Chapter 7

An Environmentally Benign Catalytic Polyoxometalate Technology for Transforming Wood Pulp into Paper

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An environmentally benign technology, based on a solution of equilibrated polyoxometalate (POM) salts and oxygen, is being developed to bleach wood pulps for use in the manufacture of paper. Unlike conventional chlorine-based technologies, this biomimetic chemistry uses only oxygen and water and produces no liquid waste. This research constitutes a new general approach to the design of soluble transition metal catalysts for aerobic oxidation in water. The POM-based catalyst is thermodynamically stable under the operating conditions and is the first catalyst designed to act as *its own buffer*.

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Introduction

Wood is composed of structural polysaccharides (primarily cellulose) and cross-linked methoxylated phenyl propane polymers (lignin). Cellulose is the most abundant constituent of the cell wall and is the key component of the natural fiber from which paper is made. It imparts strength to trees and papers. Natural and industrial processes alike focus on the removal of lignin, which is the primary encrusting cell wall matter in higher plants, with minimal damage to cellulose (high-quality paper is composed of lignin-free cellulose fibers).

Delignification of wood (*1*) is a remarkably complex process (2). At the same time, it is one of the largest-scale chemical transformations in nature and in industry. The most desirable bleaching conditions involve removal of lignin with little or no damage to the cellulose and other polysaccharides. A number of factors make delignification very difficult: the intrinsically complex organic structure of lignin, the presence in the wood cell wall structure of covalent linkages between lignin and polysaccharide, and the complex morphology of the cell wall with its physical and structural integration of lignin- and polysaccharide-rich structural domains on molecular to macroscopic scales. Biological delignification (via fungi) can be highly selective (*3–5*) and is environmentally friendly. Lignin-degrading fungi secrete metalloenzymes, which oxidatively cleave the lignin polymer to water-soluble fragments via single-electron transfer steps. These extracellular enzymes include Cu-containing oxidases (laccases) (*6*) and heme-containing peroxidases (lignin and Mn peroxidases) (*7, 8*). Once the lignin polymer is broken down into water-soluble fragments, additional enzymes convert these fragments to CO_2 and H_2O (*9*).

This chapter discloses the first technology that selectively delignifies pulp fibers in water using only O_2 (*10*) and produces no liquid waste or toxic byproducts (Scheme 1) (*11–15*). This technology involves the use of a multi-component, transition metal oxygen-anion cluster (polyoxometalate, or POM), $Na_6[AlVW_{11}O_{40}]$ (henceforth **1**).

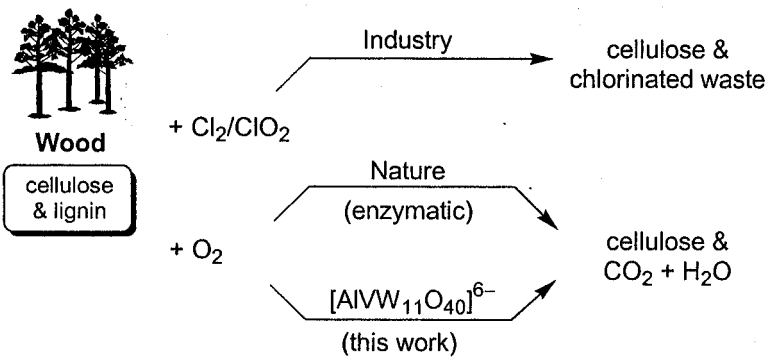
Polyoxometalates

POMs are an important and rapidly growing class of inorganic cluster compounds (16). The most common and most investigated class of POMs are the Keggin compounds. The Keggin structure is comprised of MO_6 octahedra linked together by one or two bridging oxygen atoms. The complex, **1**, is formed by substituting one of the d^0 W(VI) ions that makes up the inorganic skeleton of a parent Keggin compound, $Na_5[AlW_{12}O_{40}]$, by a d^0 V(V) ion.

While POMs range in size from 0.9 nm to over 5 nm, the Keggin structure has a diameter of about 1.1 nm, one similar to that of typical phenyl propane units in lignin.

