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

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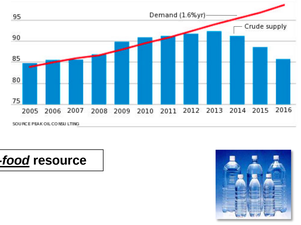
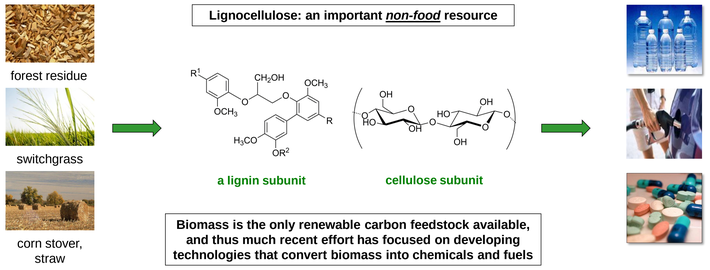
Biorenewable Replacements for Petrochemical Feedstocks

Escalating global demand for energy, diminishing petroleum reserves, and concern over rising CO_2 emissions are driving interest in the use of nonfood-based biorenewable chemicals and fuels.[1] Lignocellulose is a particularly important resource, with US production potential estimated at 1 billion tons/year.[2] However, breakdown of the highly functionalized polymers lignin and cellulose for use in biofuels and chemical applications is a major challenge.[1,3] Some promising technologies that have emerged utilize C-O bond cleavage, such as in enzymatic and acid-catalyzed hydrolysis, as well as pyrolysis/gasification.[4,5] Less attention has been directed at lignocellulose disassembly by selective C-C bond cleavage, which could provide alternative bioderived feedstocks.

Our aim is to pursue a metal-catalyzed oxidative disassembly of lignocellulose. Discovering new methods to convert lignin directly to value added products represents a major breakthrough towards the production of bio-derived chemicals and fuels.





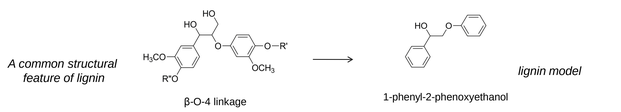
Vanadium Catalyzed Oxidative C-C Bond Cleavage

The use of an earth-abundant (non-precious) metal catalyst and air as an oxidant would represent a significant advance in our ability to break carbon-carbon bonds in 1,2-hydroxyether compounds such as lignin.

Air:
- inexpensive
- environmentally friendly
- (H_2O is the only by-product)

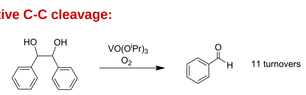
Vanadium:
- non-precious metal
- high oxidation potential of +5 state
- non-toxic

Model compounds are needed as test substrates because breakdown of the highly functionalized polymers lignin and cellulose is challenging



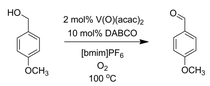
Precedent for vanadium-mediated catalytic, aerobic oxidative C-C cleavage:

Catalytic oxidative cleavage of 1,2- diphenyl-2-methoxyethanol using vanadium oxo trisisopropoxide provided 83% yield of the aldehyde with 11 turnovers of the catalyst.



Bregeault and coworkers *C. R. Acad. Sci. Paris* **1989**, *309*, 459.

Precedent for aerobic alcohol oxidation catalyzed by vanadium:

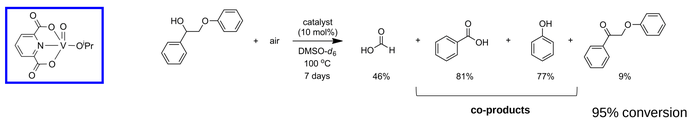


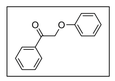
[bmim]PF_6 = 1-butyl-3-methylimidaxolium PF_6

Aerobic oxidation of 4-methoxy benzyl alcohol showed 98% conversion to the aldehyde in 91% yield. The catalyst was readily recyclable for three runs with only a slight drop in catalytic activity.

Ragauskas and coworkers *J. Org. Chem.* **2007**, *72*, 7030.

