmol^{-1} catalyst, for Na$_q$[WZnM$_2$(H$_2$O)$_2$(ZnW$_9$O$_{34}$)$_2$] and M = Zn (II), Fe(III), Mn(II), V(IV)=O and Co(II), respectively. In the oxidation of a model substrate, 2-pentanol to 2-pentanone, [1 mmol 2-pentanol, 5 mmol (~17% wt) H$_2$O$_2$, 4 µmol catalyst, 1 mL water, 75 °C, 7 h) the conversions were 93, 92, 80, 29 and 14 mol for Zn(II) ~ Fe(III) > Mn(II) > Co(II) > V(IV)=O. Thus, as a general rule the order of catalytic activity for

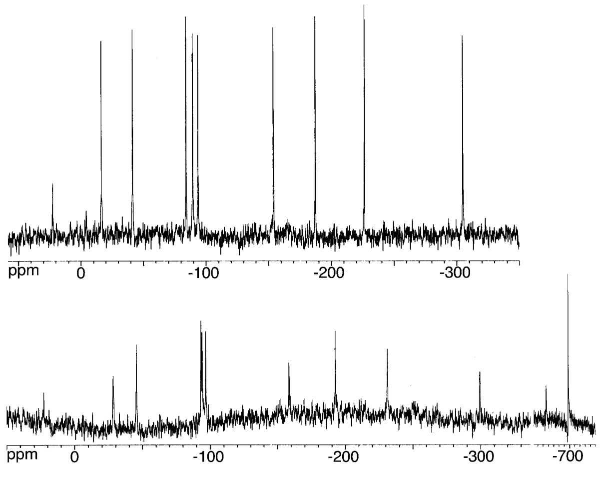


Figure 1. ^{183}W NMR spectra of Na$_{12}$[(WZn$_3$(H$_2$O)$_2$][(Zn$_9$O$_{34}$)$_2$] alone (*top*) and with addition of H$_2$O$_2$ (*bottom*).

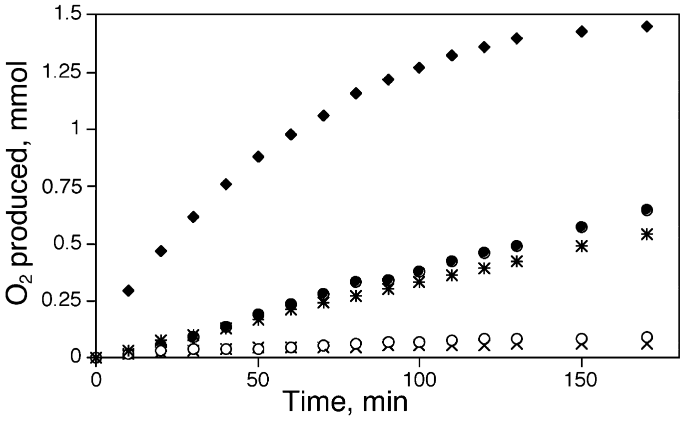


Figure 2. Decomposition of H$_2$O$_2$ by the [WZnM$_2$(H$_2$O)$_2$-(ZnW$_9$O$_{34}$)$_2$]$^{q-}$ polyoxometalates. Reaction conditions: 3.52 mmol H$_2$O$_2$, 4 µmol Na$_q$[WZnM$_2$(H$_2$O)$_2$(ZnW$_9$O$_{34}$)$_2$], 1 mL H$_2$O. [M = Zn(II), ×; M = Fe(III), ○; M = Mn(II), ✳; M = V(IV)=O, ●; M = Co(II), ◆].

$Na_q[WZnM_2(H_2O)_2(ZnW_9O_{34})_2]$ could be nicely and inversely correlated to the rate of hydrogen peroxide dismutation in the absence of a substrate, except for $Na_q[WZn(VO)_2(ZnW_9O_{34})_2]$ which was exceptionally less reactive. Since the $Na_{12}[(WZn_3(H_2O)_2][(ZnW_9O_{34})_2]$ polyoxometalate appeared stable in aqueous solution and in the presence of hydrogen peroxide, and showed only relatively slow decomposition of the later, the $Na_{12}[(WZn_3(H_2O)_2][(ZnW_9O_{34})_2]$ compound was used as a catalyst for the aqueous biphasic oxidation of various organic compounds with different functional units as outlined in Scheme 1.

