Equillbrating metal-oxide cluster ensembles for oxidation reactions using oxygen in water

Ira A. Weinstock*, Elena M.G. Barbuzzi†, Michael W. Wemple†, Jennifer J. Cowan†, Richard S. Reiner‡, Dan M. Sonnen‡, Robert A. Heintz‡, James S. Bond* & Craig L. Hill†

** Chemistry and Pulping Research Work Unit, USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin 53705, USA*
† Department of Chemistry, Emory University, Atlanta, Georgia 30322, USA
‡ Department of Chemical Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA

Although many enzymes can readily and selectively use oxygen in water-the most familiar and attractive of all oxidants and solvents, respectively–the design of synthetic catalysts for selective water-based oxidation processes utilizing molecular oxygen[1–4] remains a daunting task[5,6]. Particularly problematic is the fact that oxidation of substrates by O_2 involves radical chemistry, which is intrinsically non-selective and difficult to control. In addition, metallo-organic catalysts are inherently susceptible to degradation[5] by oxygen-based radicals, while their transition-metal-ion active sites often react with water to give insoluble, and thus inactive, oxides or hydroxides[7]. Furthermore, pH control is often required to avoid acid or base degradation of organic substrates or products. Unlike metallo-organic catalysts, polyoxometalate anions are oxidatively stable and are reversible oxidant[8,9] for use with O_2 (refs 8–10). Here we show how thermodynamically controlled self-assembly of an equilibrated ensemble of polyoxometalates, with the heteropolytungstate anion[11,12] $[AlV^{V}W_{11}O_{40}]^{6-}$ as its main component, imparts both stability in water and internal pH-management. Designed to operate at near-neutral pH, this system facilitates a two-step O_2-based process for the selective delignification of wood (lignocellulose) fibres. By directly monitoring the central Al atom, we show that equilibration reactions typical of polyoxometalate anions[13,14] keep the pH of the system near 7 during both process steps.

An effluent-free process using O_2 and H_2O would be an attractive alternative to ClO_2-based pulp bleaching[15], which is globally one of the largest industrial oxidation processes and generates considerable waste. To explore fundamental questions concerning the suitability of poloxometalate (POM) ions for delignification processes, we use $[AlV^{V}W_{11}O_{40}]^{6-}$ (**1** in Fig. 1), which can be spectroscopically monitored in solution.

Like many[8] POM ions, **1** is a reversible oxidant, capable of undergoing repeated cycles of reduction and re-oxidation[9]. The electrochemical potential for the one-electron reduction of **1** to $[AlV^{IV}W_{11}O_{40}]^{7-}$ (**2** in Fig. 1) at pH7 in water (0.480V versus the normal hydrogen electrode, NHE) lies below that of the O_2/H_2O couple (0.815 V versus NHE). Thus, whereas electron transfer from a variety of inorganic or organic substrates (such as lignin) to **1** can be highly selective (that is, the relative rates of these oxidation reactions span a wide range of values), electron transfer from 2 to O_2 (reoxidation of **2** to **1)** proceeds spontaneously[10]. These steps—anaerobic reduction of **1** by substrate and reoxidation of **2** by O_2—sum to electron transfer from substrate to O_2. Further, the reduction of O_2 by reduced heteropolytungstate anions ('heteropolyblues') such as **2** initially gives O_2^-, and subsequently and rapidly H_2O_2 (refs 10, 16, 17). By making use of the inevitable and highly reactive intermediates of radical-chain oxidation (for example, O_2^-, HO, their organic analogues and others)[18], the reoxidation of **2** by O_2 can be carried out under conditions (time, temperature and O_2 pressure) that oxidatively eliminate (mineralize) the inevitable by-products of substrate oxidation[19]. In the effluent-free process shown in Fig. 1, solutions of **1** selectively depolymerize lignin in wood fibres by direct oxidation (step 1, reduction of **1** to **2** by lignin; no O_2 present) and subsequently catalyse the O_2-oxidation of solubilized lignin fragments to their biosynthetic precursors CO_2 and H_2O (step 2).

