Design and Optimization of Catalysts: Using Modeling to Improve Performance

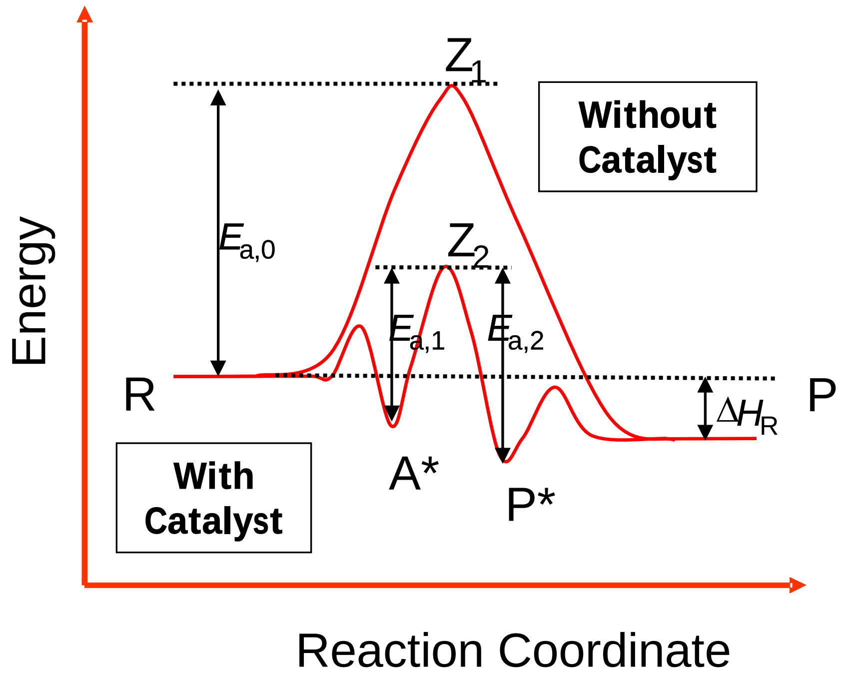
George Fitzgerald
Accelrys

Introduction

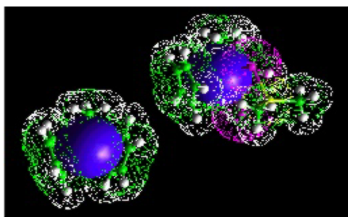
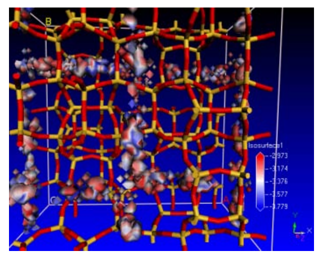
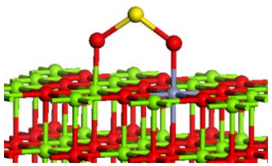
- Catalysis is critical to modern chemical industry
  - 60% of chemical products
  - 90% of chemical processes
  - Responsible for $2 billion/year in product sales
- Drivers for improvement
  - Rising cost of energy
  - Rising cost of feedstock
  - Environmental regulation
- The role of modeling
  - Obtain results faster and cheaper
  - Explore broader range of material
  - Gain insight at the atomic level

Catalysis from a QM Point of View

- Catalyst lowers the reaction energy barrier, increases rate
- Thermodynamics unchanged
- Modeling can provide
  - Reaction energies ΔH_R
  - Energy barriers E_a
  - Location of intermediates
- Modeling allows you to explore *in silico*
  - Effect of catalyst composition
  - Effect of poisons or promoters
  - Efficiency of catalyst for alternative **R**



Areas of Catalysis Modeling

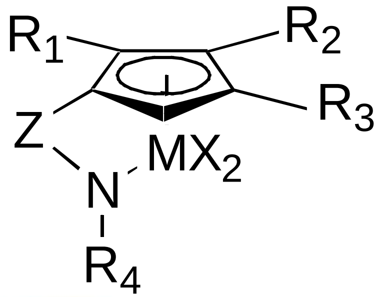
Homogeneous	Heterogeneous: Zeolites	Heterogeneous: Surfaces
		

Roles of modeling:

