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## Upcoming ACS Webinars®

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Wednesday, July 22, 2015

### **“Panorama Nanotecnológico: Desarrollo de Sistemas Biológicos y la Nanomedicina”**

*Spanish Language Broadcast*

**David Quintanar Guerrero**, Professor of Engineering and Technology, Universidad Nacional Autónoma de México

**Lena Ruiz Azuara**, President, Sociedad Química de México



Thursday, July 23, 2015

### **“The Creator’s Code: The Six Essential Skills of Extraordinary Entrepreneurs”**

**Amy Wilkinson**, Author, Entrepreneur, and Strategic Advisor, Stanford Graduate School of Business

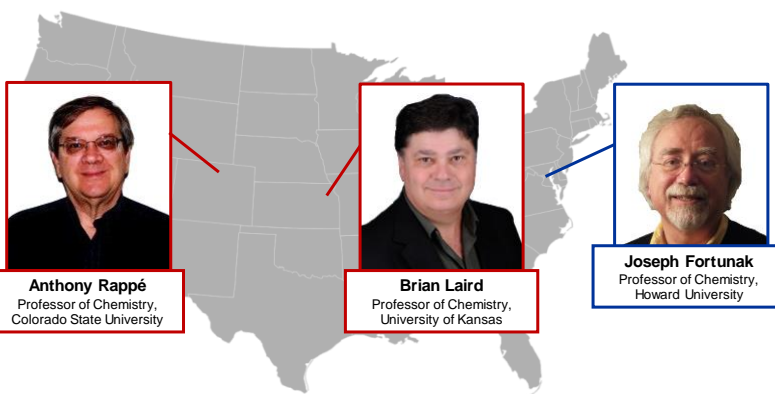
**Brian Morin**, President & COO, Dreamweaver International

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### **“Catalyzing Innovation through Molecular Design”**



**LIVE from the 19th Annual Green Chemistry & Engineering Conference**  
[www.acs.org/acswebinars](http://www.acs.org/acswebinars)

This webinar is co-produced with the ACS Green Chemistry Institute

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## Catalysis Collaboratory for Light-activated Earth-Abundant Reagents

(aka C-CLEAR)



**NSMDS:** Computational design and synthetic exploitation of Earth-abundant-sourced photocatalysts for carbon-heteroatom activation

- Catalytic processes
- Solar photon energy source (driving force, activation energy)
- Earth abundant materials
- Reduction in auxiliary agents

**Goal:** novel chemistry for pharmaceutical industry

Enantioselectivity

Saturated C-H bond activation

**Approach:**

Coordination chemistry (Shores)

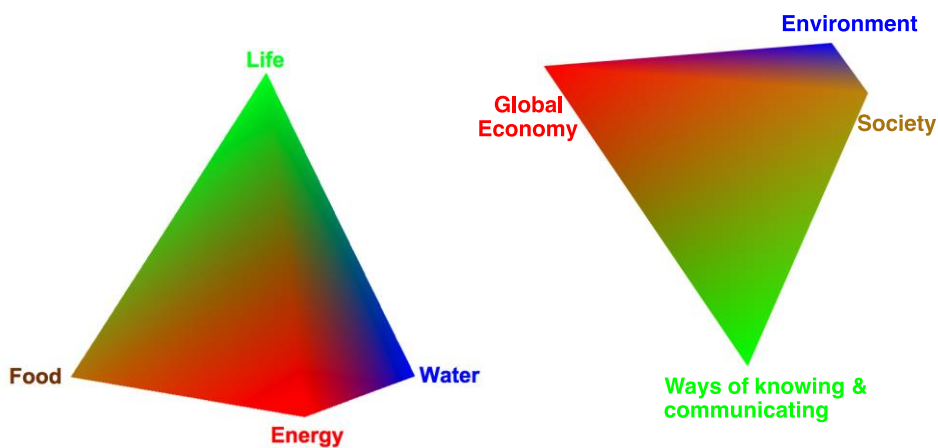
Transient absorption spectroscopy (Damrauer)

Theory (Rappé)

Organic synthetic methods development (Ferreira, Rovis)

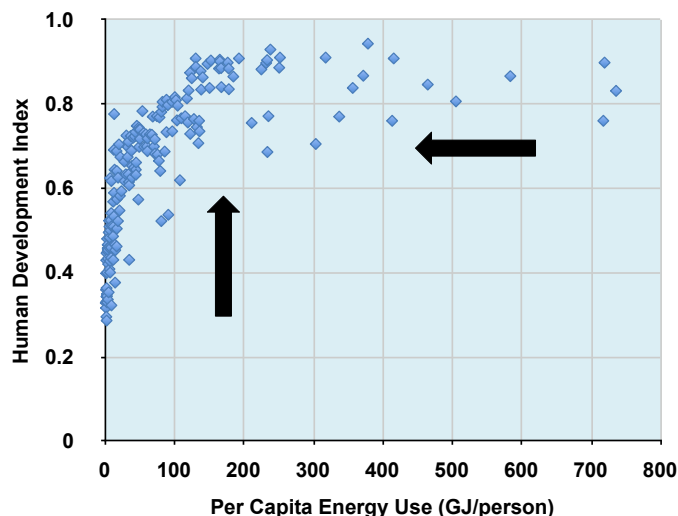


## Sustainability



## Challenge

Figure 3.2 — Human Development Index vs. Per Capita Energy Use



*Society: Must raise HDI for developing nations  
while increasing efficiency in developed nations*

<http://energywhattheworldneedsnow.com>

## 12 Principles of Green Chemistry

1. **Prevention** Prevent rather than treat waste.
2. **Atom Economy** Maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Synthesis**
4. **Designing Safer Chemicals**
5. **Safer Solvents and Auxiliaries** The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible.
6. **Design for Energy Efficiency**
7. **Use of Renewable Feedstocks** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.
8. **Reduce Derivatives** Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. **Catalysis** Selective catalytic reagents are superior to stoichiometric reagents.
10. **Design for Degradation**
11. **Real-time Analysis for Pollution Prevention**
12. **Inherently Safer Chemistry**

Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*, Oxford University Press, 1998.



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## Scale

### Annual US petroleum production $\sim 10^9$ metric tons

15% used in petrochemicals

<0.1% used in pharmaceuticals



### Annual US food consumption $\sim 7 \times 10^7$ metric tons

### Annual US natural gas consumption $\sim 5 \times 10^8$ metric tons

30% for chemicals (~half for fertilizer)

### Global Annual Revenue

Chemical Shipments \$5.2 T

Pharmaceuticals \$1 T

Energy \$6 T

*Pharma: small volume but high value*



## Selectivity

Waste/energy reduction →

Catalysis → sub-stoichiometric reagents, less energy

Improved selectivity → atom economy

→ reduce auxiliary agents

→ product control

reduce side products

→ stereo control

make the enantiomer you want

reduce waste by  $\frac{1}{2}$

improve product safety

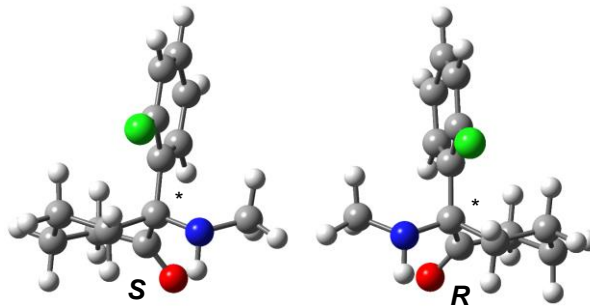
increase pharmacodynamic understanding



*Selectivity a key concept*



## Stereoselectivity



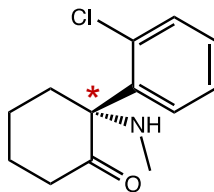
**In general, stereoisomers possess different biological activity:**

- most benign option: 50% waste
- alternatively, one isomer is active, the other provides (-) side effects
- isomers can have opposite effects

*Need stereocontrol during discovery as well as production*

Ariëns "Stereochemistry, a Basis for Sophisticated Nonsense in Pharmacokinetics and Clinical Pharmacology" Eur. J. Clin. Pharmacol. 1984, 26, 663-668

## Ketamine

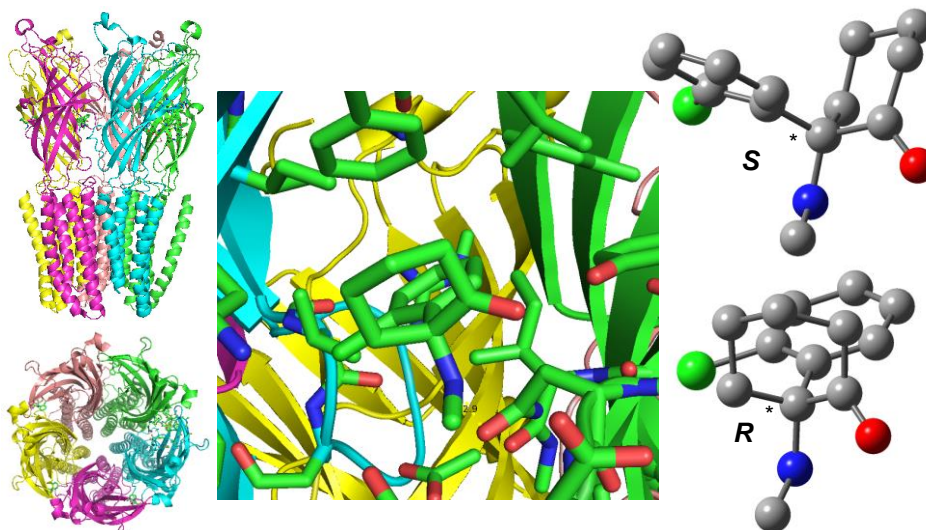


- Induces unconsciousness and amnesia.
- Also induces analgesia and psychedelic hallucinations.  
→ Often a drug of abuse (club drug)
- Unlike other anesthetics, does not reduce blood pressure;  
→ Important for critically ill surgery patients.
- *S* enantiomer associated with analgesic properties
- *R* enantiomer associated with psychedelic hallucinations

Ariëns "Stereochemistry, a Basis for Sophisticated Nonsense in Pharmacokinetics and Clinical Pharmacology" Eur. J. Clin. Pharmacol. 1984, 26, 663-668



## Ketamine



*Wrong enantiomer doesn't fit*

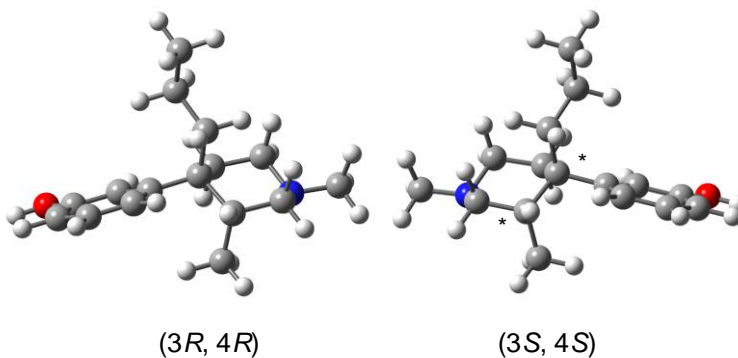
Pan, J.; Chen, Q.; Willenbring, D.; Mowrey, D.; Kong, X. P.; Cohen, A.; Divito, C. B.; XU, Y.; Tang, P. "Structure of the pentameric ligand-gated ion channel GLIC Bound with anesthetic ketamine", *Structure*, **2012**, 20, 1463.