POMs are attractive for use in the bleaching process for several reasons. First, they are easily prepared in a single step in H_2O from inexpensive, minimally toxic, readily accessible precursors such as WO_3 and $NaVO_3$. Second, their physical properties, including redox potentials, acidities, charges, and solubilities, can be controlled by the choice of precursors and synthetic conditions. Third, POMs are resistant to oxidation (only d^0 metal ions are present), yet they can be reversibly reduced by lignin and a host of other organic substrates (*17*). Finally, one or more of the d^0 metal ions (W(VI) ions in the case of 1) can be replaced by other d^0 or d-electron containing transition-metal ions.

As a result, the appropriately optimized POMs can selectively remove electrons from organic substrates such as lignin and facilitate their transfer to O_2. As such, the POM in our technology performs the same function as does the ensemble of extracellular enzymes in wood-rotting fungi (Scheme 1).

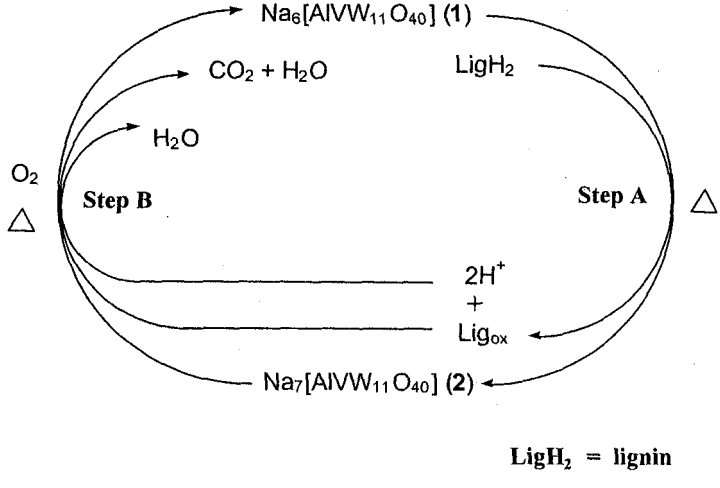


Scheme 1

POM Bleaching

Pulp bleaching by POMs is a two-step technology that is being developed at the Forest Products Laboratory of the U.S. Department of Agriculture and the Department of Chemistry at Emory University. The selective removal and mineralization of lignin by a solution of 1 and O_2 is accomplished in two steps that sum to the selective transfer of electrons from lignin to O_2 (Scheme 2).

In the first step (step A, Scheme 2), a slurry of unbleached pulp fiber is heated anaerobically in an aqueous solution of the fully oxidized catalyst, 1. Electron transfer from lignin converts 1 to its reduced form, $Na_7[AlVW_{11}O_{40}]$ (2). As in nature (degradation by fungal enzymes), the lignin is cleaved by single-electron transfer and subsequent hydrolysis reactions. Prior to step B, the high quality (high viscosity, etc.) delignified fiber is collected. In step B, 2 is reoxidized to 1 by O_2, and the combined reaction of **1, 2,** and dioxygen results in the complete oxidative mineralization of the dissolved lignin fragments to CO_2 and H_2O (*18*). As in all organic oxidation reactions in H_2O, protons are generated during substrate oxidation (step A). During the reduction of 0, to water, these protons are consumed such that over a complete cycle (steps A and B), the concentration of H^+ in the system remains unchanged.



Scheme 2

However, to avoid acid-catalyzed hydrolysis of the a -D-glucopyranoside linkages in cellulose during delignification, a pH buffer is needed in step A. In previous work we demonstrated that $[SiV^{V}W_{11}O_{40}]^{5-}$ is effective in step A, but it is rapidly degraded by the phosphate buffer needed to maintain the pH of the solution near neutral (*14*). Moreover, the reoxidation of $[SiV^{IV}W_{11}O_{40}]^{6-}$ by dioxygen (step B) is very slow, precluding effective catalytic turnover (steps A + B). We also evaluated the POM $[PV_2Mo_{10}O_{40}]^{5-}$ in early studies because the reduced form was known to be reoxidized quickly by reaction with 0,.

Unfortunately, this POM is stable only at the acidic pH values at which cellulose hydrolysis occurs, and thus the pulp does not survive step A (*14*). The catalyst reported here is an equilibrium mixture of POM clusters in which 1 is the major product. It is capable of sustained activity at near-neutral pH values in both the steps A and B. The ability of POM to maintain such pH values in the absence of an exogenous buffer involves acid-base reactions associated with the self-assembly synthesis of the POM itself. We refer to this unprecedented ability of a redox reagent to maintain the pH of its own redox reactions as 'self-buffering'. The equilibrated POM-based catalyst system in this chapter is not the most efficient system for the bleaching process; other POMs (mixed Mo and W systems) provide better results. We have focused on equilibrated solutions of 1 because they afford three effective complementary spectroscopic handles for detailed and quantitative analysis of the chemistry: ^{27}Al, ^{51}V and ^{183}W NMR (*19*).