Development of the equilibrated solutions is summarized in Fig. 2. In order to optimize and fully characterize all components of the desired equilibrated solution, isomerically pure samples of

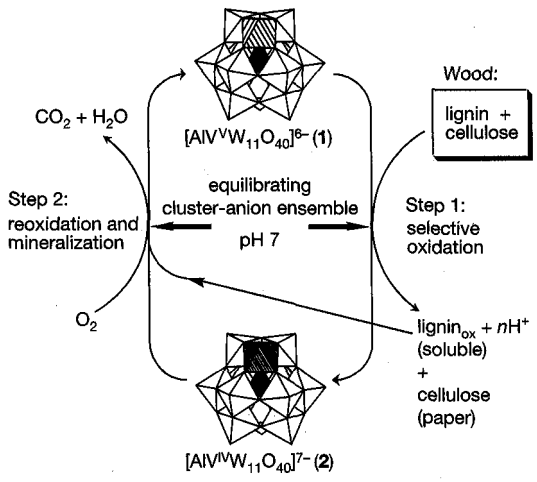


Figure 1 Proposed two-step process for conversion of lignin in wood to CO_2 and H_2O. (Wood is a composite of lignin and cellulose[15].) The structures of polyoxometalates (POMs) a -$[AlV_{V}W_{11}O_{40}]^{6-}$ and a -$[AlV_{IV}W_{11}O_{40}]^{7-}$ (a - **1** and a **-2**) are shown in polyhedral notation. The central, tetrahedrally coordinated Al atoms are shown in black. Step 1 (right) is the selective anaerobic oxidation of substrate (lignin) and reduction of POM **(1" 2).** Step 2 is the reoxidation of POM **(2" 1)** by O_2 with simultaneous POM-catalysed oxidation of the lignin fragments to CO_2 and H_2O (mineralization). Reversible acid-condensation reactions of cluster-anions (POM species) in equilibrium with **1** and **2** maintain the pH near neutral.

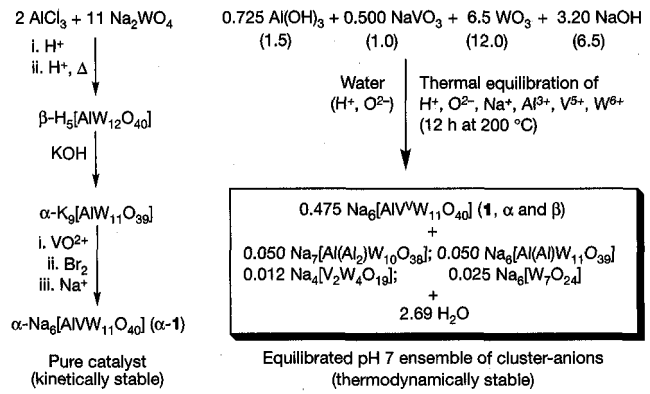
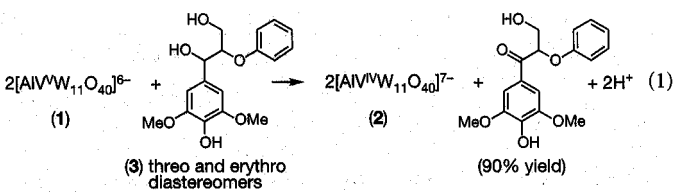


Figure 2 Stepwise synthesis of kinetically stable pure **1,** and equilibration to give a thermodynamically stable reaction medium. Three attributes of the reaction medium (right), pertinent to transition-metal-mediated transformations in water, follow: (1) it is uniquely stable with respect to precipitation of redox-active metal ions (all elements present, H, Na, Al, V, Wand O are in thermal equilibrium with one another), (2) it is stable to oxidative degradation (all main-group and transition-metal cations present, H^+, Na^+, $Al_{(III)}$ and the d^0 cations $V_{(V)}$ and $W_{(VI)}$, are in their highest accessible valence states), and (3) the cluster anions necessary for internal H^+ management are themselves integral components of the thermodynamically controlled (equilibrating) reaction medium. As such, self-buffering is an inherent and reversible property of the electron transfer and catalyst system as a whole, attributable to changes in the position of equilibrium of the entire molecular ensemble.

the target POM catalyst, in this case a -$Na_6[AlVW_{11}O_{40}]$ (a-Na_6 **1**[12]), as well as precursors'' and, closely related derivatives must first be isolated. This is accomplished using the method by which POMs have traditionally been prepared[11,12]—sequential, kinetically controlled steps of acid-condensation and base-hydrolysis (Fig. 2, left).