## Picnadol

An Opioid Analgesic

agonist

antagonist



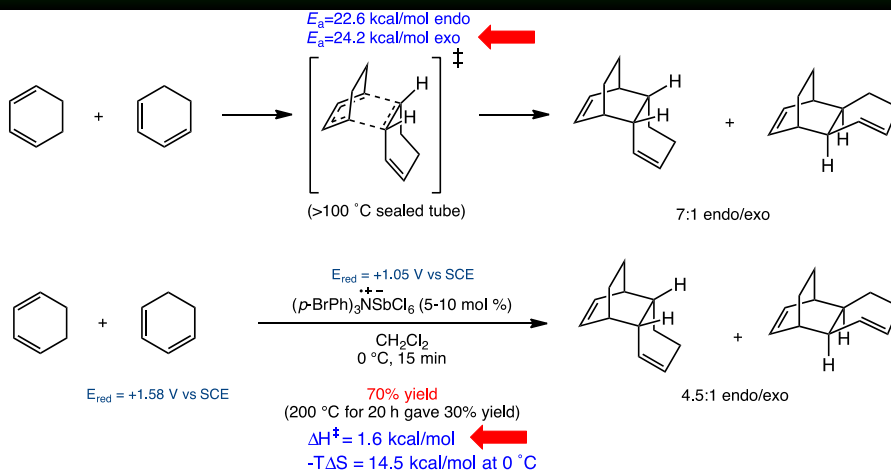
The racemate is a weak agonist

*Difficult to sort out impact*

Ariëns "Stereochemistry, a Basis for Sophisticated Nonsense in Pharmacokinetics and Clinical Pharmacology" *Eur. J. Clin. Pharmacol.* **1984**, 26, 663-668



## Catalysis

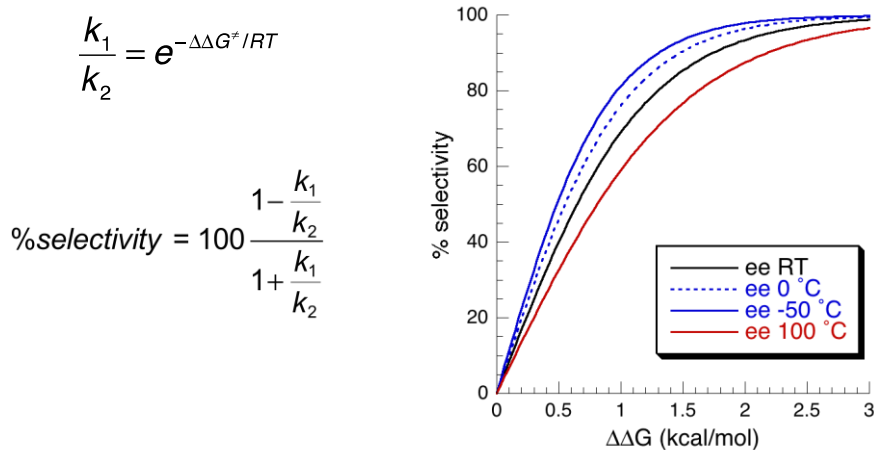


Adding a step lowers the barrier, reduces energy need ( $T$ ) for the reaction

Can lead to increased selectivity  $\frac{k_1}{k_2} = e^{-\Delta\Delta G^\ddagger / RT}$

Kläerner, F.-G.; Dogan, B.M.J.; Ermer, O.; Doering, W.E.; Cohen, M.P. *Angew. Chem. Int. Ed. Engl.* **1986**, 25, 108.  
 Bellville, D. J.; Wirth, D. W.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, 103, 718-720.

## Selectivity

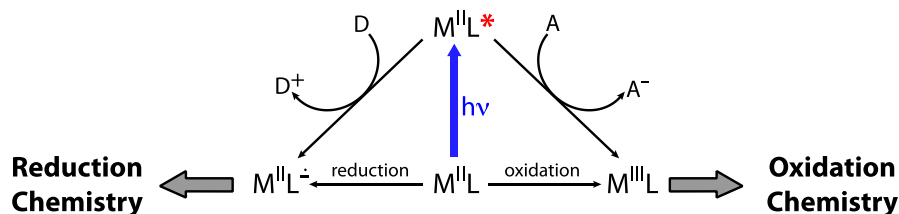


Selectivity increases with increasing  $\Delta\Delta G$   
 Selectivity decreases with increasing  $T$





# Photoredox Catalysis



Compared to “photovoltaics + electrochemistry”, photoredox catalysis has the potential for increased efficiency & product selectivity

Reviews:

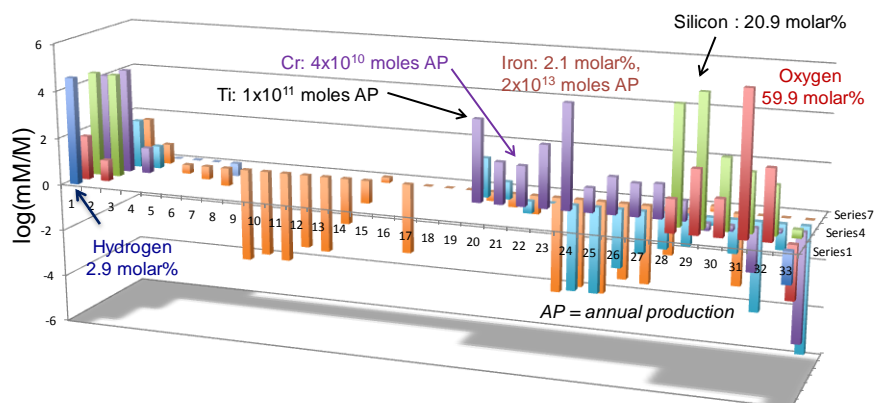
Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. “Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis” *Chem. Rev.* **2013**, 113, 5322-5363.

Douglas, J. J.; Nguyen, J. D.; Cole, K. P.; Stephenson, C. R. J. “Enabling novel photoredox reactivity via photocatalyst selection” *Aldrichimica Acta*, **2014**, 47, 15-25.

Xuan, J.; Xiao, W.-J. “Visible-Light Photoredox Catalysis”, *Angew. Chem. Int. Ed., Engl.* **2012**, 51, 6828.



# Abundance



Aspirational Goal: Ti and Fe

Data from: Carmichael, R. S., Ed., CRC Practical Handbook of Physical Properties of Rocks and Minerals, CRC Press, Boca Raton, FL, 1989.



scandium 21	titanium 22	vanadium 23	chromium 24	manganese 25	iron 26	cobalt 27	nickel 28	copper 29	zinc 30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
44.956	47.867	50.942	51.996	54.938	55.845	58.933	58.693	63.546	65.38

Titanium:  $1 \times 10^{11}$   
moles AP

Chromium:  $4 \times 10^{10}$   
moles AP

Iron: 2.1 molar %,  $2 \times 10^{13}$  moles AP

### Compared to 2<sup>nd</sup> and 3<sup>rd</sup> row analogues, 1<sup>st</sup> row transition metal complexes:

- are more abundant (the metals, anyway)
- are more reactive (weaker bonds)
- undergo redox in 1 e<sup>-</sup> increments (lower barriers)
- are electron spin active
- have low-lying photo-inactive excited states

### Solutions? Approaches?

- learn how to control (use to our advantage) spin
- associated molecular magnetism, spin-crossover applications
- involve the ligands in redox events

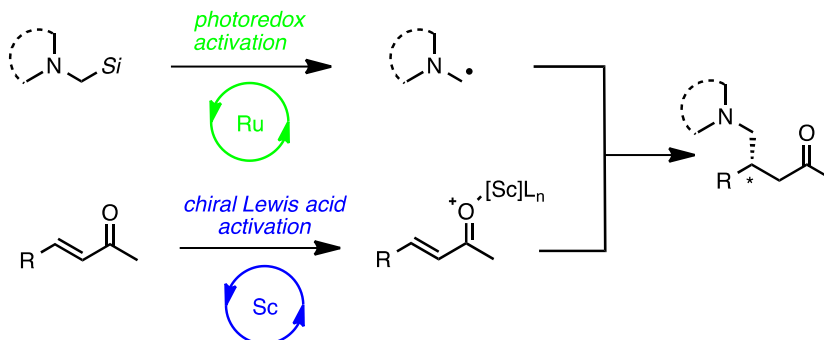
### 1<sup>st</sup> Row Metals in Catalysis Reviews:

Special Issue: "Earth Abundant Metals in Homogeneous Catalysis" *Accounts of Chemical Research* 2015, 48, 886-1775.

Chirik, P. J. "Iron- and Cobalt-Catalyzed Alkene Hydrogenation: Catalysis with Both Redox-Active and Strong Field Ligands" *Acc. Chem. Res.* **2015**, 48, 1687-1695.

Hennessy, E. T.; Liu, R. Y.; Iovan, D. A.; Duncan, R. A.; Betley, T. A. "Iron-mediated intermolecular N-group transfer chemistry with olefinic substrates" *Chem. Sci.*, **2014**, 5, 1526-1532.