This system based on the POM I exhibits most of the features of an ideal environmentally benign oxidation catalyst: (1) O_2 is the only oxidant used; (2) water is the only solvent required; (3) the catalyst, 1, possesses no organic ligands or components and is consequently thermodynamically stable toward oxidative degradation; (4) a single molecule, 1, facilitates the repeated operation of multiple functions: delignification (bleaching) and catalytic wet oxidation of the dissolved lignin fragments (aerobic mineralization); (5) the catalytically active species, 1, is in equilibrium with its synthetic precursors under operation conditions (a rare situation in catalysis); should it be degraded during turnover, its optimal form is spontaneously reconstituted; and (6) the catalyst system (1, its precursor, and other species present at equilibrium) functions as its own pH buffer (i.e., the system is self-buffering).

Experimental Approach

General

All materials used were reagent grade. The pulp was an unbleached mixed-pine kraft pulp with a kappa number of 32.4 and a viscosity of 3 1.1 mPa•s. The bleaching and wet oxidation reactions were performed in a 300-mL Parr 4843 Reactor. The UV-vis spectra were acquired using a Hewlett-Packard 8452A spectrophotometer. All pH measurements were made using an Orion model 250A pH meter.

Acquisition of ^{27}Al ^{51}V ^{183}W NMR Spectra

The spectra were obtained using a Varian UNITY 400 NMR at 16.66 MHz. External references were, for ^{27}Al, 0.10 M $AlCl_3$•$6H_2O$ ($[A1(H_2O)_6]^{3+}$ d = 0 ppm), for ^{51}V, 10 mM $H_4[PVMo_{11}O_{40}]$ in 0.60 M NaCl (d = -533.6 ppm), and for ^{183}W, 0.2 M Na_2WO_4•$2H_2O$ (WO_4^{2-}(aq), d = 0 ppm).

Results and Discussion

It is possible to obtain an isomerically pure sample of **1** by the standard method of POM synthesis: sequential kinetically controlled acid condensation and/or base-hydrolysis steps. Importantly, it is also possible to obtain equilibrium solutions of **1** by preparing the catalyst at the concentration and temperature at which it is designed to operate. The rationale behind this approach is that a catalyst system prepared in this manner should be thermodynamically stable under turnover conditions. Eq. 1 gives the stoichiometry for the equilibrium self-assembly synthesis of **1** from simple metal oxide precursors. This reaction is carried out in a single hydrothermal step in which the synthetic precursors are heated at 200 °C for 12 hours in water.

$$Al(OH)_3 + NaVO_3 + 11\ WO_3 + 5\ NaOH \rightarrow Na_6[A1VW_{11}O_{40}] + 4\ H_2O \qquad (1)$$

Use of the stoichiometry in eq. 1 provides an equilibrated solution that contains **1** as the major product (95% relative to the total vanadium present (0.25M V(V))), along with a small concentration $Na_5[AlW_{12}O_{40}]$ (mixture of a and b isomers, 5% relative to the total aluminum present (0.25 M Al(III))), $Na_5[V_3W_3O_{19}]$ and $Na_4[V_2W_4O_{19}]$ (both 1% relative to the total vanadium present). The pH resulting from the stoichiometry in eq. 1 is 3.9, a pH too low for use in delignification. To increase the pH and to optimize the self-buffering properties, the concentration of each component was varied systematically. The optimized stoichiometry, given in eq. 2, was achieved by increasing the relative ratio of $Al(OH)_3$, WO_3, and NaOH.

$$0.725\ Al(OH)_3 + 0.500\ NaVO_3 + 6.50\ WO_3 + 3.20\ NaOH \rightarrow$$
$$0.475\ Na_6[AlVW_{11}O_{40}]\ (\mathbf{1}) + 0.012\ Na_4[V_2W_4O_{19}] + 0.050\ Na_6[Al_2W_{11}O_{40}] +$$
$$0.050\ Na_7[Al_3W_{10}O_{38}] + 0.025\ Na_6[W_7O_{24}] + 2.69\ H_2O \qquad (2)$$

A key to this chemistry is the aluminum concentration in solution. The aluminum concentration must be sufficient to avoid precipitation of the tungsten

species and simultaneously must be adequate to facilitate the formation of species important in the self-buffering process. The amount of tungsten was also optimized to achieve the highest concentration of catalyst **1.** Additional POM species in solution were quantified by ^{27}Al and ^{51}V NMR (see Figures 1 and 2).