Next, **1** is prepared in one step using a thermodynamically c.ontrolled process: the thermal equilibration of component main-group and transition-metal oxides and hydroxides in water (Fig. 2, right). The final position of equilibrium, which dictates the pH and self-buffering properties of the medium, is controlled by adjusting the relative concentrations of the component precursors. Use of the molar concentrations shown as prefixes in Fig. 2 (stoichiometric ratios are in parentheses) gives a thermally equilibrated pH7 solution of **1** (90 ± 5% relative to $NaVO_3$; mixture of a and b isomers) as its major constituent. Final solution concentrations were determined to within 25% by ^{27}Al, ^{51}V and ^{183}W NMR spectroscopy[12,21]; data concerning $Na_7[Al(A1_2)W_{10}O_{38}]$ are available as Supplementary Information. The cluster anions in equilibrium with 1 are shown in the box at the bottom right in Fig. 2. Any H^+ or OH^- ions introduced during use (Fig. 1; that is, reversible reduction of **1** by substrate or subsequent reoxidation by O_2) are consumed, respectively, by reversible acid-condensation or base-hydrolysis reactions which are typical of these cluster-anions[22]. Analogous reactions have been quantified in fundamental studies of cation speciation and cluster-anion formation[13]. In the reaction system in Fig. 1, these physical properties are incorporated by design to provide inherent stability and internal H^+ management during Electron transfer[10] and catalysis. Thus, the position of equilibrium of the reaction medium changes in response to the addition of H^+ simultaneous with the addition of electrons (Fig. 1, step 1; electron transfer from substrate to **1**), and to the addition of "O^{2-} equivalents'' simultaneous with the removal of electrons (Fig. 1, step 2; electron transfer from **2** to O_2)[14].

In a typical laboratory-scale delignification reaction, unbleached softwood pulp from red pine and jack pine (5% lignin by weight) was heated in an equilibrated pH 7 solution of **1** (prepared as in Fig. 2; 0.01 g of pulp per ml of 0.475 M 1) at 130 °C for three hours under argon. During the reaction, 75% of the lignin[23] present in the unbleached pulp fibres is oxidatively depolymerized to water-soluble fragments, while ~15% of cluster **1** is reduced to **2.** The oxidation of lignin or other organic compounds in H_2O releases H^+ ions, as illustrated by equation (l), which shows the partial oxidation by **1** (12h at 22°C) of a dimeric model[24] **(3)** for polymeric lignin:



Although the reaction in equation (1) demonstrates the need for pH management, **3** is more readily oxidized, and thus represents a less stringent delignification test than the non-phenolic lignin models, such as veratryl alcohol derivatives, that are commonly used in pulp bleaching studies. Moreover, POM delignification requires cleavage of the lignin polymer, and by inference, of **3** as well. Room-temperature cleavage of **3** by the POM a-$Na_5[SiVW_{11}O_{40}]$, a close analogue of **1,** occurs via two sequential one-electron oxidation steps to give the- corresponding cyclohexadienyl cation, followed by hydrolysis to give monomeric 2,6-dimethoxy-*p*-benzoquinone and other products[24]. Reaction of **3** with **1** at higher temperatures gives mixtures of products, including 2,6-dimethoxy- *p*-benzoquinone.

As is evident from equation (1), the number of H^+ ions released during lignin oxidation and cleaveage in water correspond to the number of equivalents of **1** reduced to **2.** Thus, during dlignification of the unbleached fibres, 0.07 moles per litre of H^+—15% conversion of **1** (4.475 M) to **2**— are generated (equation (2a)). Meanwhile, the pH of the solution remains unchanged as H^+ ions are converted to water by reaction with the oxo ligands of cluster-anions present in the equilibrium mixture (equation (2b), a process quantified by ^{27}Al, ^{51}V and ^{183}W NMR spectroscopy):

$$4[AlV^{V}W_{11}O_{40}]^{6-}(\mathbf{1}) + 2\text{ligninH}_2 \rightarrow 4[AlV^{IV}W_{11}O_{40}]^{7-}(\mathbf{2}) + 2\text{lignin}_{ox} + 4H^+ \quad (2a)$$

$$4H^+ + [V_2W_4O_{19}]^{4-} + [Al(Al)W_{11}O_{39}]^{6-} + [W_7O_{24}]^{6-} \rightarrow 2[AlVW_{11}O_{40}]^{6-}(\mathbf{1}) + 2H_2O \quad (2b)$$