## Photoredox Stereocontrol

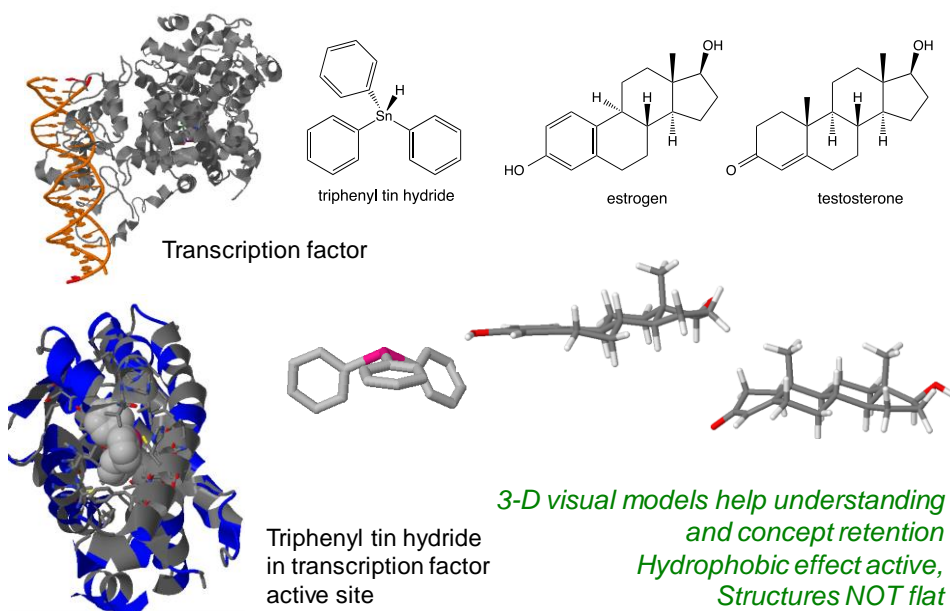


### Tandem photocatalysis achieves stereocontrol

Ruiz Espelt, L.; McPherson, I. S.; Wiensch, E. M.; Yoon, T. P. "Enantioselective Conjugate Additions of  $\alpha$ -Amino Radicals via Cooperative Photoredox and Lewis Acid Catalysis" *J. Am. Chem. Soc.* **2015**, 137, 2452.

Wang, C.; Zheng, Y.; Huo, H.; Rçse, P.; Zhang, L.; Harms, Hilt, K. G.; Meggers, E. "Merger of Visible Light Induced Oxidation and Enantioselective Alkylation with a Chiral Iridium Catalyst" *Chem. Eur. J.* 2015, 21, 7355.

## Models & Modeling (pictures)



## Electronic Structure Theory

### Modeling is internally calibrating

experiment → theoretical model → suggest experiment

### Catalysts

structure  
where are the unpaired electrons

### Transition States

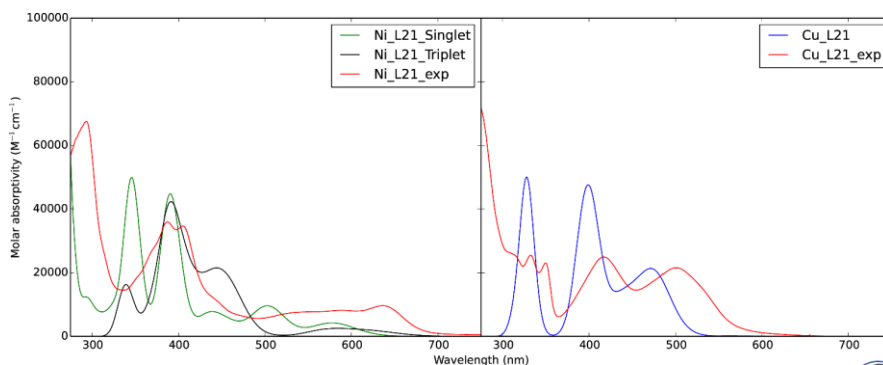
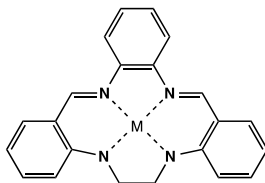
structure  
reaction path  
where are the unpaired electrons

### Excited States

what do the spectra look like  
peak positions  
intensities  
where does the excited electron come from and go to  
APFD DFT model using a 6-311+g(d) basis



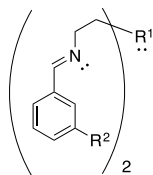
# Theory versus Experiment



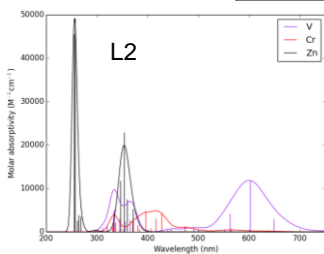
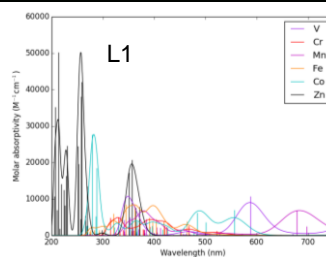
Only qualitative agreement, but useful



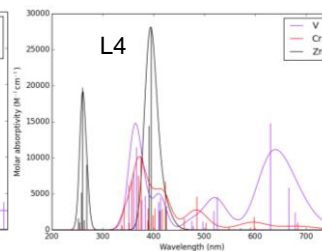
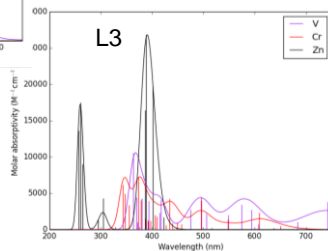
## Ligand Screening



Ligand	R¹	R²
L1	NCH <sub>3</sub>	OH
L2	O	OH
L3	NCH <sub>3</sub>	NHCH <sub>3</sub>
L4	O	NHCH <sub>3</sub>

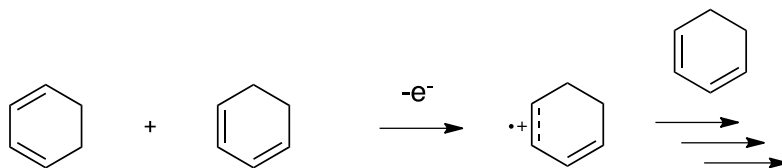


Zn: shorter wavelengths (less in visible)  
V: greater intensity than Cr  
Salen-derived L1 seems most promising



Collette Nite

## Electrochemical Oxidation Diels-Alder Reactions of Electron-Rich Dienophiles



Electrode	Potential (V)	Diels-Alder product (%)	Polymer (%)	M <sub>w</sub> 2 <sup>nd</sup> fraction/3 <sup>rd</sup> fraction
Pt	1.5	Trace	43.7	900/2000
Pt	1.7	Trace	51.2	550/1200
graphite	1.7	13.1	4.4	1200/ND

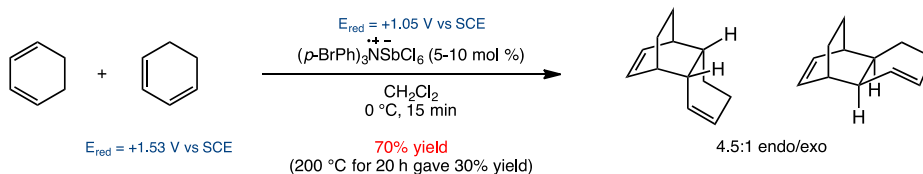
0.4 M 1,3-cyclohexadiene, 0.08M Bu<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub>

*No useful selectivity/control*

Nigenda, S. E.; Schleich, D. M.; Narang, S. C.; Keumi, T. J. *Electrochem. Soc.* **1987**, 2465-2470.



## Chemical Oxidation Diels-Alder Reactions of Electron-Rich Dienophiles

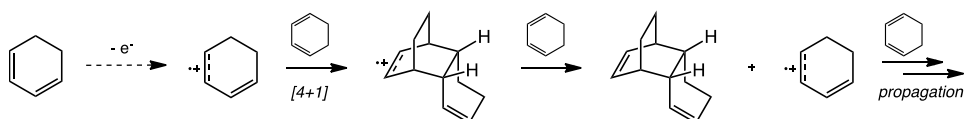


*Uphill, but happens at low T, not high T*

Bellville, D. J.; Wirth, D. W.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, 103, 718-720.



## Proposed Mechanism

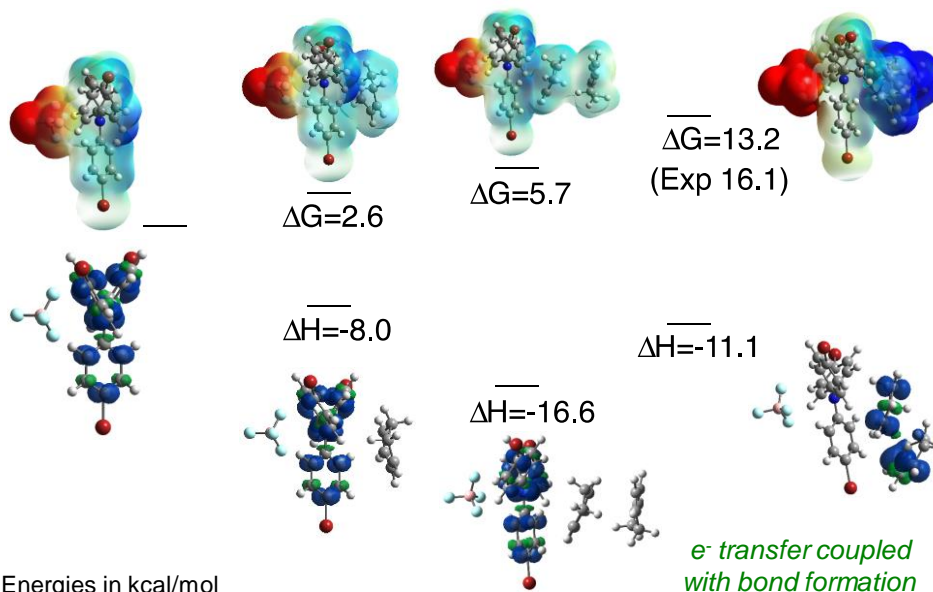


*Radical chain*

Bellville, D. J.; Wirth, D. W.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, 103, 718-720.