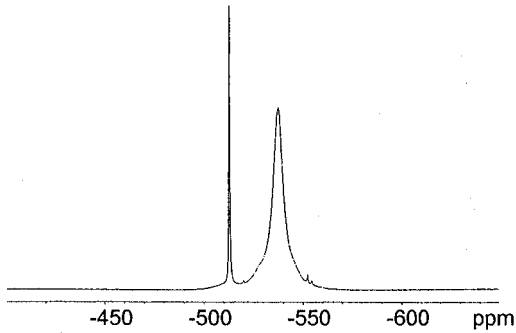


*Figure 1. ^{51}VNMR spectrum of **1** prepared by hydrothermal synthesis. The minor peak at -511 ppm is $Na_4[V_2W_4O_{19}]$, and the major peak at -536 ppm is $Na_6[AlVW_{11}O_{40}]$.*

When softwood kraft pulp (kappa number of 32.4 and a viscosity of 31.1 mPa•s) is heated as a slurry in an equilibrated 0.5 M solution of **1** at 130 °C for 130 min under anaerobic conditions (argon atmosphere) to eliminate non-selective autoxidation, 78% of the residual lignin in the unbleached pulp fibers is oxidatively depolymerized to water soluble fragments, while about 15% of the **1** in solution is reduced to **2.** The decrease in the lignin component of the pulp fibers was assessed by kappa number, and the damage to cellulose was assessed by viscosity. After minimum optimization, the low kappa number pulps (kappa numbers of 6) obtained possessed final viscosities of 23 mPa•s. These values are comparable to those typically obtained industrially using chlorine compounds and far exceed those possible using O_2 (final viscosities of less than 15 mPa•s).

This new catalyst system is designed for continuous circulation of the POM solution. Before the POM is used in a new bleaching step, however, **2** is reoxidized to **1** by O_2 under conditions that result in complete mineralization of dissolved lignin fragments to CO_2 and H_2O (see Scheme 2). The POM solution used in the delignification experiment described above was reoxidized by heating at 210 °C for three hours under O_2 (2 MPa). As a model for continuous operation, this same POM solution was used to perform seven additional

bleaching-mineralization cycles with fresh samples of unbleached pulp used in each bleaching step. The results are summarized in Figures 3 and 4, The CO_2 produced was measured during each of the eight cycles and compared with the amount expected based on the masses of lignin removed and the yields of delignified pulp samples (Figure 3). It is noted that during each bleaching step, the pH of the POM solution remained nearly constant throughout the eight cycles.

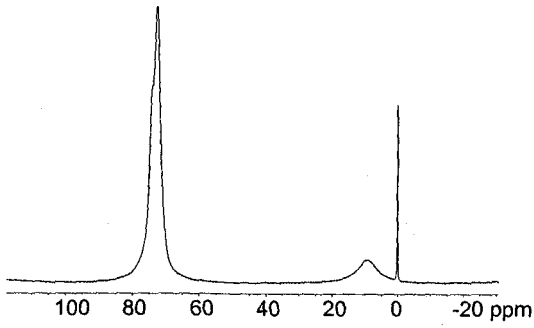


*Figure 2. ^{27}Al NMR spectrum of **1** prepared by hydrothermal synthesis. The peak at 0 ppm is $AlCl_3$ (external standard), the peaks at 8.5 ppm and 73.5 ppm are $Na_6[Al_2W_{11}O_{39}]$, and the one at 73.2 ppm is $Na_6[AlVW_{11}O_{40}]$.*

If left unbuffered, the pH would have dropped to about 1.2 during each bleaching reaction (the theoretical drop of the pH is simply based on the percentage reduction of the POM solution). It was independently determined that each molecule of 1 was reduced by one electron to form 2, and 2 only, with the simultaneous generation of one equivalent of H^+.