In Table 1 are presented the results for the selective oxidation of secondary alcohols to the corresponding ketones. In general the method was highly successful for oxidation of simple acyclic, cyclic and benzylic secondary alcohols to the corresponding ketones. The presence of two non-vicinal alcohol moieties, e.g., in 2,5-hexanediol, led to the formation of the corresponding diketone, 2,5-hexanedione. Notably, however, a solid alcohol such as menthol was hardly reactive. Assuming logically that the reaction either occurs at the interface between the organic substrate and catalyst-containing aqueous phase where the alcohol moiety is "presented" to the organic phase or by dissolution of a small amount of the alcohol in the aqueous phase, we conclude that menthol is mostly inactive due to physical considerations, i.e., lack of possible interaction between the alcohol moiety and the aqueous catalyst. Dissolution of menthol in toluene leads to an increased conversion, but remained lower than with the similar cyclohexanol. This is presumably due to physiochemical considerations, either lower solubility in the aqueous phase or reduced, rate-related, reactivity at the interface due to dilution. There is very high chemoselectivity in this reaction in reference to oxidation at a secondary alcohol in the presence of a primary alcohol as is evident in the oxidation of 2-ethyl-1,3-hexanediol to 2-ethyl-3-oxo-1-hexanol. However, primary alcohols can be oxidized cleanly to the corresponding carboxylic acids in nearly quantitative yields in the absence of a secondary alcohol moiety. Thus, 1-pentanol, benzyl alcohol and 4-hydroxymethylimidazole were oxidized to the corresponding pentanoic acid, benzoic acid and imidazole-4-carboxylic acid, respectively, in upwards of 95% yields under the following reaction conditions: 1 mmol substrate, 5 mmol (~17% wt) H_2O_2, 4 μmol $Na_{12}[WZnZn_2(H_2O)_2(Zn_9O_{34})_2]$, 1 mL water, 75 °C, 7 h. Similarly, 1,6-hexanediol was oxidized to the corresponding dicarboxylic acid in essentially quantitative yields.

Table 1. Oxidation of secondary alcohols catalyzed by $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$.

Substrate	Conversion, mol %
2-pentanol	94
2-butanol	93
2-octanol	91
2,5-hexanediol	99
1-phenylethanol	~100
cyclohexanol	~100
cyclooctanol	95
2-ethyl-1,3-hexanediol[a]	~100
menthol[b]	4 (20)[a]

Reaction conditions: 1 mmol substrate, 5 mmol (~17% wt) H_2O_2, 4 μmol $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$, 1 mL water, 75 °C, 7 h. Selectivity to ketones was ~100%; conversions were determined by GC.

[a] Products were 2-ethyl-3-oxo-1-hexanol, 95% and butanoic acid, 4%.

[b] 0.1 mL toluene added. The efficiency of H_2O_2 utilization was >75%.

Since peroxometal reaction pathways are typically observed for early transition metal compounds with a d^0 configuration,[18] one may assume that such a mechanism is also viable in this case. Preliminary support for such a mechanism was obtained from a kinetic isotope effect value, $k_H/k_D = 3.1$ for the oxidation of 2-octanol *versus* the oxidation of 2-octanol-d_2. Thus, one may hypothesize that the rate-determining step is hydrogen abstraction at the α-carbon position by the peroxotungstate intermediate. The high reaction selectivity, that is oxidation at a secondary position *versus* oxidation at a primary carbon, also tends to negate the probability of a hydroxy radical as active species, although a radical pathway, e.g., autooxidation may be operating in the aldehyde to carboxylic acid transformation as indicated by supression of carboxylic acid formation upon addition of TEMPO as a radical chain inhibitor. Thus, the addition of catalytic amounts of TEMPO (nitroxyl radical) to a reaction mixture, for example, in the oxidation of 1-pentanol {1 mmol pentanol, 0.02 mmol TEMPO, 5 mmol (~17% wt) H_2O_2, 4 μmol $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$, 1 mL water, 75 °C, 7 h} led to pentanal (63 mol %) as the major reaction product *versus* formation of pentanoic acid only (100 mol %) in the absence of TEMPO.

