Computational Studies of Catalysts for Oxygen Pulping of Wood

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Wood pulping using the alkaline kraft process has been the predominant technology for chemical pulping for decades. While kraft pulping is efficient with respect to energy and inorganic chemical recovery it is also capital-intensive, degrades non-cellulosic polysaccharides and requires odor abatement operations due to the production of mercaptans.

It has been proposed that catalytic methods may offer a viable alternative to conventional kraft pulping, and eliminate the formation of odor-causing mercaptans. While catalysts based on transition metals may be initially expensive, with adequate turnover numbers and selectivity (*i.e.*, lignin removal with polysaccharide preservation) they may become cost-effective.

While the overall objective of the current work is the development of catalysts for pulping wood as an alternative to conventional pulping methods, the specific objective of this paper is the establishment of quantitative structure-performance relationships for known and proposed catalysts. This is being accomplished through a coupled experimental/computational approach. The former determine the efficacy of the catalysts while the latter compare performance with geometric and electronic structure of the catalysts and lignin models. Correlations established between experimental and computational results are used to design and predict the performance of prospective catalysts prior to synthesis, thus accelerating the development process.

Due to reported activity toward lignin, work to date has concentrated on a series of copper-phenanthroline and cobalt-salen oxidation catalysts. Density functional calculations have revealed a relationship between delignification and the unpaired orbital density of the copper-phenanthrolines. Based on these results, performance has been predicted for a number of previously untested phenanthroline ligands, and these are currently being tested experimentally. Among the cobalt-salen catalysts, there is considerable geometric distortion with axial substitution, which was found to be related to product yield. Axial ligands which increase this distortion and increase oxygen activation may offer opportunities for enhanced performance.