The consumption of H^+ ions introduced during oxidation of lignin by 1 in step A and of OH- anions formed upon reduction of 0, by 2 in step B is due to the reversible reaction of metalate species summarized in eq. 3. $Na_4[V_2W_4O_{19}]$, $Na_6[Al_2W_{11}O_{39}]$ and $Na_6[AlVW_{11}O_{40}]$ (**1**) were quantified using ^{51}V and ^{27}Al NMR (Figures 5 and 6).

$$4\,H^+ + Na_4[V_2W_4O_{19}] + Na_6[Al(Al)W_{11}O_{39}] + Na_6[W_7O_{24}] \Leftrightarrow$$
$$2\,Na_6[AlVW_{11}O_{40}]\ (\mathbf{1}) + 2\,H_2O + 4Na^+ \qquad (3)$$

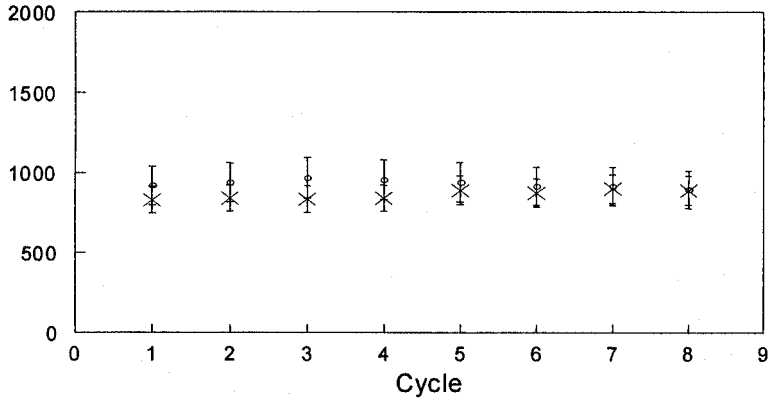


Figure 3. Quantification of the CO_2 produced by aerobic mineralization of dissolved lignin fragments during reoxidation of 2 to 1 in 8 delignification/ reoxidation cycles. The theoretical CO_2 values were calculated for each point from a combination of pulp yields and decreases in lignin content. Experimental $[CO_2]$ values were determined by reaction of head gases with solutions of $Ba(OH)_2$.

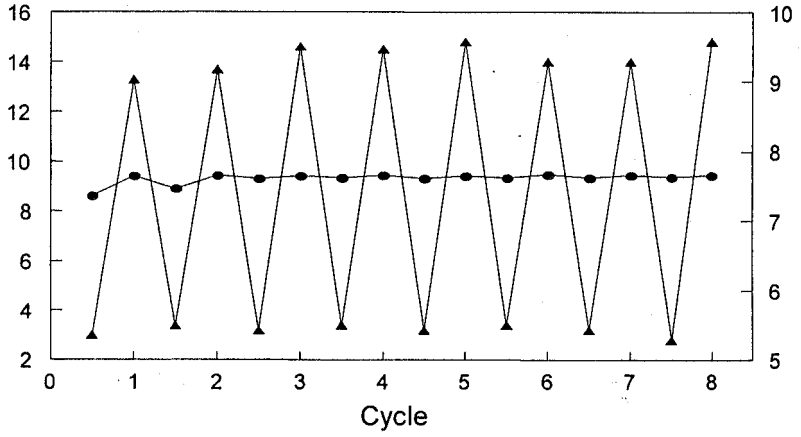


*Figure 4. A single 0.5 M solution of $Na_6[AlVW_{11}O_{40}]$ (**1**) used repeatedly in successive delignification and O_2-reoxidation (8 complete cycles). These two steps (delignification plus reoxidation) constitute one complete cycle shown on the abscissa. Concentrations of $Na_7[AlVW_{11}O_{40}]$ (**2**) and pH were determined after each step from UV-visible spectroscopy (ε(680nm) = 180 $cm^{-1}M^{-1}$) (left scale percent reduction = p ; right scale, pH = l).*

