Homogeneous Vanadium-based Aerobic Oxidation Catalysts and Derivatives for Silica Supported Systems

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Biorenewable Replacements for Petrochemical Feedstocks

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Supply and Demand

Vanadium Catalyzed Oxidative C–C Bond Cleavage

Silica Supported Vanadium Catalyst

Mechanistic Study of Alcohol Oxidation

Development of More Effective Catalysts

Microelectrode Xingiang cathode greatly accelerates the reaction of 1° with air to generate V°.

Varying Solvent and Additives

Hydroxyquinoline Ligand Derivatives

Preliminary reactivity tests with the vanadium dioxide-dihydroxyquinoline (DEA) silica are promising. Refining a suspension of a vanadium-DEA silica with a DMSO:2 solvent under an argon show moderate activity for catalytic C–C bond cleavage of glucose.

Varying the Catalyst Using 4-Dimethoxyphenyl Alcohol as a Test Substrate

Silica Supported Vanadium Catalyst

Potential Benefits:

Site Accessibility – Some silica supports have large surface areas (900 m2/g) and pore sizes (2 nm to 50 nm) allowing easily accessible anchored functional groups
Stability – The support can withstand elevated temperatures in the presence of water without losing order.
Reusability – The catalyst can be recycled and used in other oxidation processes.

Vanadium – DEA Modification Silica

Preliminary reactivity tests with the vanadium-dihydroxyquinoline (DEA) silica are promising. Refining a suspension of a vanadium-DEA silica with a DMSO:2 solvent under an argon show moderate activity for catalytic C–C bond cleavage of glucose.

Vanadium – NO Modification Silica

Synthesis of 5-Chloromethyl hydroxyquinoline (5-CHQ)

Tethering 5-CHQ to organo modified silica

Conclusion

Successful catalytic, aerobic oxidation C–C bond cleavage of lignin model complexes has been demonstrated, while the precise mechanisms of the oxidations continue to be the subject of ongoing detailed experimental and computational investigations. The homogenous nature of the catalyst provides new opportunities for ligand design to optimize activity and selectivity in these reactions. Future work will focus on the design of more active catalysts and extension of this catalytic oxidation reaction to more complex model systems and lignins.

Supporting the vanadium catalysts will provide a means of catalyst recycle, and may provide additional mechanistic insight by isolating the vanadium centers and impeding bimolecular reactions.