After our initial research on the oxidation of alcohols in the aqueous biphasic media, the scope of the catalytic method for oxidation of additional functional moieties was investigated. Thus, in Table 2 are presented results for the oxidation of vicinal diols that were also effectively and catalytically oxidized by $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$ with aqueous H_2O_2. Carbon-carbon bond cleavage products were obtained in high yields for most cases, that is the oxidation of 1-phenyl-1,2-ethanediol, *cis*-1,2-cyclooctanediol, *cis*-1,2-cyclopentanediol and 2-methoxycyclohexanol. *cis*- and *trans*-cyclohexanediol were oxidized with similar efficiency. For the more hydrophobic 1,2-octanediol, some 2-oxo-1-octanol was also formed. In fact it would appear that the α-hydroxy ketones are the initial oxidation products in these reactions. For example, oxidation of 1-phenyl-1,2-ethanediol at room temperature {1 mmol 1-phenyl-1,2-

ethanediol, 5 mmol (~17% wt) H_2O_2, 4 μmol $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$, 1 mL water, 22 °C, 7 h} yielded, 2-oxo-2-phenylethanol, benzaldehyde and benzoic acid in an approximately 1:3:3 ratio after 27% conversion.

Above, we have discussed the oxidation of alcohol moieties in aqueous biphasic media. In efforts to extend this methodology we attempted to oxidize simple reactive alkenes such as cyclohexene and cyclooctene. Unfortunately, they did not react. Since "sandwich" type polyoxometalates, e.g., $[WZnMn_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$,[9] are known catalysts for these epoxidations when dissolved in organic media, the lack of reactivity in the biphasic aqueous system was attributed to lack of miscibility at the interface. We, thus, turned to oxidation of additional polar functional moieties such as amines. Oxidation of aliphatic tertiary amines has been reported with hydrogen peroxide, but oxidation of aromatic tertiary amines, i.e., pyridine derivatives, usually requires use of peracids. For the latter, some catalytic systems are known using, for example, methylrhenium oxide[19] or perfluorinated ketones[20] as catalysts in organic media. Our results for the oxidation of pyridine derivatives in the aqueous biphasic reaction medium are summarized in Table 3. From the results, one may observe that in general electron-rich pyridine derivatives reacted to yield the expected *N*-oxides cleanly, whereas electron-deficient compounds like 2-chloropyridine and especially 2,6-dichloropyridene were hardly reactive.

The oxidation of primary amines with hydrogen peroxide is known to be catalyzed by soluble salts of tungstic and molybdic acid.[21] In this way the primary amine has been oxidized to the oxime, which can then be hydrolyzed under acidic conditions to the corresponding carbonyl compound. Indeed, in the aqueous biphasic oxidation of 1-octylamine a 70:30 mixture of octanoic acid:octanal at 100% conversion was formed (1 mmol 1-octylamine, 5 mmol (~17% wt) H_2O_2, 4 μmol $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$, 1 mL water, 75 °C, 7 h). Interestingly in the identical oxidation of benzylamine an approximately 50:50 mixture of benzaldehyde oxime and the Schiff base, $PhCH_2N{=}CHPh$, was formed. The latter product assumingly came from the condensation of benzylamine and benzaldehyde formed in the oxidation plus hydrolysis of benzylamine. Also notable is the observation that *t*-butylamine (2-amino-2-methylpropane) was oxidized quantitatively to the respective nitro derivative, 2-nitro-2-methylpropane.

The oxidation of aniline and its derivatives catalyzed by the $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$ in an aqueous biphasic reaction medium was also successful, see Table 4. Aniline, alkyl-substituted aniline and halogen-substituted aniline derivatives all yielded the dimeric azoxy compounds as major products at high conversions.

Table 2. Oxidation of vicinal alcohols catalyzed by $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$.

Substrate	Conversion, mol %	Product (selectivity, mol %)
cis-1,2-cyclopentanediol	>98	glutaric acid (~100)
1-phenyl-1,2-ethanediol	>98	benzoic acid (>95)
cis-1,2-cyclooctanediol	>98	suberic acid (>98)
cis-1,2-cyclohexanediol	>98	adipic acid (>95)
trans-1,2-cyclohexanediol	>98	adipic acid (>98)
2-methoxy-cyclohexanol	>98	methyl adipate (>95)
1,2-octanediol	67	2-oxo-1-octanol (33), heptanal (10), heptanoic acid (57)

Reaction conditions: 1 mmol substrate, 5 mmol (~17% wt) H_2O_2, 4 μmol $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$, 1 mL water, 75 °C, 7 h. The efficiency of H_2O_2 utilization was >85% except for 1,2-octanediol were it was 63%.

Table 3. Oxidation of pyridine derivatives catalyzed by $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$.