- Identify catalysts
  - Catalytic material
  - Mechanism
  - Active sites
- Optimize catalyst
  - Increase yield and/or specificity
- Optimize processes
  - Diffusion
  - Deactivation

Homogeneous Catalysis

- Design and optimization of homogeneous catalysts such as metallocenes
- Typically designing ligands for
  - Control of activity
  - Control of molecular weight
  - Control of tacticity
- Modeling has played a significant role in improving processes, generation of patents, gaining understanding



M= metal, such as transition metal

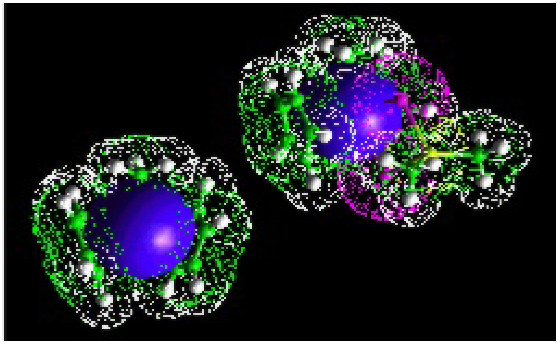
Z= bridging group such as SiR_2, C_2H_4

X = halide, CH_3

Olefin Polymerization via Metallocene Catalysis

Problem:

- Catalytic efficiency of metallocenes depends upon choice of metal, ligand, concentration of co-catalyst
- 2 forms of catalyst exist: cationic & bimetallic
- Reaction mechanism is poorly understood
- How to produce optimal catalyst?



Solution:

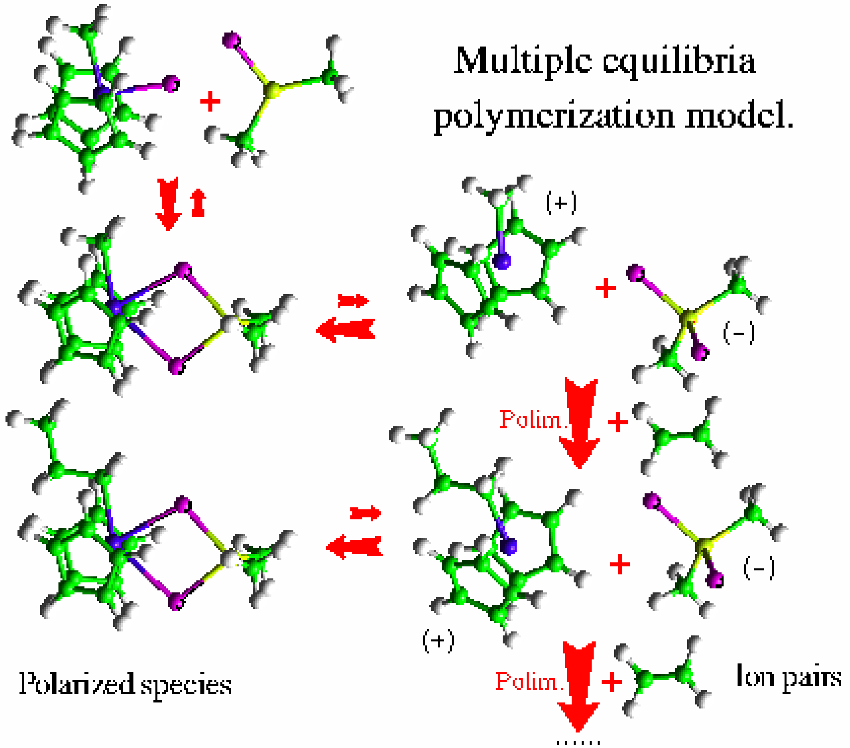
- Study both cationic vs. bimetallic forms with *theory and experiment*

"The multidisciplinary effort discussed here allowed our molecular modeling group … to contribute substantially to the deposit of patents…"
Drs. Longo, Fusco, & Accomazzi, EniChem

Fusco, R. & Longo, L, *Macromol. Theory Simul.*, **3**, 895 (1994)