(Note that the target catalyst, **1,** is itself a product.) To ensure reversibility, precipitation of fully condensed tungsten oxide (that is, solid WO_3) must be prevented. This is accomplished by preferential co-condensation of W(VI) with Al(III) to give soluble tungstoaluminate cluster-anions[25] (for example, **1** in equation (2b)). Hence, at greater percentages of reduction, the more Al-rich anion, $Na_7[(Al)(A1_2)W_{10}O_{38}]$ (Fig. 2; effectively a reservoir for Al), reacts as well. If not for these acid-induced, POM self-assembly reactions, the pH of the solution would decrease to 1.15. At this low pH value, the b-D-glycosidic linkages between glucose units in cellulose would be readily cleaved and thus, the desired product would be degraded.

The use of **1** and other POMs ensures highly selective oxidation of lignin alone, whereas bleaching of wood pulp by O_2 has been considered not useful for delignification to low percentages of lignin[26], because it results in the oxidative degradation of cellulose fibres by non-selective radical-chain autoxidation reactions. Degradation of cellulose fibres is typically indicated by a decrease in pulp viscosity[23]—this viscosity is a nonlinear function of the average chain-length of the cellulose polymer. After reaction of unbleached fibres (initial viscosity 31 mPas) with **1** (0.01 g of pulp per ml of 0.475 M equilibrated **1** for 50 min at 145 °C) followed by filtering, washing, and mild extraction with dilute aqueous NaOH, 81% of the lignin is removed. The final viscosity is 22 mPa s. These values are comparable to those typically obtained industrially using chlorine compounds and far exceed those obtained using O_2 directly (final viscosities of less than 15 mPa s).

If systems such as **1** are to be used commercially, one issue that must be addressed is the need for near-quantitative recovery of cluster anions from delignified wood fibres, given that the cluster-anions mediate the delignification reactions stoichiometrically, rather than in a truly catalytic fashion. Keggin anions (close-packed structures) possess hydrodynamic radii in water of ~5.6Å (ref. 27), similar in size to typical lignin monomers (ring-methoxylated and side-chain hydroxylated phenylpropane derivatives) and small enough to diffuse freely between cellulose fibres within the wood-cell wall. In addition, due to the organic acids present on their surfaces, the polysaccharide polymers (cellulose and hemi-celluloses) present in wood fibres possess a net negative charge at near-neutral pH values. Hence, as a consequence of both size and charge, the POM clusters are easily washed from fibre samples at diffusion-controlled rates. In preliminary washing studies (see Supplementary Information), 0.12 p.p.m. V and 4.0 p.p.m. W were detected in fibres after washing and alkali extraction (a standard industry practice). These values are comparable to naturally occurring levels in the environment[28,29] and in selected foods[28,29].

After removing the delignified cellulose fibres, reoxidation of **2** to **1** by O_2 is carred out in a separate step (step 2 Fig. 1). The four-electron reduction of O_2 in H_2O results in the production of 4 equivalents of OH^- (effectively the reaction of the two "O^{2-}- equivalents" with 2 H_2O). Each equivalent of **2** reoxidized to **1** thus introduces a

like quantity of OH^-. In the absence of a mechanism for managing pH, reduction of O_2 by the pH-neutral 0.07 M solution of **2** (and the production of 0.07 M HO^-) would thus result in t an increase in pH to 12.8. This increase is prevented, however, by rapid base-hydrolysis of the cluster-anions formed during deligification. These hydroysis reactions, effectively the reaction of "O^{2-}-equivalents" from reduction of O_2 with previously condensed cluster-anions, return the system to its initial postition of equilibruim:

$$4[AlV^{IV}W_{11}O_{40}]^{7-}(\mathbf{2}) + O_2 \rightarrow 2[AlV^{V}W_{11}O_{40}]^{6-}(\mathbf{1}) + [V_2W_4O_{19}]^{4-} + [Al(Al)W_{11}O_{39}]^{6-} + [W_7O_{24}]^{6-} \quad (3)$$