Substrate	Conversion, mol %	Product
pyridine	96	pyridine-1-oxide
2-picoline	~100	2-picoline-1-oxide
4-picoline	43	4-picoline-1-oxide
2,6-lutidine	~100	2,6 lutidine-1-oxide
quinoline	82	quinoline-1-oxide
8-hydroxyquinoline	94	8-hydroxyquinoline-1-oxide
2-chloropyridine	10	2-chloropyridine-1-oxide
2,6-dichloropyridine	0	—

Reaction conditions: 1 mmol substrate, 5 mmol (~17% wt) H_2O_2, 4 μmol $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$, 1 mL water, 75 °C, 7 h. Selectivity to the *N*-oxide was ~100%.

Table 4. Oxidation of aniline derivatives catalyzed by $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$.

Substrate	Conversion, mol %	Product (selectivity mol %)
aniline	95	diphenyldiazine 1-oxide (93)
2-ethylaniline	97	di-2-ethylphenyldiazine 1-oxide (85)
3-methylaniline	~100	di-3-methylphenyldiazine 1-oxide (100)
3-fluoroaniline	86	di-3-fluorophenyldiazine 1-oxide (85)
3-nitroaniline	66	1,3-dinitrobenzene (100)
4-ethoxyaniline	58	di-4-ethoxyphenyldiazine 1-oxide (76), 4-ethoxy-nitrobenzene (20)
4-hydroxyaniline	49	4-nitrophenol (100)
4-methoxy-2-nitroaniline	20	4-methoxy-2-nitrobenzene (100)

Reaction conditions: 1 mmol substrate, 5 mmol (~17% wt) H_2O_2, 4 µmol $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$, 1 mL water, 75 °C, 7 h.

On the other hand aniline with electron-donating substitution (ethoxy, hydroxy) or electron-withdrawing nitro substitution tended to yield the corresponding nitro derivatives at reduced conversions.

In any catalytic process, it is important to survey the potential for catalyst recycle. In this case recovery and reuse of the catalyst can be carried out by simple phase separation after the reaction and addition of more organic substrate. Here since water is a product of the reaction its accumulation in the system will need to be rectified by evaporation after several reaction cycles. An illustration of the effectiveness of the aqueous catalyst phase was carried out using 2-pentanol as model substrate. Thus reaction of 10 mmol 2-pentanol, 50 mmol H_2O_2, 40 µmol $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$, 10 mL water, 75 °C, 7 h followed by phase out separation of the organic phase and re-addition of 2-pentanol (10 mmol) and hydrogen peroxide (50 mmol) showed 95, 90, and 96% conversions over three reaction cycles with 2-pentanone as only product. There was no discernible loss in activity or selectivity.

Conclusion

An aqueous biphasic reaction system has been developed for the oxidation of alcohols, vicinal diols, and amines catalyzed by a stable, recoverable and recyclable, water-soluble polyoxometalate, $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$, and hydrogen peroxide as terminal oxidant. Primary and secondary alcohols were oxidized to carboxylic acid and ketones, respectively. Oxidation of vicinal diols yielded carbon-carbon bond cleavage products. Pyridine derivatives were oxidized to *N*-oxides and anilines were oxidized to azoxy derivatives or nitro compounds depending on the substitution pattern in the aromatic ring.

Experimental Section

The $Na_q[WZnM_2(H_2O)_2(ZnW_9O_{34})_2] \cdot x\,H_2O$ polyoxometalates were prepared according to the published literature procedure.[16] Reactions were carried out in 10-mL flasks using the amounts of compounds and conditions as described in the sections above. For example, in the oxidation of alcohols and diols, the substrate (1 mmol) was placed in the reaction flask and 0.6 mL of water was added followed by the addition of 0.1 mL of a 40 mM stock solution of $Na_q[WZnZn_2(H_2O)_2(Zn_9O_{34})_2] \cdot x\,H_2O$ and 0.3 mL of 60% aqueous H_2O_2. The flask was then emerged in a preheated oil bath and vigorously stirred with a magnetic stirrer. At the designated time the flask was cooled and the organic phase was analyzed by GLC after dilution with ~1 mL ethyl acetate. Reactions were quantified by GLC (HP 6890) using a 30 m 5% phenylmethyl silicone capillary column with an ID of 0.32 mm and 0.25 µm coating (Restek 5MS) and products were identified by GC-MS (HP 5973) with the same column and conditions. The ^{183}W NMR (16.671 MHz) spectra were measured on a Bruker Avance 400 spectrometer in D_2O with Na_2WO_4 in D_2O as external standard. The decomposition of hydrogen peroxide was measured by using a gas burette.

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