Polymerization Model

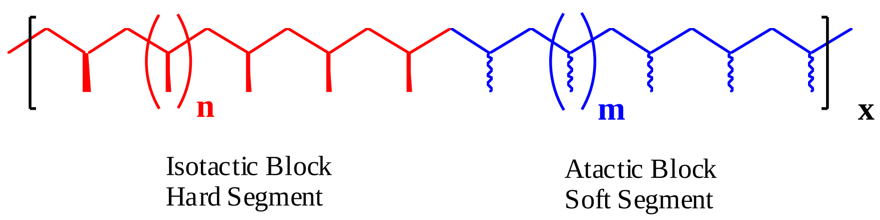
- Experiment
  - ^{1}H and ^{13}C NMR to identify species
  - Mass spec to study interaction of ionic catalyst + ethylene
  - EPR to identify deactivation mechanism
- Computation
  - Binding energies
  - Activation barriers
  - Comparison of reaction pathways for multiple metals, co-catalysts
- Understanding of mechanisms, working in conjunction with experiment led to
  - Understanding of mechanism
  - Several patents
  - Improved catalysts

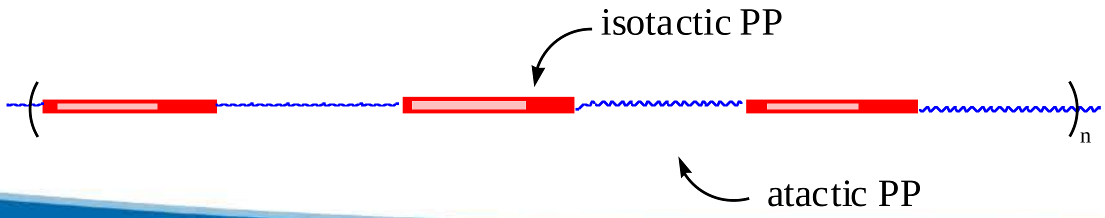


R. Fusco and L. Longo, *Macromol. Theory Simul.*, **3**, 895 (1994)

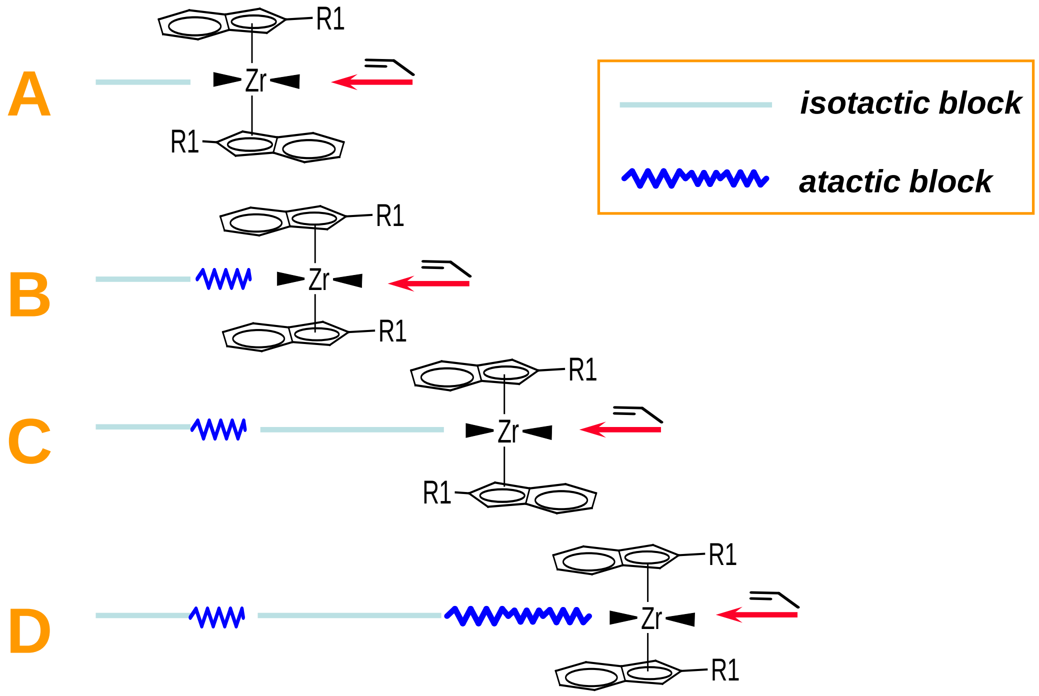
EHPP

- Elastomeric homopolypropylene
  - A rubbery form of polypropylene
  - Composed of alternating blocks of isotactic (hard) and atactic (soft) PP in the same polymer chain
- Applications in
  - Nonwovens for Diapers
  - Films for Diaper Components
  - Medical Tubing (PVC replacement)
  - Medical Film and Food Packaging