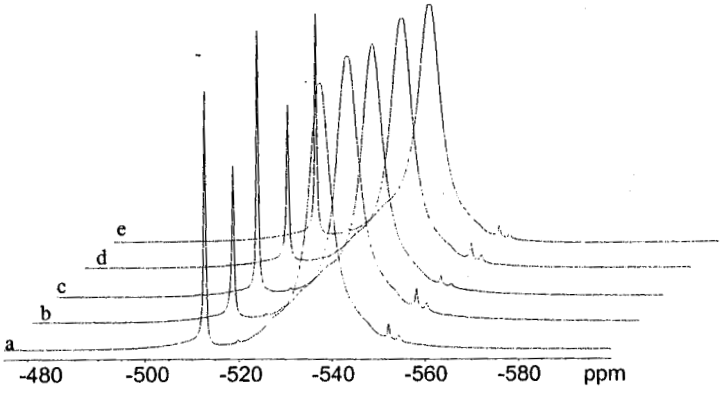


Figure 5. ^{51}*VNMR of (a) a solution offreshly prepared* ***1,*** *(b) the solution after reduction by lignin in cycle 1, (c) after reoxidation by* O_2 *in cycle 1, (d) after the final delignification step (cycle 8), (e) afterfinal reoxidation (cycle 8).*

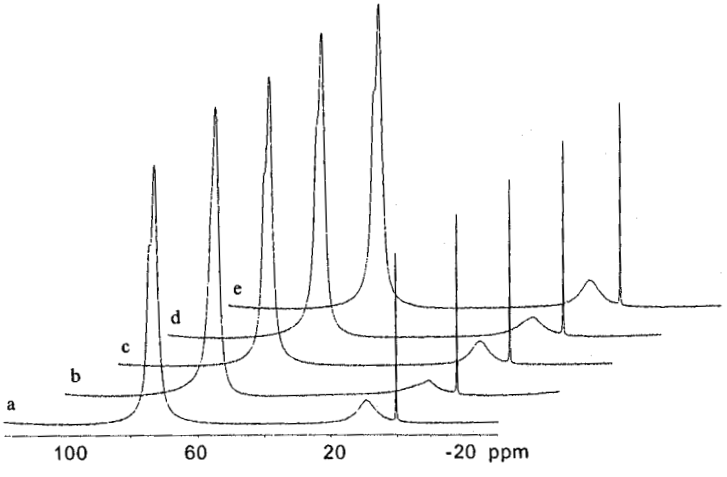


Figure 6. ^{27}*Al NMR of (a) a solution offreshly prepared* ***1,*** *(b) the solution after reduction by lignin in cycle 1, (c) after reoxidation by* O_2 *in cycle 1, (d) after thefinal delignification step (cycle 8), (e) after final reoxidation (cycle 8).*

Eq. 3 explains most of the chemistry responsible for the self-buffering. However, complete delineation of this complicated chemistry (quantitation of all POM species present including those in trace amounts) is extraordinarily difficult. The POM speciation responsible for self-buffering is satisfactorily modeled by reduction of a 0.5 M solution of **1** by CO. Use of CO, unlike heterogeneous reactions with pulp, results in a 100% reduction of **1.** Thus study with CO oxidation facilitated the quantification of the POM species responsible for this internal pH management chemistry. In the absence of self-buffering, the pH at 100% of reduction would have been 0.3. During reduction of a 0.5 M solution of **1** by CO, the pH remains near neutral (40% reduction) and then gradually decreases to pH 6 at 50%, 5 at 70% and 4 at 100%. Clearly this POM system has considerable self-buffering ability. The products from reduction of **1** by CO (200 °C and 5 hours) are CO_2 and H_2O, just as when lignin was used as the substrate.

After a careful analysis of the completely reduced and oxidized solution by ^{27}Al, ^{51}V and ^{183}W NMR (see representative experiments in Figures 7 and 8), we were able to better understand and rationalize the self-buffering properties. $Na_4[V_2W_4O_{19}]$ is a limiting reagent in eq. 3. During complete reduction of **1,** it disappears by reaction with $Na_6[Al_2W_{11}O_{39}]$. The remaining $Na_6[Al_2W_{11}O_{39}]$ is consumed by reaction with paratungstate (eq. 4).

$$Na_6[Al_2W_{11}O_{39}] + (^1/_7)Na_6[W_7O_{24}] + (^{34}/_7)H^+ \Leftrightarrow$$
$$Na_5[AlW_{12}O_{40}] + Al^{3+} + (^{13}/_7)Na^+ + (^{17}/_7)H_2O \qquad (4)$$