## Transition State



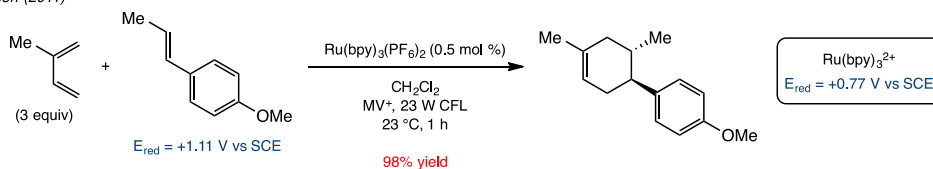
Energies in kcal/mol

Spin density plots  $\rho(\uparrow)$ - $\rho(\downarrow)$ : blue net  $\rho(\uparrow)$  & green net  $\rho(\downarrow)$

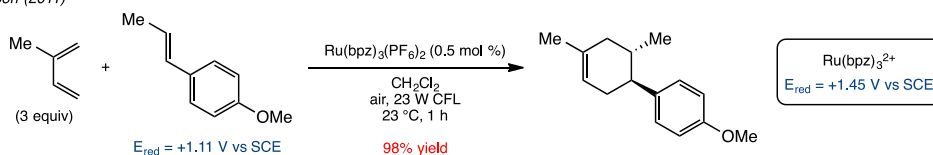
Sung Hi Jo

## Photochemical Diels-Alder Reactions of Electron-Rich Dienophiles

Yoon (2011)



Yoon (2011)

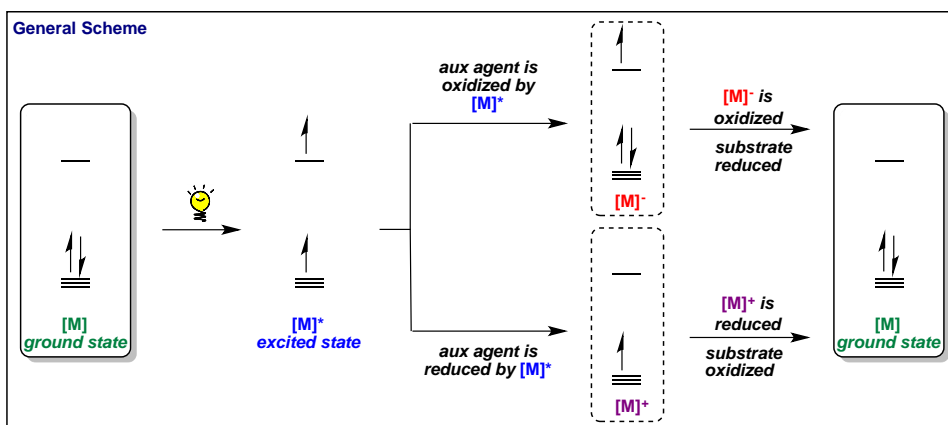


$[\text{Ru}(\text{bpy})_3]^{2+}$  + methyl viologen (MV) or stronger oxidant +  $\text{O}_2$

Lin, S.; Ischay, M. A.; Fry, C. G.; Yoon, T. P. *J. Am. Chem. Soc.* **2011**, 133, 19350-19353.



## Outer-Sphere Photocatalysis



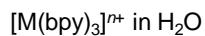
Auxiliary agent beats redox potential lifetime issues

Review: Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, 113, 5322-5363.



## Emissive States

Metal	Lifetime (ns)	Emission $\lambda_{\max}(\text{nm})$
Cr(III)	69,000	729
Fe(II)	0.81	???
Ru(II)	600	613, 627
Os(II)	19	715

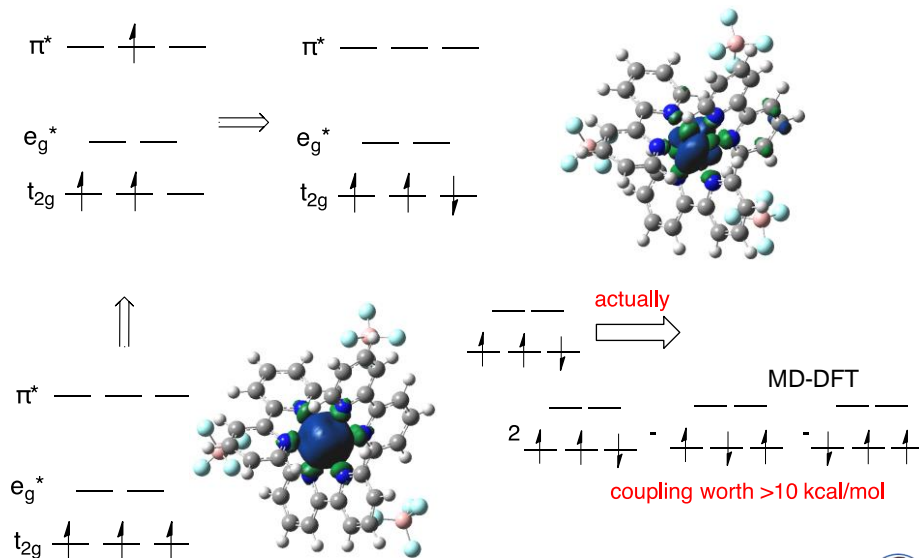


*Low spin Cr(III) excited state provides long lifetime*

Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. "Lifetimes, Spectra, and Quenching of the Excited States of Polypyridine Complexes of Iron(II), Ruthenium(II), and Osmium(II)" J. Am. Chem. Soc. 1980, 102 1309-1319

McDaniel, A. M.; Tseng, H.-W.; Damrauer, N. H.; Shores, M. P. "Synthesis and Solution Phase Characterization of Strongly Photooxidizing Heteroleptic Cr(III) Tris-Dipyridyl Complexes" Inorg. Chem. 2010, 49, 7981-7991.

## $[\text{Cr}(\text{bpy})_3]^{3+}$ Potential Oxidative Dye



*Low spin Cr(III) excited state tough to model*





## Questions for C-CLEAR

(aka Catalysis Collaboratory for Light-activated Earth-Abundant Reagents)

- Can a first row metals be used in photoredox catalysis?
- Can the longer lifetime of Cr(III) be exploited to eliminate auxiliary agent?
- Can stereocontrol be achieved?
- Can differentiated (novel) reactivity be observed?

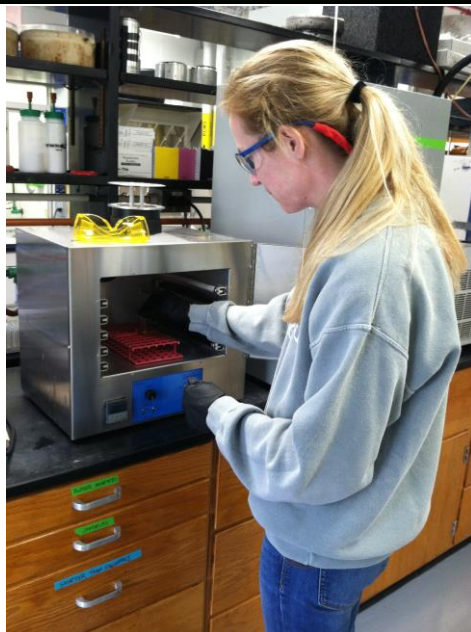


## Catalyst Synthesis



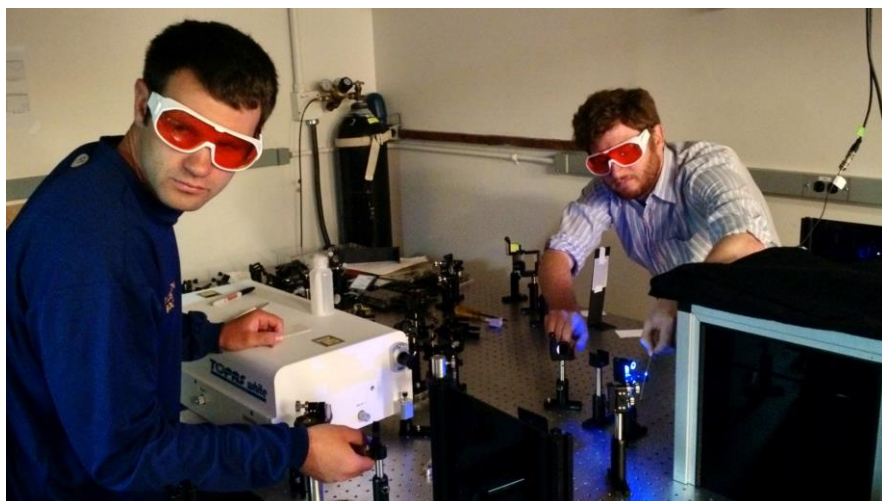
David Boston, Robert Higgins

## Photocatalyst Screening



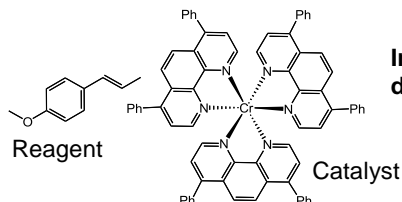
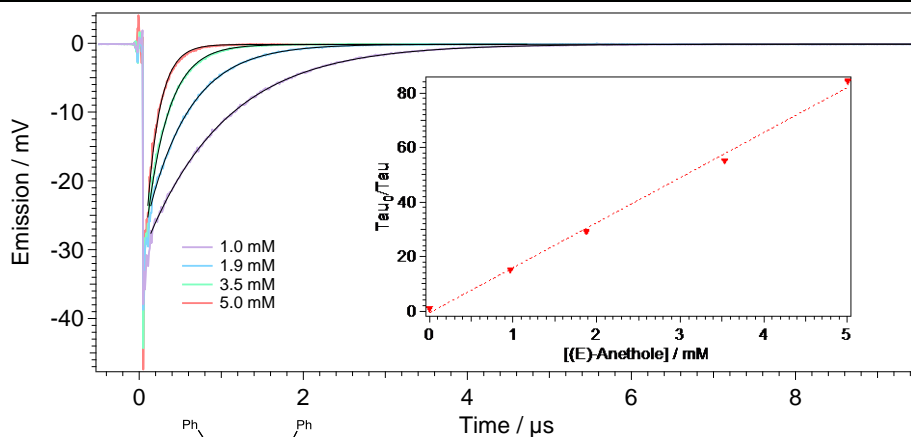
Suzie Stevenson