Stereoblock Polypropylene



- *Substituent orientation leads to high isotactic vs. syndiotactic*
- *Unique opportunity for control: different polymers can be made by controlling side groups*
- *Isotacticity (% mmmm) very sensitive to K_{eq}*
  ⇨If we can compute K_{eq}, we can predict isotacticity

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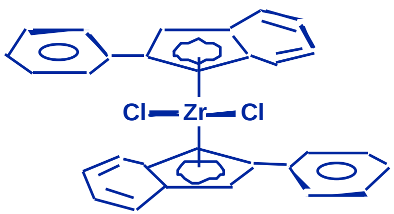
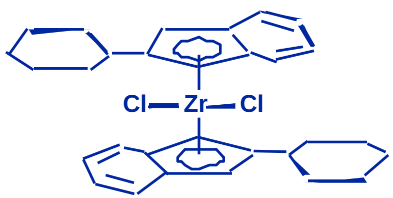
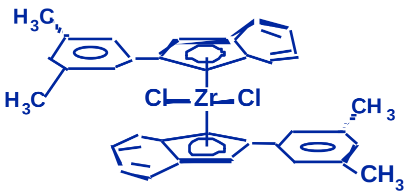
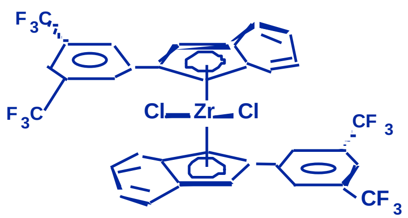
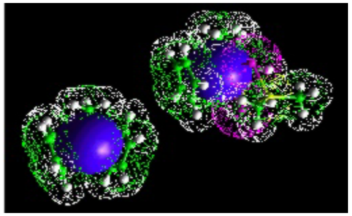
Prediction vs. Experiment: Excellent Correlation

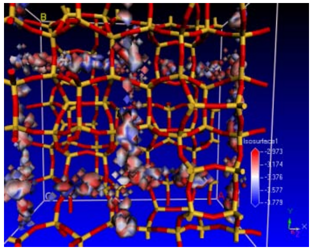
Metallocene	$E_{iso} - E_{atactic}$ (kcal/mol)	Predicted polymer type	Observed polymer type	Predicted %mmmm	Observed %mmmm
	-0.92	elastomeric	elastomeric	medium	39%
	+1.6	atactic	atactic	low	12%
	-0.29	elastomeric	elastomeric	medium	31%
	-5.3	isotactic	isotactic	high	75%

Areas of Catalysis Modeling

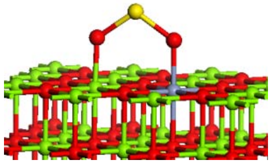
Homogeneous



Heterogeneous:
Zeolites



Heterogeneous:
Surfaces



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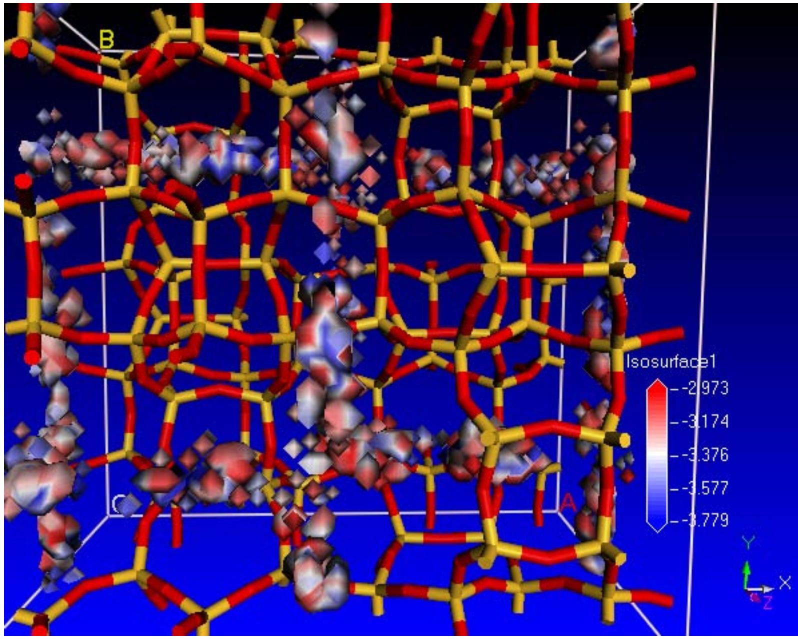
Adsorption & Catalysis in Microporous Materials