Eq. 4 by itself accounts for ~50% of the H^+ consumed by the POM system. After complete reduction, the concentration of $Na_7[Al_3W_{11}O_{38}]$ changes slightly. It was possible to rationalize this behavior via eqs. 5 through 8:

$$Na_7[Al_3W_{10}O_{38}] + Na^+ \Leftrightarrow Na_{10}[Al_2W_{10}O_{38}] + Al^{3+} \qquad (5)$$

$$7\ Na_{10}[Al_2W_{10}O_{38}] + Na_6[W_7O_{24}] + 34H^+ \Leftrightarrow$$
$$7\ Na_9[Al_2W_{11}O_{39}] + 7\ Al^{3+} + 15\ Na^+ + 17\ H_2O \qquad (6)$$

$$Na_9[Al_2W_{11}O_{39}] + (^1/_7)Na_6[W_6O_{24}] + (^{34}/_7)H^+ \Leftrightarrow$$
$$Na_5[AlW_{12}O_{40}] + (^{34}/_7)Na^+ + (^{17}/_7)H_2O \qquad (7)$$

$$Al^{3+} + (^{12}/_7)Na_6[W_7O_{24}] + (^{16}/_7)H^+ \Leftrightarrow Na_5[AlW_{12}O_{40}] + (^{37}/_7)Na^+ + (^8/_7)H_2O \qquad (8)$$

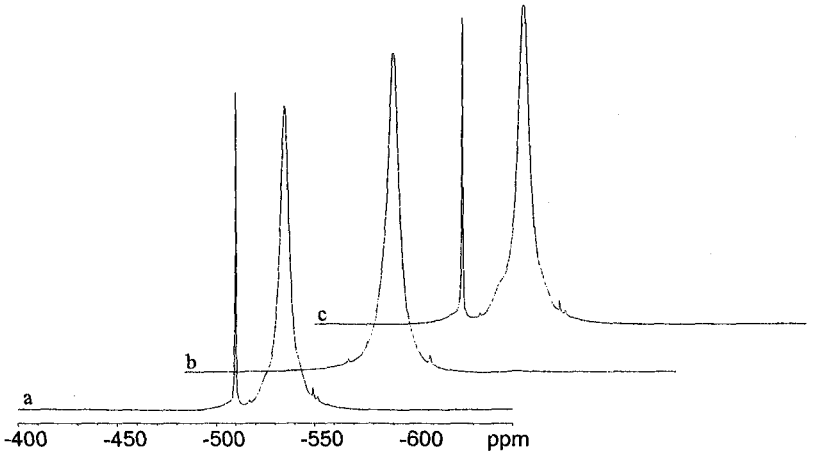


Figure 7. ^{51}*V NMR of (a) a solution of freshly prepared* ***1****, (b) the solution after complete reduction by CO, and (c) the solution after the complete subsequent reoxidation.*

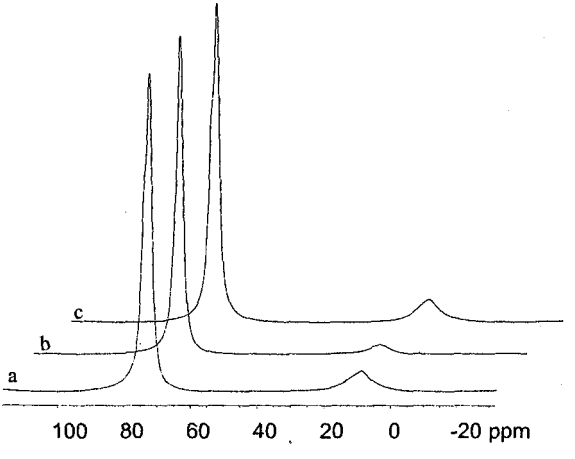


Figure 8. ^{27}*Al NMR of (a) a solution of freshly prepared* ***1****, (b) the solution after complete reduction by CO, and (c) the solution after the complete subsequent reoxidation.*

Conclusions

An environmentally friendly and economically attractive technology, using POMs, for the conversion of wood pulp into paper has been described. Unlike the current chemistry that uses corrosive chlorine compounds and generates considerable toxic chlorinated organic waste, this chemistry produces no liquid waste or toxic effluent.

The approach used is unique: an equilibrated solution of POMs, simply using oxygen as the oxidant and water as the solvent, is able to facilitate the selective delignification of wood pulp, generating only H_2O and CO_2 as by products.

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