## Time-Resolved Spectroscopy



Sam Shepard, Steve Fatur

## Time-Resolved Spectroscopic Studies for Efficient Catalysis



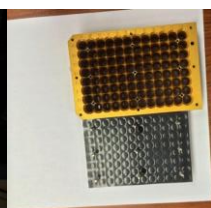
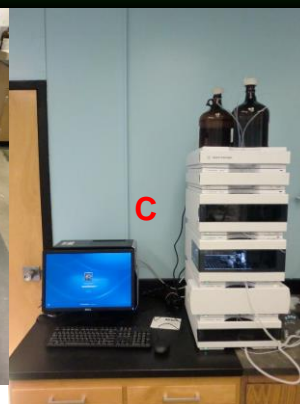
**Increasing the concentration of reagent decreases catalyst emissive lifetime.**

- Measures photo-oxidation rate constant
- All data fit to single exponential functions

## High Throughput Experiment Facilities



A. Dry/Wet Box  
B. Tumble Stirrer  
C. HPLC  
D. Photo plate

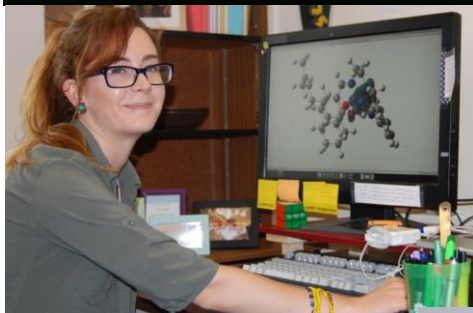


Rapid scan of ligand, metal, solvent, auxiliary agents ( $H^+$  source, salt, etc.),

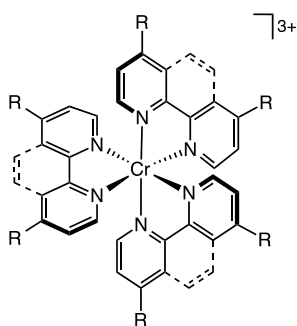
Kyle Ruhl



## Theory



## Photooxidizing Cr(III) Complexes



•absorb visible light

$\lambda_{\text{max}}$  300-420 nm

$\text{Ru}(\text{bpy})_3^{2+}$

452

•long excited state lifetimes

$\tau_{\text{obs}}^*$  ( $\mu\text{s}$ ) 425-8

1.1

•high excited state reduction potentials

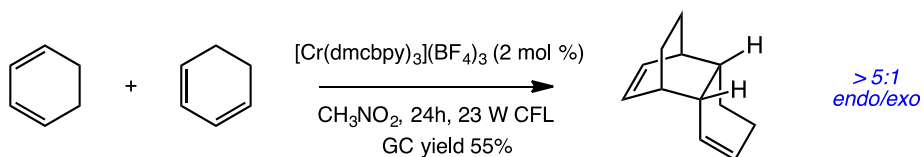
$[\text{M}]^+ / [\text{M}]^{\cdot+}$  (V vs. SCE) 1.4-1.84

+0.77

McDaniel, A. M.; Tseng, H.; Damrauer, N. H.; Shores, M. P. *Inorg. Chem.* **2010**, 49, 7981-7991.  
 Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, 113, 5322-5363.



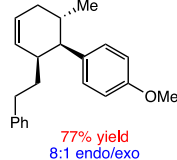
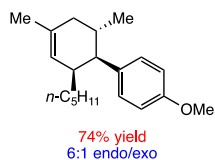
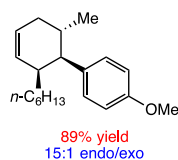
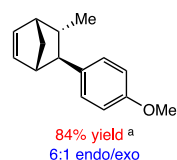
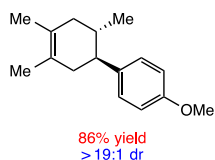
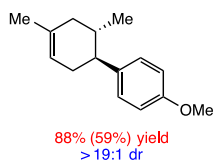
## Dimerization of Cyclohexadiene



Stevenson, S. M.; Shores, M. P.; Ferreira, E. M. "Photooxidizing Chromium Catalysts for Promoting Radical Cation Cycloadditions," *Angew. Chem. Int. Ed.* **2015**, 54, 6506–6510 .



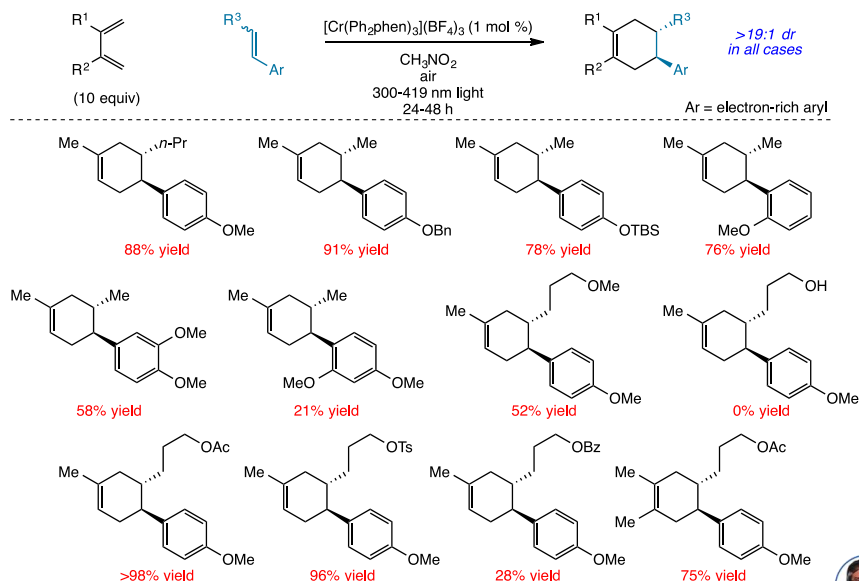
## Diene Scope



<sup>a</sup> 5 mol % catalyst was used.  
 (Yields in parenthesis were obtained with a 23 W CFL as the light source.)

Stevenson, S. M.; Shores, M. P.; Ferreira, E. M. *Angew. Chem. Int. Ed.* **2015**, 54, 6506–6510 .

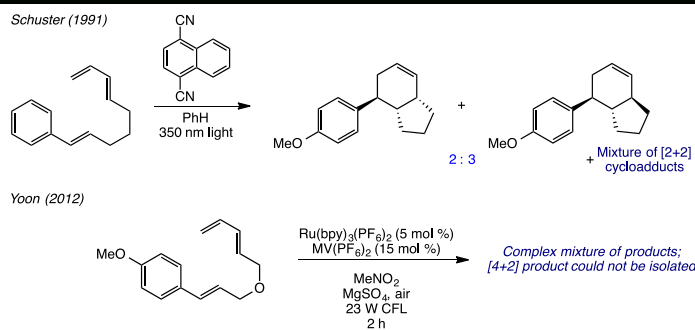
## Dienophile Scope



Stevenson, S. M.; Shores, M. P.; Ferreira, E. M. *Angew. Chem. Int. Ed.* **2015**, *54*, 6506–6510.

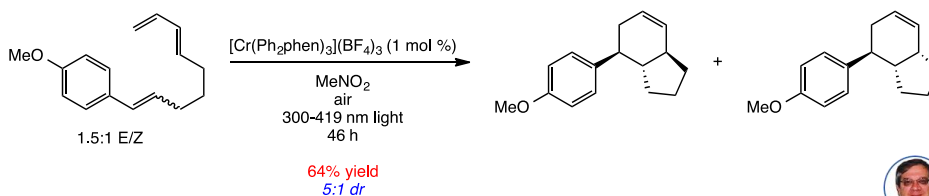


## Differential (Novel) Reactivity



Wölfle, I.; Chan, S.; Schuster, G. B. *J. Org. Chem.* **1991**, *56*, 7313-7319.

Lin, S.; Padilla, C. E.; Ischay, M. A.; Yoon, T. P. *Tetrahedron Lett.* **2012**, *53*, 3073-3076.

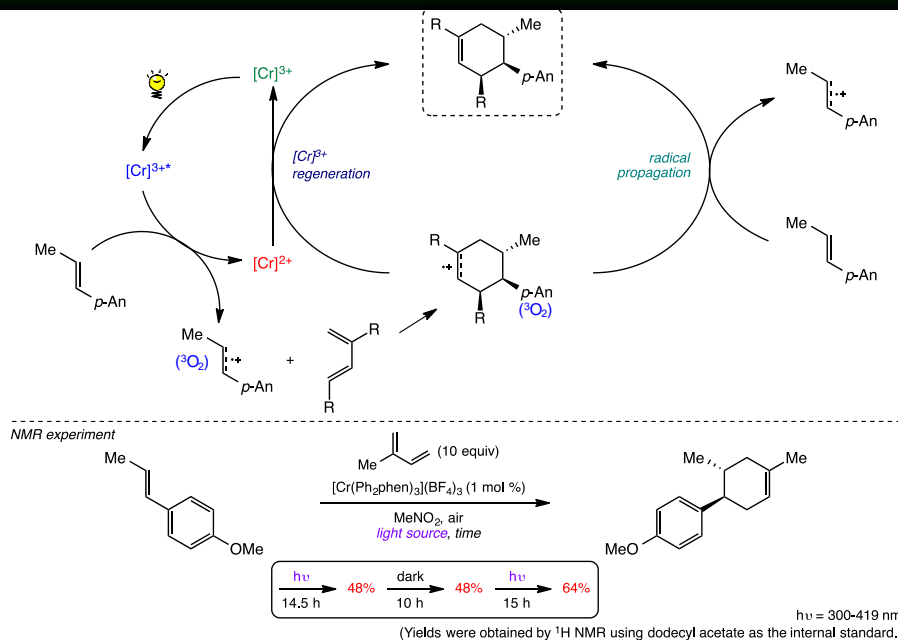


Stevenson, S. M.; Shores, M. P.; Ferreira, E. M. *Angew. Chem. Int. Ed.* **2015**, *54*, 6506–6510.