Equations (2) and (3) sum to equation (4), the selective oxidation of lignin (ligninH$_2$) by O_2 to give water-soluble lignin fragments (lignin,) and H_2O:

$$2\ \text{ligninH}_2 + O_2 \rightarrow 2\ \text{lignin}_{ox} + 2H_2O \quad (4)$$

Moreover, when the reaction shown in equation (3) is carried out at 210°C for 3h under O_2 (2 MPa), **1** catalyses the conversion of solubilized lignin fragments (lignin, in equations (2a) and (4)) to CO_2 and H_2O (oxidative mineralization). The amount of CO_2 evolved (930 ± 40 mg CO_2 per 1) corresponds to the mass (lignin and some polysaccharides) earlier removed from the pulp fibres (see ref. 19 and work cited therein). These reactions (equations (2–4) and mineralization) define a process currently achieved only in nature: the complete and selective O_2-oxidation of lignin to CO_2 and H_2O.

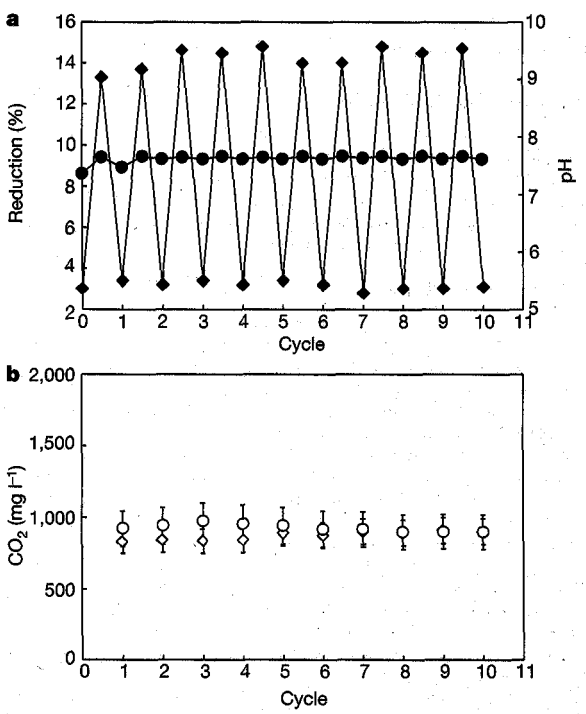


Figure 3 Oxidation of lignin in wood-pulp fibres to CO_2 and H_2O. Details are given in Methods. A single equilibrated solution of **1** prepared as shown in Fig. 2 was used in 10 successive two-step cycles of delignification (anaerobic oxidation by **1**) and subsequent O_2-reoxidation/lignin mineralization. In the first step of each cycle, unbleached pulp was heated in a solution of **1.** Lignin is oxidatively cleaved and solubilized by **1,** which is thereby reduced. The delignified cellulose fibers were then removed and O_2 was used (second step of each cycle) to reoxidize **2** to **1** and convert solubilized lignin fragments to CO_2 and H_2O. **a,** Percentage reduction of **1** to **2** (diamonds, left scale) and solution pH values (circles, right scale). Reversible acid-condensation (self-buffering) reactions keep the pH near neatrual thoughout all 10 cycles. **b,** Measured (circles) and theoretical (diamonds) values of CO_2 producted during the catalytic mineralization of sulubiliazed lignin fragments.

As a model for continuous operation, the equilibrate solution was used in nine additional cycles of delignification and reoxidation/mineralization (Fig. 3). Notably, the pH of the POM solution remained nearly constant throughout the ten cycles (Fig. 3a, right scale). The CO_2 produced in each mineralization step was comparable to the amount expected on the basis of the masses of lignin removed and yields of the delignified pulp samples (Fig. 3b; see Methods and Supplementary Information).