Catalytic Oxidation of 1-Phenyl-2-Phenoxyethanol by Dipicolinate Vanadium (V)



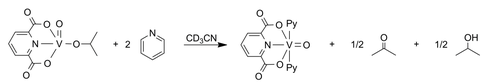


Detected as an intermediate: 80% yield at 50% conversion

Control (no vanadium): no reaction after 1 week at 100 °C

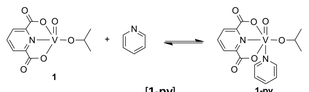
(1) (a) Dodds, D. R.; Gross, R. A. *Science* **2007**, *318*, 1250–1251. (b) Huber, G. W.; Corma, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 7184–7201. (c) Corma, A.; Iborra, S.; Velty, A. *Chem. ReV.* **2007**, *107*, 2411–2502.
(2) Perlack, R. D.; Wright, L. L.; Turhollow, A. F.; Graham, R. L.; Stokes, B. J.; Erbach, D. C. *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply.* US Department of Energy Report, 2005, available online at http://www.eere.energy.gov/biomass/publications.html.
(3) (a) Emsley, A. M. *Cellulose* **2008**, *15*, 187–192. (b) Zhang, Y. H. P. *J. Ind. Microbiol. Biotechnol.* **2008**, *35*, 367–375.
(4) (a) Li, C.; Zhao, Z. K. *AdV. Synth. Catal.* **2007**, *349*, 1847–1850. (b) Dhepe, P. L.; Fukuoka, A. *Catal. SurV. Asia* **2007**, *11*, 186–191. (c) Fukuoka, A.; Dhepe, P. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 5161–5163. (d) Zhang, Y. H. P.; Lynd, L. R. *Biotechnol. Bioeng.* **2004**, *88*, 797–824.
(5) Chheda, J. N.; Huber, G. W.; Dumesic, J. A. *Angew. Chem., Int. Ed.* **2007**, *46*, 7164–7183.

Mechanistic Study of Alcohol Oxidation



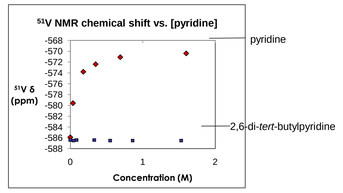
With no added base:
no reaction (25 °C)
Less than 25% reacts after 3 weeks at 100 °C

Evidence for pyridine coordination:



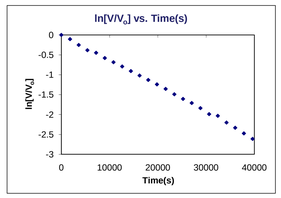
$$K_{eq} = \frac{[\mathbf{1\text{-}py}]}{[\mathbf{1}][\text{pyridine}]}$$

K_{eq} = 15(±2) M^{-1}

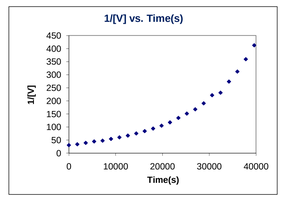


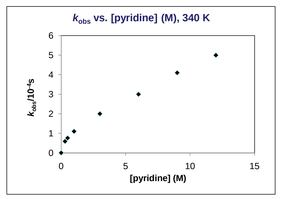
Determination of Reaction Order

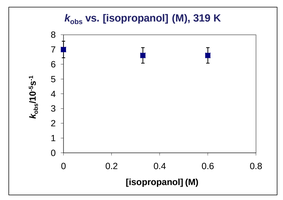
Fit to first order rate law:



Fit to second order rate law:





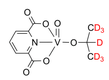


Activation Parameters:

$\Delta H^{\ddagger}$ = 85(4) kJ/mol = **20(2) kcal/mol**

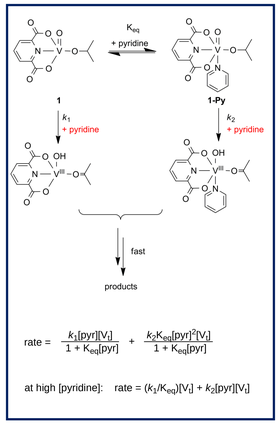
$\Delta S^{\ddagger}$ = -57(6) J/mol = **-14(1) eu**

Temperature (K)	k_{obs} (s^{-1})
319	7.0(5) x 10^{-5}
331	2.1(1) x 10^{-4}
340	5.0(3) x 10^{-4}
351	1.7(1) x 10^{-3}
360	2.7(2) x 10^{-3}