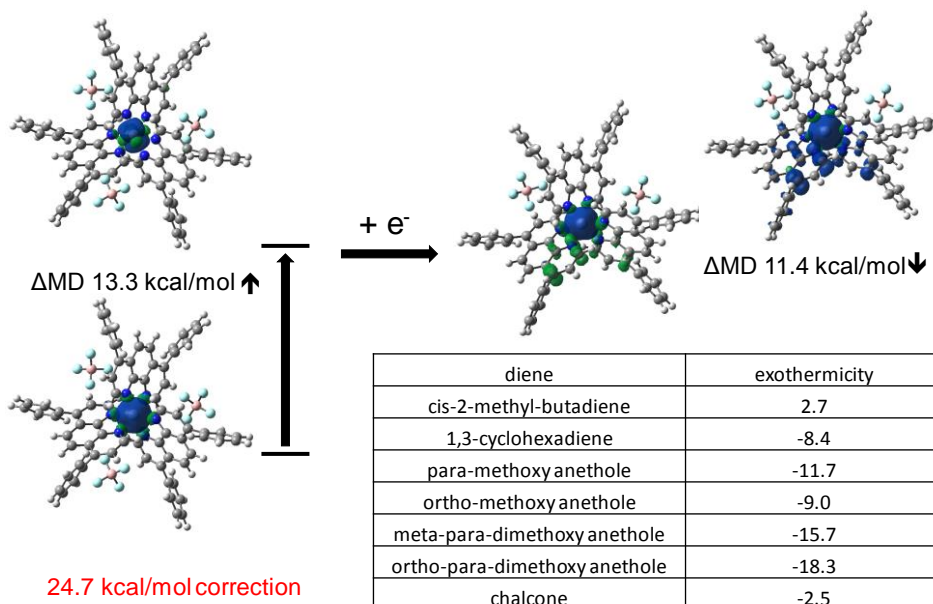




## Catalyst Regeneration vs. Radical Propagation



## Oxidation Process





## Summary

So far 1<sup>st</sup> row transition metal photocatalysis gives:

- product selectivity
- energy reduction
- reagent reduction
- diastereoselectivity

Can a first row metals be used in photoredox catalysis? **yes**

Can the longer lifetime of Cr(III) be exploited to eliminate auxiliary agent? **yes**

Can stereocontrol be achieved? **diastereocontrol yes**

Can differentiated (novel) reactivity be observed? **yes**



## NSMDS: Sustainable Chemical Innovations by an Integrated Design Approach

*Industry-driven, resource-efficient, cost-competitive*



**Brian Laird (PI)**

Ward Thompson, Jon Tunge, R.V. Chaudhari & Bala Subramaniam (co-PIs)

The University of Kansas Center for Environmentally Beneficial Catalysis (CEBC)

# KU NSMDS: Project Faculty Team

## Molecular-Scale Modeling:



**Brian Laird (PI)**  
Computational materials science  
and applied statistical mechanics



**Ward Thompson (co-PI)**  
Theoretical chemical dynamics  
and nanostructured materials

## Catalysis and Reaction Engineering



**Bala Subramaniam (co-PI)**  
Green catalysis, reaction media,  
reactor engineering, life-cycle  
analysis (LCA)



**R.V. Chaudhari (co-PI)**  
Multiphase catalytic reactors,  
catalyst design, reaction kinetics

## Synthesis of Organic Materials:



**Jon Tunge (co-PI)**  
Organic synthesis, catalyst  
design, reaction mechanisms

## Postdoctoral Associates



Xin  
Jin



Swarup  
Maiti



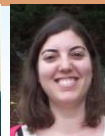
Tapan  
Maji



Pansy  
Patel



Krista  
Steenbergen



Maria  
Tenorio



Zhenxing  
Wang

## Graduate Students



Jesse  
Kern



Hiranya  
Mendis



Ziwei  
Song



Wenjuan  
Yan

## Undergrads



Ethan  
Zolotor



Tom  
Flynn

## Professional Staff



Claudia  
Bode



Chris  
Lyon

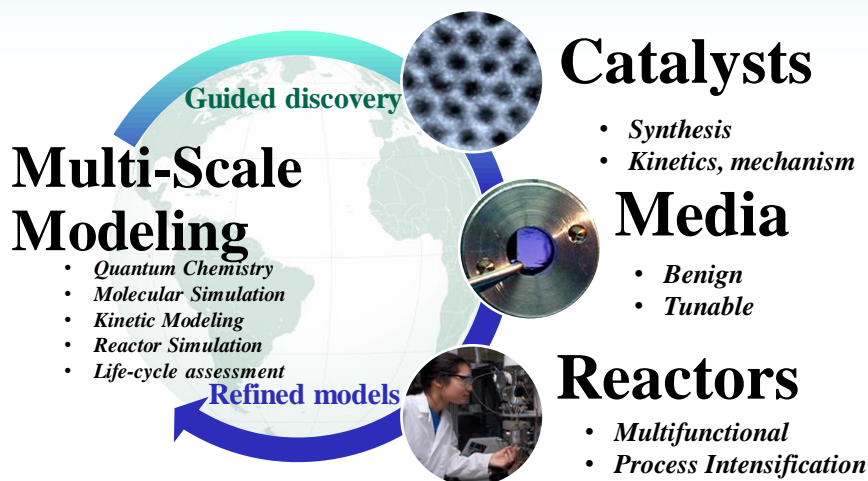


Anand  
Ramanathan



Andrzej  
Rokicki

# Integrated Design Approach



## CEBC's Industry partners Guide Science and Enhance Training



Scientists and engineers from companies across the value chain form our Industry Advisory Board. They travel to KU twice a year to hear updates from faculty, students and research staff.

At the spring meeting, all research projects are evaluated by both the Industry Advisory Board and the Scientific Advisory Board.

Students and postdocs present their research, gain feedback from industry experts, and improve their communication skills.



## Leveraging Resources at CEBC



**Mission:** Invent cleaner, safer, energy-efficient technologies for commodity chemicals that protect the planet and human health.

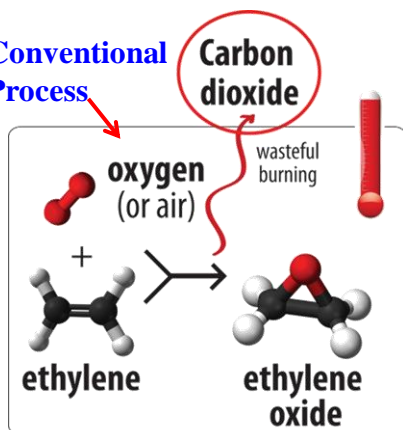
**\$31** million in R&D total  
**22** industry partners total  
**44** inventions  
**12** patents  
**~35** students & postdocs



## Example of a Grand Challenge in the Chemical Industry

### Epoxidation of Ethylene to Ethylene Oxide

Conventional Process



(2<sup>nd</sup> largest emitter of CO<sub>2</sub> in commodity chemical production)

**15%**  
feedstock &  
product wasted  
**\$2 billion/yr**  
lost opportunity



**Project Goal:** Apply integrated design approach to *grand challenges* in the chemical industry

**Test bed A: Non-phosgene CO<sub>2</sub>-based route to dimethyl carbonate (DMC)**

**Test bed B: Cleaner, atom-economical route for butadiene to adipic acid**



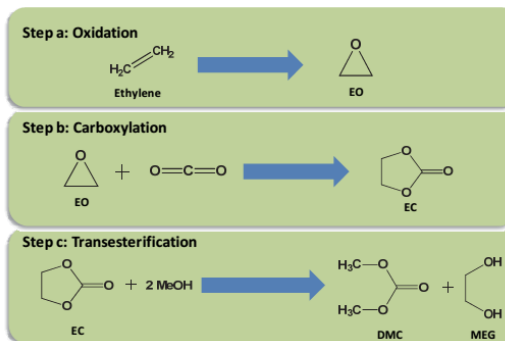
### Test Bed A: Non-phosgene Route from Ethylene to DMC

Develop a novel *atom economical, non-phosgene* catalytic route for making DMC from ethylene, CO<sub>2</sub> and methanol using the following steps:

**Step 1: Ethylene to ethylene oxide (EO) using methanol as a solvent**

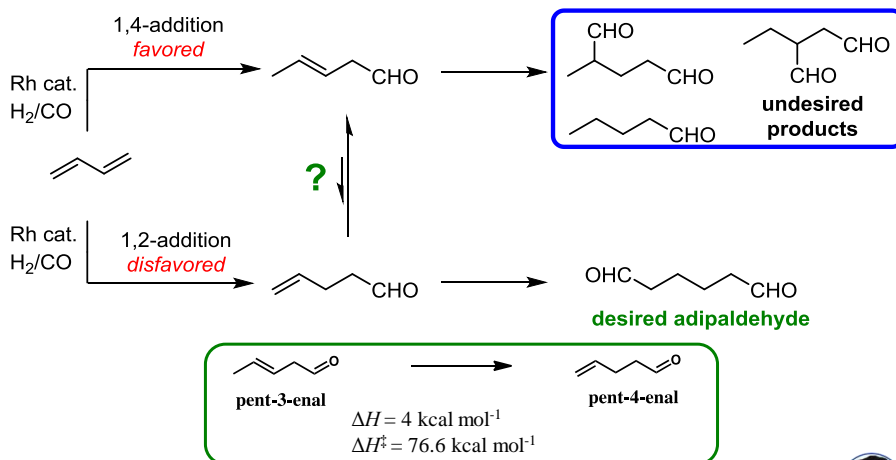
**Step 2:** Carboxylation of EO to ethylene carbonate (EC) using CO<sub>2</sub>

**Step 3:** Transesterification of EC using methanol to DMC



## Test Bed B: Adipic Acid from Butadiene

- Conventional routes for adipic acid use cyclohexane and nitric acid  
→ generates significant chemical waste and emissions
- Need atom-economical route with high selectivity for adipaldehyde



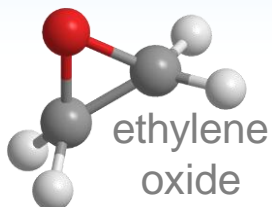
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## Integrated Catalyst Design in Action