Four indices plotted in Fig. 3, all of which remained constant, provide evidence that the integrity of the catalyst system was retained throughout the multi-cycle experiment: (1) the amount of **1** reduced during delignification; (2) the pH of the solution; (3) the amount of **2** reoxidized by O_2; and (4) the amount of CO_2 produced. In addition, the amount of lignin removed in each cycle remained constant (75 ± 5%). More direct observation of the reversible behaviour and stability of the equilibrating system is provided by ^{27}Al, ^{51}V and ^{183}W NMR analysis of the solution before, during and after the ten-cycle experiment (^{27}Al and ^{51}V NMR spectra are shown in Fig. 4).

Although the spectroscopically accessible prototype system is

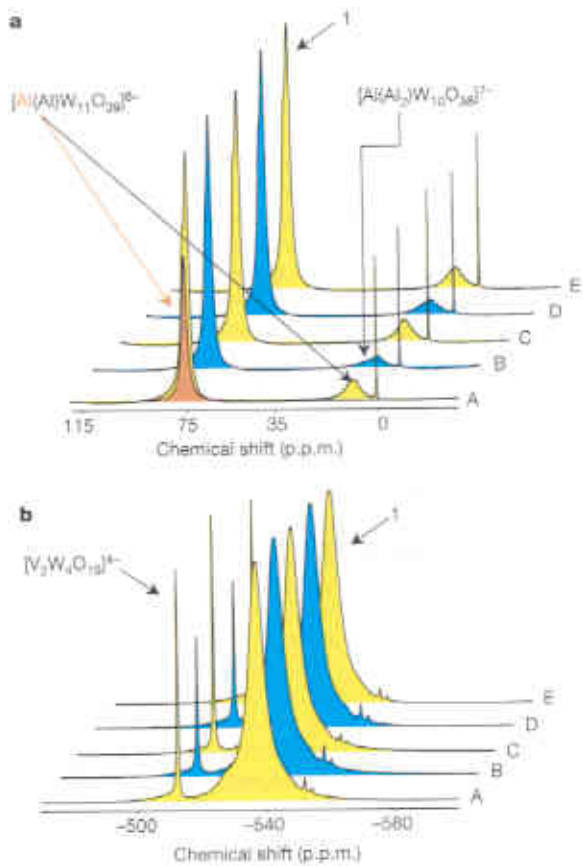


Figure 4 NMR analysis of the solution used in the 10-cycle experiment in Fig. 3. Samples were analysed by high-field ^{27}Al and ^{51}V NMR spectroscopy: **a,** ^{27}Al NMR spectra of the freshly prepared solution (spectrum A), after reduction by lignin in cycle 1 (reoxidized by Br_2 at room temperature) (B), after O_2-reoxidation/mineralization in cycle 1 (C), after reduction by lignin in cycle 10 (D) and after final O_2-reoxidation/mineralization in cycle 10 (E). **b,** ^{51}V NMR spectra of the freshly prepared solution (spectrum A), after reduction in cycle 1 (reoxidized by Br_2 at room temperature) (B), after reoxidation in cycle 1 (C), after reduction in cycle 10 (D) and after final reoxidation in cycle 10 (E). See Methods for assignments. Integration of ^{27}Al and ^{51}V NMR signal Intensities and spectral deconvolution (an example is shown in orange in ^{27}Al NMR spectrum A) were used to quantify the reactions in equations (2b) and (3). Signals due to cluster-anions present in freshly prepared or O_2-oxidized solutions are shown in yellow, while those due to cluster-anions in solutions reduced by lignin (subsequently reacted with Br_2 at room temperature) are shown in blue.

ideal for characterizing the chemical changes (Fig. 4 and equations 2 and 3) involved, any practically useful POM ensemble will need to be able to delignify more concentrated pulp mixtures (that is, 80–120 g pulp per 1) with greater efficiency (defined as lignin solubilized per mole of POM clusters; Fig. 1, step 1). Moreover, practical implementation will require milder operation conditions and faster turnover rates (T < 250°C and t < 1 h) in wet oxidation (Fig. 1, step 2), and near-quantitative yet efficient and economic POM recovery from teh treated pulp in industrial settings.