- Properties of zeolites determined by
  - Pore size
  - Acidity
  - Extra framework cation
  - Framework composition
- Simulation reveals
  - Locations of adsorption sites
  - Interaction energies
  - Diffusivity of molecules in the pores
- Simulation provides a way to correlate these microscopic properties with observed activity

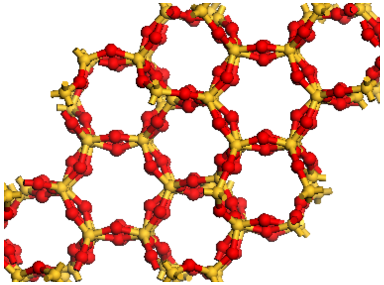


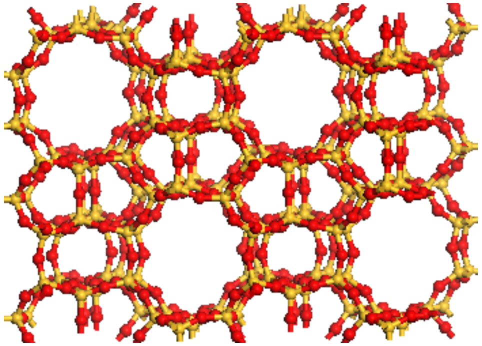
Adsorption of an organic molecule in zeolite MFI.

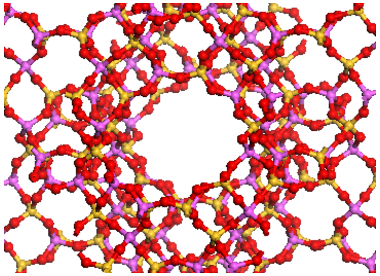
Preferred adsorption sides are colored blue

Shape Selectivity vs. Activity

- Controlling selectivity in hydrocracking in zeolites (Benazzi, et al., *J. Catal.* **217**, 376 (2003))
- Compare cracking vs. isomerization
- Activity increases with acidity, but…
- No correlation with selectivity
- Adsorption energy inversely proportional to pore size
  - Small pore, high energy → cracking
  - Large pore, low energy → isomerization
- Modeling helps guide you to the best material based on rules, trends, correlations deduced from results







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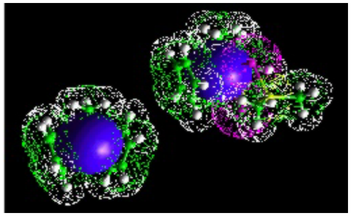
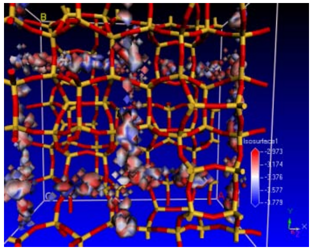


Heterogeneous: Zeolites



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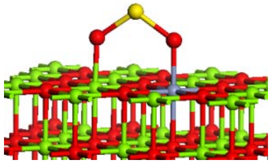

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DeSO$_x$ Catalyst Design using Simulation

- Background
  - SO_2 is a major air pollutant arising from sulfur in fuels
  - Causes acid rain with negative impact on ecosystem, human health and buildings and monuments
- Oxides can be used to catalyze DeSOx reactions
  - Key goal is activation of the S-O bond in SO_2
  - Simulations and experiments have been used to understand the chemistry of SO_2 on oxide surfaces