### Epoxidation of ethylene to ethylene oxide



**\$30 billion**

per year; growing by 5%

**14<sup>th</sup> largest**

volume organic chemical

**Essential**

chemical building block

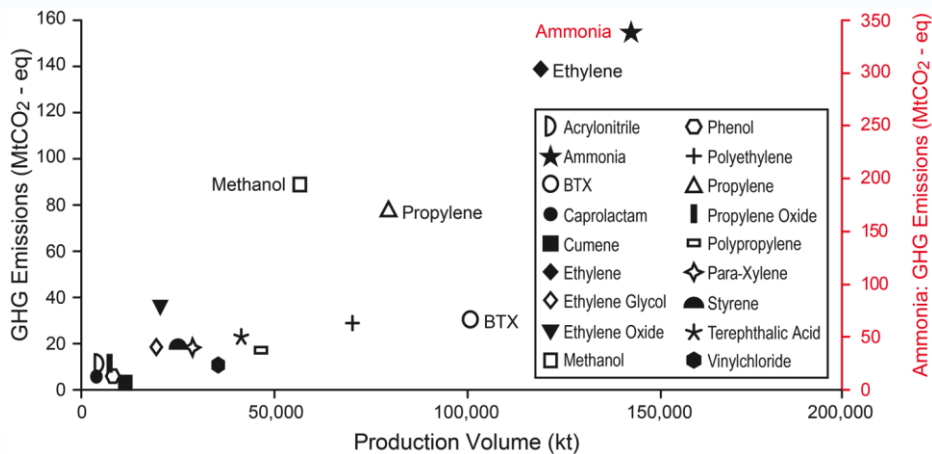


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## GHG Emissions of Top 18 Large-Volume Chemicals

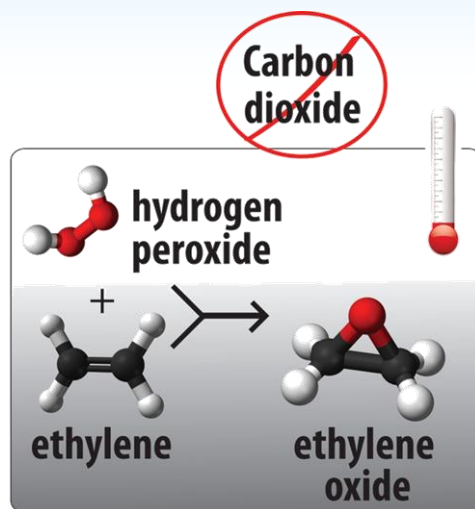


www.dechema.de/dechema\_media/Chemical\_Roadmap\_2013\_Final\_WEB-p-4584-view\_image-1-called\_by-dechema2013-original\_site-dechema\_eV-original\_page-136220.pdf



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## Recent CEBC Alternate Technology



Rhenium (MTO) catalyst, 50 bar, 35°C, methanol

\*M. Ghanta, et al., *Ind. Eng. Chem. Res.*, 2012, **52**, p:18-29

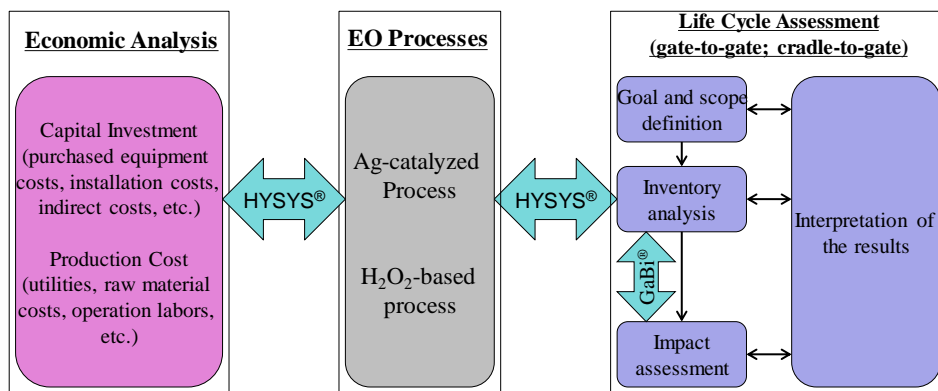
**Eliminates**  
CO<sub>2</sub> emissions  
**Conserves**  
resources

### Downside

- expensive catalyst
- Cradle to gate LCA shows total GHG emissions not better than conventional process if H<sub>2</sub>O<sub>2</sub> production included

**Need to do better**

## Economic and Environmental Impact (LCA) Assessments



## CEBC H<sub>2</sub>O<sub>2</sub> Process can be Cost-competitive

Economics already on par with conventional process, and projected to cost **17%** less with use of the following:

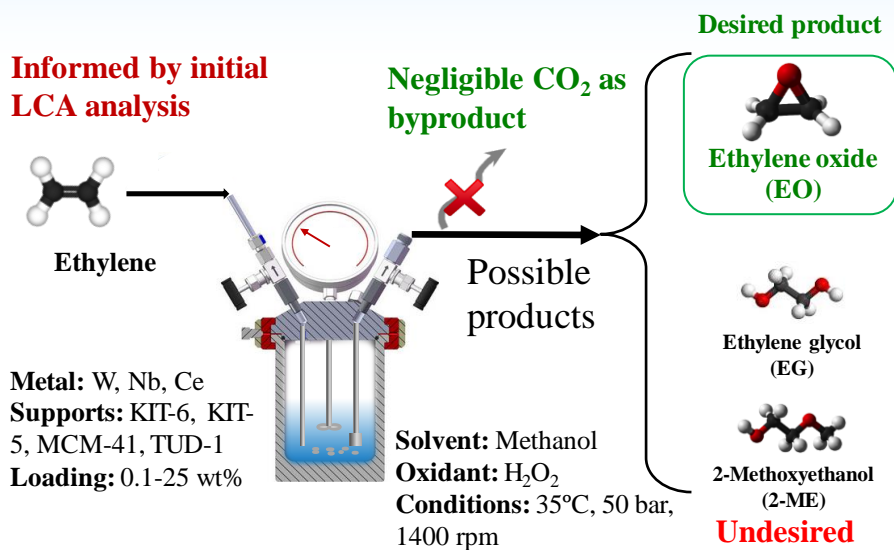


Would also lead to 25% reduction in GHG emissions (LCA)

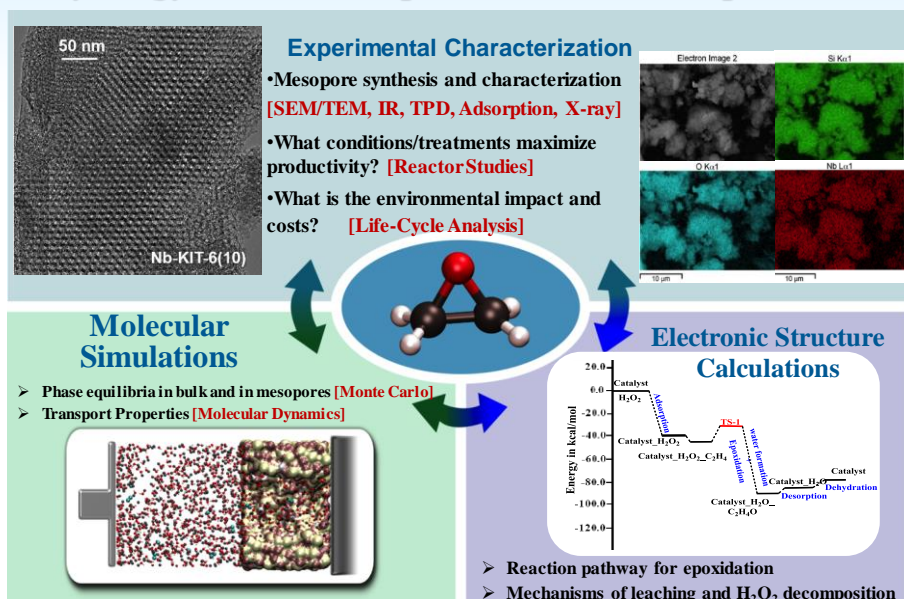




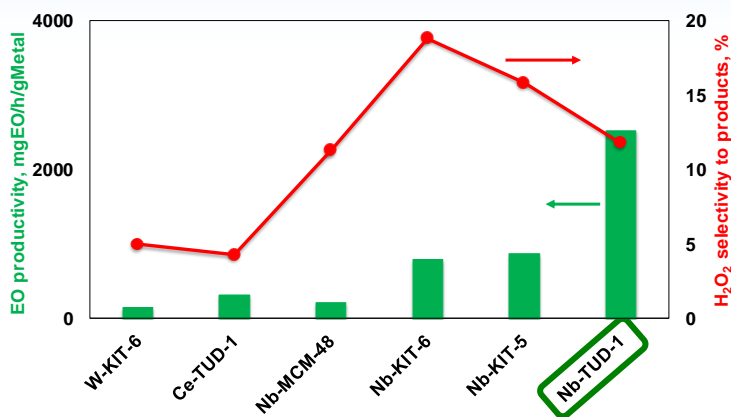
## New Process: Selective Ethylene Epoxidation Over Metal Incorporated Mesoporous Catalysts



## Synergy Between Experiment and Computation

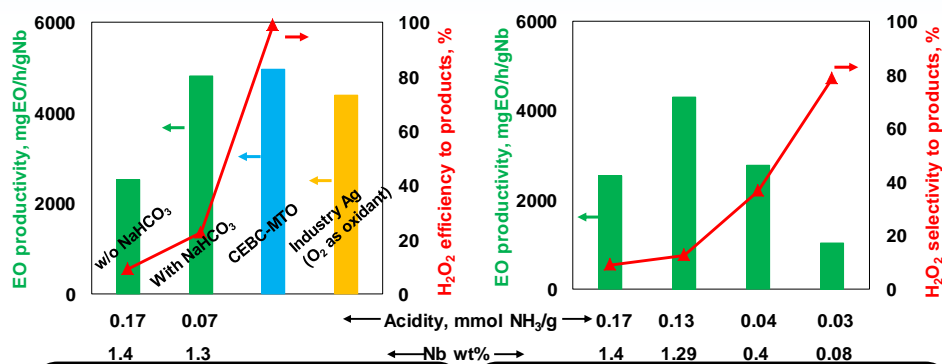


## Mesoporous Catalysts are Active but Decompose $\text{H}_2\text{O}_2$



- **Nb-TUD-1** showed highest activity.
- **Problems: Metal leaching and  $\text{H}_2\text{O}_2$  decomposition**
- **Is catalyst acidity the main reason of  $\text{H}_2\text{O}_2$  decomposition?**