Systems developed further to meet some of these demanding criteria for practicality include a pH 5.5 equilibrating ensemble, designated "$Na_{6.9}SiV_{0.9}Mo_{1.0}W_{10.1}$" in which the dominant species are Keggin anions, structurally analogous to 1, formula $[SiVMoW_{10}O_{40}]^{5-}$ and/or $[SiVW_{11}O_{40}]^{5-}$ (see Methods and Supplementary Information). Unlike solutions of 1, the optimized systems are difficult to study by NMR because they include isostructural clusters containing both W(VI) and Mo(VI), a relatively NMR-insensivite Si(IV) heteroatom and, as below, paramagnetic Mn cations. The "$Na_{6.9}SiV_{0.9}Mo_{1.0}W_{10.1}$" system was used to delignify commercial fibre samples (20-litre reactions at 30 g pulp per 1) supplied by three paper manufacturers (key fibre properties indicative of high selectivity are available as Supplementary Information). Typically, pH values of the reaction medium increase during delignification from 5.5 to near 6 (addition of H^+, Fig. 1, step 1; 1.5 h at 140 °C), and decrease to their original values during reoxidation (addition of "O^{2-} equivalents").

More rapid rates of POM reoxidation by O_2 (Fig. 1, step 2; 0.5–1.0h, 210°C, 300 p.s.i. O_2), were achieved in model reduction–oxidation cycles upon partial replacement of W(VI) by 0.05 to 0.10 molar equivalents of Mn(III) (see Methods), which is known to catalyse wet-ocidation reactions[18]. Upon complete (~100%) reduction of a 0.5M solution by gaseous CO (4-8 eqiv. at 200°C reduction of all V(V) present to V(IV)), the pH increased from about 5.5 to 6.8 during the effective addition of ~0.5 M H^+. Reoxidation by O_2 (and the effective addition of 0.5 M OH^-) resulted in a decrease in pH to its initial value (5.5). These values are directly transferable to delignification systems and are a good indication of expected performance in actual practice. Although 100% reduction is difficult to achieve under laboratory conditions, similar results (reoxidation rates and self buffering) are observed. The superficially counter-intuitive pH changes, previously observed in reductions of labile molybdovanadophosphate systems[14,30], are due to changes in teh relative H^+-dependent thermodynamic stabilities of cluster anions upon reduction and reoxidation—reduced anions are typically stable at higher pH values[30].

Although industiral use of POM-based delignification systems will require further development, the data in Figs 2-4 show that the thermodynamically controlled self-assembly of inorganic oxides can yield complex, yet highly organized, supramolecular systems that behave as stable, pH-controlled and multi-functional (electron transfer and catalyst) aqueous reaction media. □

Methods

Multi-cycle experiment in Fig. 3

In the first step of each cycle, unbleached pulp (5% lignin by weight was stirred under argon in a 0.475 M solution of 1 (0.01 g pulp per ml; initially 2.5 g pulp (dry weight), in 250 ml solution) in a 1.0 -litre Parr high-pressure vessel and heated for three hours at 130°C. During each reaction, ~75% of the lignin was oxidatively cleaved and solubilized by 1, which was thereby reduced (Fig. 3a, % reduction of 1 to 2 (diamonds), left scale; determined by UV-visible spectroscopy, ε_{680} = 180 $cm^{-1}M^{-1}$, and solution pH values (circles), right scale). The delignified cellulose fibres were then removed and washed. To avoid irreproducible losses of volatile organic compounds, the small volumes of POM solution washed from the fibres were discarded rather than concentrated and returned—as practical operation would require–to the system. Removal of analytical samples also contributed to the total decrease in volume of the POM solution to 187 ml (reacted with 1.87 g unbleached pulp) at the begining of cycle 10. In the second step of each cycle, O_2 was used to reoxidize 2 to 1 (Fig. 3a, (diamonds), left scale) and to convert solubilized lignin fragments to CO_2 (Fig. 3b) and H_2O (see Supplementary Information). In each case, the reactor was fitted with a gas-entertainment impeller, sealed under 2 MPa O_2 (static pressure) and heated for 3 h at 210°C. Reversible cluster-anion equilibration (self-buffering) reactions keep the pH near neutral throughout all 10 cycles (Fig. 3a, (circles), right scale). Experimentally measured CO_2 values (Fig. 3b, circles) were determinded by reaction of head gases with aqueous $Ba(OH)_2$; associated uncetainties are minimum values based on titrations of $Ba(OH)_2$ solutions. Theoretical values (Fig. 3b; diamonds) were calculated by mass balance from decreased in lignin content and final pulp yelds; associated uncertainties were estimated from the variation observed in replicate measurments of identical fibre samples. For lignin, calculations were based on the molecular weight of repeating b-O-4 linked coniferyl alcohol subunits[15] ($(C_{10}H_{12}O_4)_n$ + 11 O_2 " 10 CO_2 + 6 H_2O). CO_2 from any additonal deceases in pulp mass was estimated using repeating glucose subunits, $(C_6H_{10}O_5)_n$, to represent cell wall polysccharides.

