POLYOXOMETALATE (POM) CATALYST SYSTEMS: CHEMICAL PRINCIPLES AND REACTIONS WITH LIGNIN AND OXYGEN.

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ABSTRACT. Chemical data pertinent to most-recently developed POM delignification systems will be presented. These data will be used to demonstrate the fundamental basis for the stability, self-buffering properties, versatility and high selectivity of these systems when used in combination with oxygen to convert native or residual lignin in wood or wood-pulp fibers to CO_2 and H_2O.

OVERVIEW. The potential use of polyoxometalates (POMs) as water-soluble yet oxidatively stable analogs of lignin-degrading enzymes in the chlorine-free production of high-quality delignified wood products was first described at the 2nd EWLP in 1992 (Grenoble, France).[1] A more thorough elaboration, including demonstration data, was presented at the 3rd EWLP (Stockholm, 1994).[2] Presentations in subsequent Workshops (4th and 5th EWLPs) concerned further developments and highlighted the potential of POMs for use in achieving mill closure and for replacing sulfur (new pulping processes)[3,4] During this time, numerous obstacles[5] were overcome by continued fundamenta1[6-10] and applied research.[11-12] As a result of these efforts, new POM systems suitable for use in pilot-scale (10 tons/day) demonstration and testing are now available.

SELECTIVE CATALYSIS OF O_2 OXIDATIONS IN WATER. Steady progress towards this goal has required considerable effort. The most attractive scenario for environmentally benign oxidations of lignin and other substrates involves selective and stable catalysis in water using only O_2. Indeed, the selective use of O_2 in water–the most familiar and attractive of all oxidants and solvents–is a mainstay of biochemistry. However, the design of synthetic catalysts for selective use of O_2 in water is fraught with inherent problems.[13] First, the chemistry of O_2 is intrinsically non-selective and very difficult to control. Typically organic compounds and O_2 either do not react at an appreciable rate or react via minimally selective and controllable radical-chain reactions (autoxidation, combustion, etc.). Such reactions severely limit the usefulness of O_2 when applied directly to wood fibers. Catalysis of selective O_2 oxidations that do not proceed by autoxidation is so rare and potentially significant that each case has garnered considerable interest and scrutiny.[14-16] In addition, virtually all metal-based catalysts are hydrolytically unstable in water. The reason for this instability is that water readily reacts with transition-metal ions to give insoluble oxides or hydroxides.[17] Furthermore, organic ligands such as synthetic porphyrins that might stabilize transition-metal ions in water are inherently (thennodynamically) unstable in the presence of O_2. And, even if somewhat kinetically stable to oxidation, metallo-organic complexes are typically insoluble in water. Finally, the H^+ or OH^- ions generated during the catalysis of redox reactions in water can degrade organic substrates or products. A pertinent example is the acid-catalyzed hydrolysis of b-D-glycosidic linkages in cellulose. Given these generic obstacles, it is not surprising that no chemical system that simultaneously addresses all these problems has ever been reported. Nonetheless, the need to overcome these problems continues to increase in significance in both petrochemical and agricultural contexts as demand for environmentally benign oxidation technologies grows.

EQUILIBRATED POM SYSTEMS. The POM systems now ready for use in pilot demonstration represent a new approach to the control of transition-metal complexes in water. The new POM systems are thermodynamically stable in water and self-buffering. Their use in the selective and pollution-free delignification of wood fibers involves a two-step process that uses only O_2 and addresses all of the technical issues detailed above, The operative chemistry is described by recourse to data obtained using equilibrated solutions of a new heteropolytungstate cluster anion, $[AlV^{V}W_{11}O_{40}]^{6-}$. This cluster anion and functional equilibrated solutions in which it constitutes a dominant component, were designed to elucidate and demonstrate the fundamental chemistry reflective of thermodynamic stability and responsible for the system's self-buffering properties.

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