At 340 K: k_H/k_D = 5.7

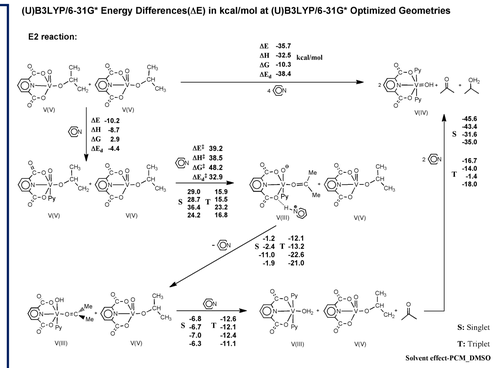
Proposed Mechanism



$$\text{rate} = \frac{k_1[\text{pyr}][V_i]}{1 + K_{eq}[\text{pyr}]} + \frac{k_2 K_{eq}[\text{pyr}]^2[V_i]}{1 + K_{eq}[\text{pyr}]}$$

at high [pyridine]: rate = $(k_1/K_{eq})[V_i] + k_2[\text{pyr}][V_i]$

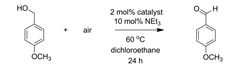
(U)B3LYP/6-31G* Energy Differences(ΔE) in kcal/mol at (U)B3LYP/6-31G* Optimized Geometries

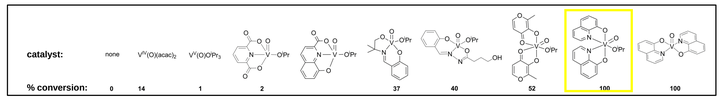


Calculations suggest that the reaction may proceed by an "E2" type pathway, where a bimolecular reaction occurs between the vanadium(V) complex and pyridine. Attack of pyridine on the C-H bond of the isopropoxide ligand forms a vanadium(III) intermediate. The details of the spin-crossover and the exact nature of the transition state in this system are still under investigation.

Development of More Effective Catalysts

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



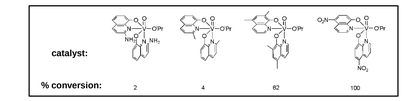


Varying Solvent and Additive

additive (10 mol%)	% conversion to aldehyde (NMR)
none	4
triethylamine	99
triethylamine (5 mol%)	99
diisopropylethylamine	99
TEMPO	99
DABCO	83
DMAP	28
NaOtBu	19
Na_2CO_3	16
DBU	5
proton sponge	6
NaOAc	1
CsF	1

solvent	% conversion to aldehyde (NMR)
1,2-dichloroethane	99
ethyl acetate	91
toluene	78
THF	96
CH_3CN	93
CH_2Cl_2	99*
1,2-dichlorobenzene	99
DMSO	69
pyridine	12

Hydroxyquinoline Ligand Derivatives



More electron-donating ligands greatly accelerate the reaction of V^{IV} with air to generate V^{V}.

Studies of the (dipic)VO^{i}Pr system demonstrated that a nitrogen base (pyridine or amine) may facilitate the alcohol oxidation step. Thus, with a combination of more electron-donating ligands and an amine additive, it may be possible to obtain more active catalysts.

Silica Supported Vanadium Catalyst

Potential Benefits:

Site Accessibility – Some silica supports have large surface areas (800 m^2/g) and pore sizes (2 nm to 50 nm) allowing easily accessible anchored functional groups

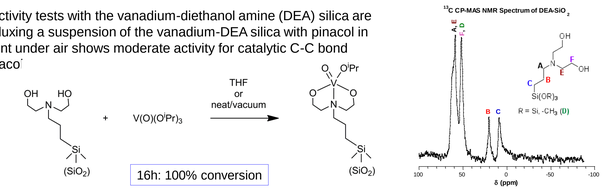
Stability – The support can withstand elevated temperatures in the presence of water without losing order.

Mechanistic Insight – Supporting the catalyst allows the potential to site isolate the vanadium centers and could prevent bimolecular reactions between two vanadium centers.

Reusability – The catalyst can be recycled and used in other oxidation processes

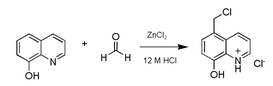
Vanadium- DEA Modification Silica

Preliminary reactivity tests with the vanadium-diethanol amine (DEA) silica are promising. Refluxing a suspension of the vanadium-DEA silica with pinacol in DMSO-d_6 solvent under air shows moderate activity for catalytic C-C bond cleavage of pinaco

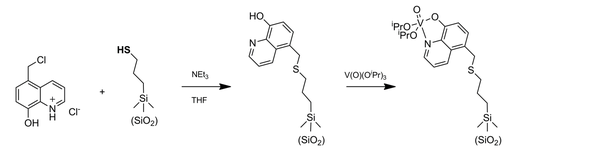


Vanadium- HQ Modification Silica

Synthesis of 5-chloromethyl hydroxyquinoline (5-CHQ)



Tethering 5-CHQ to organo modified silica



Conclusion

Successful catalytic, aerobic oxidative 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 homogeneous 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.