NMR data in Fig. 4

Samples of the solution used in the 10-cycle experiment in Fig. 3 were analysed by high-field[27] and [51] V NMR spectroscopy (paramagntic species were oxidized by Br_2). All [27]Al NMR spectra are externally referenced to 0.1 M aqueous $AlCl_3$ ($[Al(H_2O)_6]^{3+}$, d = 0 p.p.m.). The signals at 70–80 p.p.m. arise from tetrahedrally coordinated Al atoms located at the centre of the identified cluster-anions[12]; signals at 8–15 p.p.m. arise from octahedrally coordinated Al atoms. Intergration and spectral deconvolution (an example is shown in red in Fig. 4a spectrum A) was used to quantify reversible changes in the position of equilibrium upon successive addions of H^+ (delignigication, equation (2)) and of "O^{2-}-equivdents" (O_2-reoxidation, equation (3)). All [51]V NMR spectra are referenced to pure $VOCl_3$. Consumption and re-formation of $[V_2W_4O_{19}]^{4-}$ (equations (2b) and (3)) is shown by changes in intensity of the sharp signal at -511 p.p.m. The large linewidth of the signal at -535 p.p.m. (from 51in 1) is due to quadrupolar broadening 27 Al (I - 5/2)21 and to the presence of an equilibrium mixture of a- and b-keggin structural isomoers[12].

Preparation of "Na6.9SiV0.9MoW10.1"

To a Parr reactor containing ~9.90 litre water was added 1.0 equiv. (993.1 g) Na2SiO3 (anhydrous, 92.2%), 4.9 equiv. (1,500.0 g) NaOH (98%), 0.45 equiv. (618.8 g) V_2O_5 (99.2), 1.0 equiv. (1,090.5 g) MoO_3 (99%) and 10.1 equiv. (17,583.7 g) WO_3 (99.88%). The reactor vessel was sealed and heated to 200 °C for 3 hours under 100 p.s.i. (cold) of O_2 with continuous rapid stirring (about 500 r.p.m.). Before use in delignification, the solution was treated with ozone in a glass vessel and concentrated to about 0.6 M (density 2.422). When combined with pulp for use in delignification, water in the pulp fibres contributes to give a final concentration of 0.5 M relative to Si(IV).

Preperation of "$Na_{6.5}SiV_{0.9}Mn_{0.1}MoW_{10}$"

To a Parr reactor containing ~188ml water was added 1.0 equiv. Na_2SiO_3, 4.5 equiv. NaOH, 0.45 equiv. V_2O_5, 1.0 equiv. MoO_3, 10.0 equiv. WO_3 and 0.1 eqiv. MnO_2 (during synthesis, Mn(IV) is reduced, most probably by water, to Mn(III)). Oxygen (200–250p.s.i.) was added and the mixture stirred (1,000 r.p.m.) while heated to 200°C for 5 h, then cooled, vented, opened and the solution filtered. Solutions possess densities of about 2.2 g ml^{-1} and have pH values in the range 5-6.

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Correspondence and requests for materials should be addressed to I A W (e-mail: iaweinst@facstaff.wisc.edu) or C.L.H (e-mail: chill@emory.edu)

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As the result of a thorough Forest Service review, Forest Products Laboratory Director Chris Risbrudt has determined that Dr. Rajai Atalla, originally acknowledged within this article for his work on polyoxometalate (POM), should have been listed as an author. The article goes beyond the new thermally stable POM chemistry and includes the broader POM evolution implications and practical applications for which Dr. Atalla rightly deserves recognition.