## Lowering Acidity to Enhance Performance in Nb-TUD-1



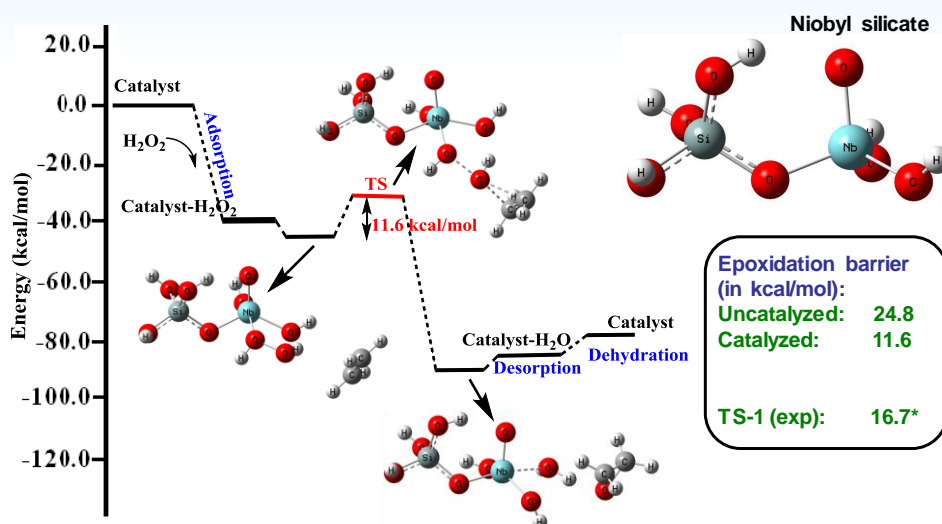
### **$\text{NaHCO}_3$ pretreatment:**

- EO productivity: 4819 mgEO/h/gNb
- $\text{H}_2\text{O}_2$  selectivity to products: 22.4%
- $\text{H}_2\text{O}_2$  decomposition significant

### **Lower Nb loading:**

- EO productivity: 1041-4304 mgEO/h/gNb
- $\text{H}_2\text{O}_2$  selectivity to products: 9.1-78.7%
- Metal leaching a problem

## Reaction Profile for Model Nb-silica Catalyst



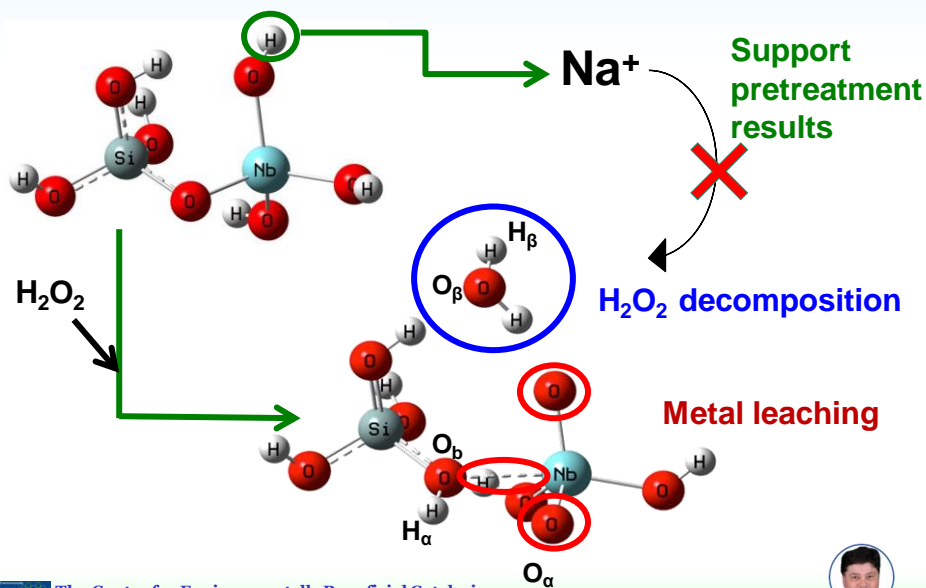
The calculations done using M06-L/aug-cc-pVDZ method and LANL2DZ basis set for Nb  
 \* A. van der Pol, J.H.C. van Hoof, Appl. Catal. A 106 (1993) 97.



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## Modeling Brønsted Acid Sites: Niobium hydroxide



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## Ongoing and Future Work

### Experiment:

- To counter metal leaching: use  $\text{CH}_3\text{OH}$  as solvent for  $\text{H}_2\text{O}_2$
- Explore other coordination motifs for Nb catalyst

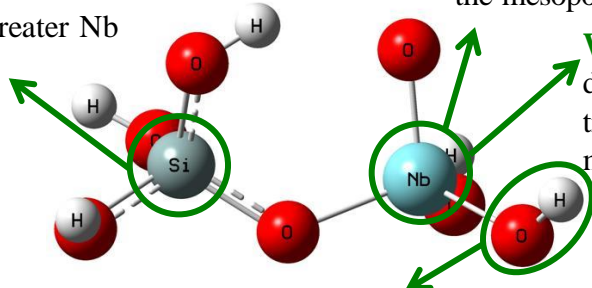
### Modeling:

**Nb:** High metal loading: greater Nb wt%

**SiOH:** model only the mesopore

**W:** effect of different transition metals

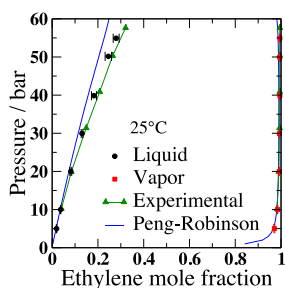
**SiH<sub>3</sub>:** increasing structural complexity: QM/MM approach



## Understanding Phase Equilibria and Transport Properties of Mesopore Catalysis

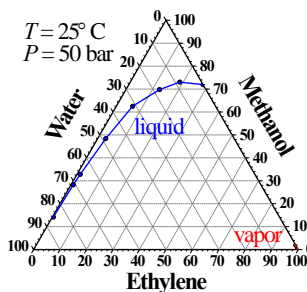
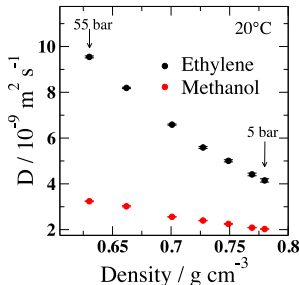
- Reactant/product mixture inside pore not accessible experimentally → modeling
- Monte Carlo (MC) and molecular-dynamics (MD) simulations on bulk to validate force fields.
- Ethylene concentration and transport favorably tuned by pressure

### Phase Diagrams



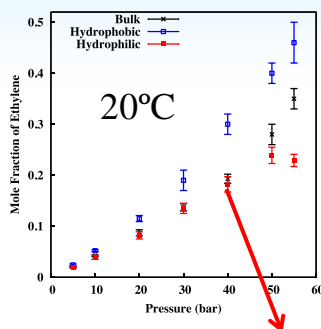
MeOH/ethylene binary

### Transport



Ternary

## Modeling of Reactant Mixture in Pore

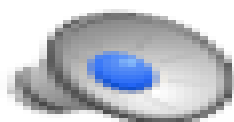


**Initial test:** MC simulations of  $C_2H_4/MeOH$  mixture in series of model amorphous  $SiO_2$  pores

- Surface chemistry modulates  $C_2H_4$  mole fraction

**Towards the full system:** 5-component mixture ( $C_2H_4$ , MeOH,  $H_2O_2$ ,  $H_2O$ , EO) in metal -doped pore

- MD simulations on pore/bulk equilibrium



Red: Ethylene

Blue: Methanol

Filled surface: Mesopore (cutout) with color representing atom charge

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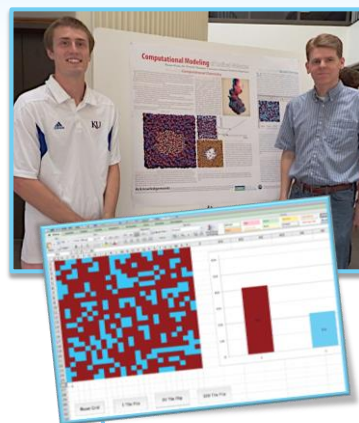
## Education and Outreach: Adding Value to Our NSF-RET Program



44 participants since 2009, 12/summer includes science teachers and undergrads training to become teachers

[cebc.ku.edu/research-experience-teachers](http://cebc.ku.edu/research-experience-teachers)

- NSMDS funding adds 2 undergrads to the 6-week program. Students gain insights from RET participants about how to communicate science and turn research into lessons/lab activities
- Teachers in the RET program gain technical advice from undergrads and learn about green chemistry and engineering from faculty to include in the new lessons they create for their students



While working with Prof. Thompson, an undergrad developed an algorithm about entropy (i.e., "coin flip" spreadsheet)

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## Community Outreach



### Carnival of Chemistry

Graduate students and staff from NSMDS team hosted hands-on activities for >500 children and their families at KU's annual Carnival of Chemistry. Activities highlighted how catalysts work and how green engineering can reduce environmental impact of chemical manufacturing.



## Concluding Remarks

- ***Emerging feedstocks*** (biomass, shale gas) provide exciting challenges for developing novel technologies with reduced environmental footprints
  - Potential game changers for the US chemicals industry
- Multi-scale approach that benefits from expertise of chemists and engineers to concurrently address all process elements (catalyst, reaction mechanisms, reactors, etc.) expedites discovery of ***resource-efficient*** technologies
- Quantitative ***sustainability assessments*** (economic, LCA) are powerful tools in guiding R&D toward practically viable processes
- ***University/Industry/Government partnerships*** that engage stakeholders across the entire value chain key for timely technology commercialization with emerging feedstocks





# Thank You!



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**Anthony Rappé**  
Professor of Chemistry,  
Colorado State University



**Brian Laird**  
Professor of Chemistry,  
University of Kansas



**Joseph Fortunak**  
Professor of Chemistry,  
Howard University

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