Claus reaction

$$2H_2S + SO_2 \rightarrow \quad 2H_2O + 3S_{solid}$$

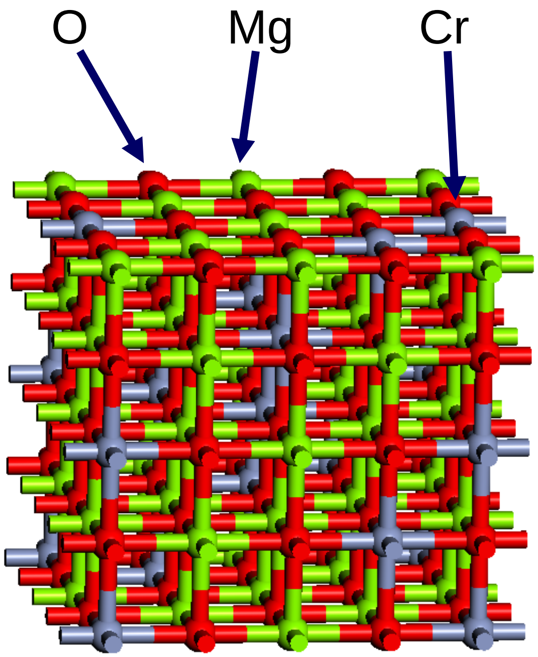
Reduction of SO_2 by CO

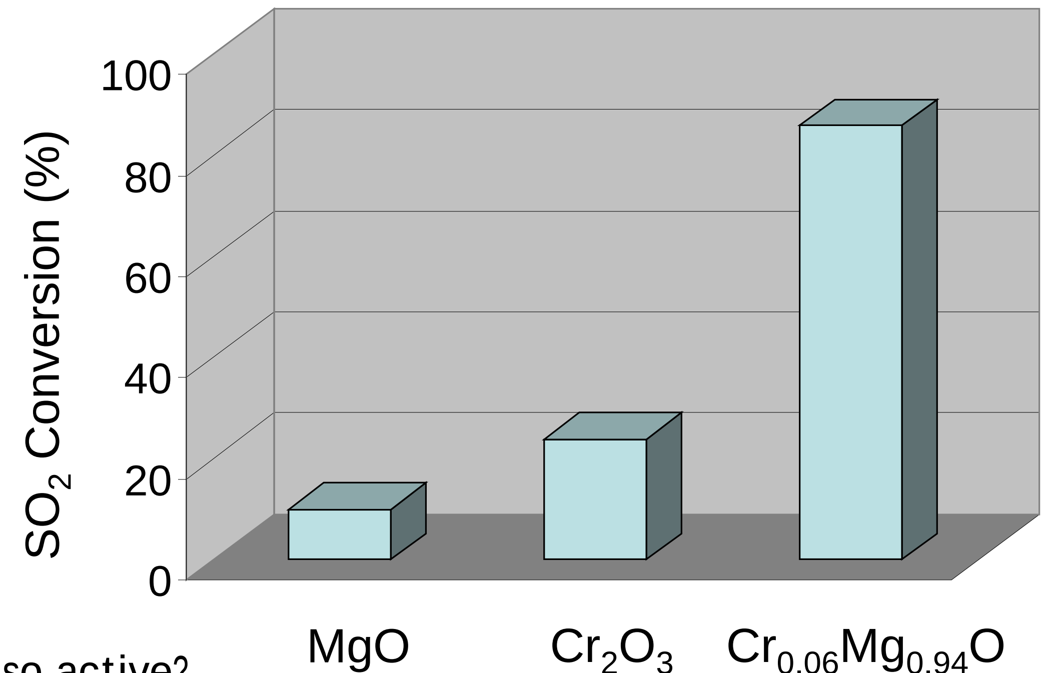
$$SO_2 + 2CO \rightarrow \quad 2CO_2 + S_{solid}$$

J. A. Rodriguez *et al.* JACS, **122**, 12362 (2000).

DeSOx Catalyst Design

$SO_2 + 2CO \rightarrow 2CO_2 + S_{solid}$ @ 500 C



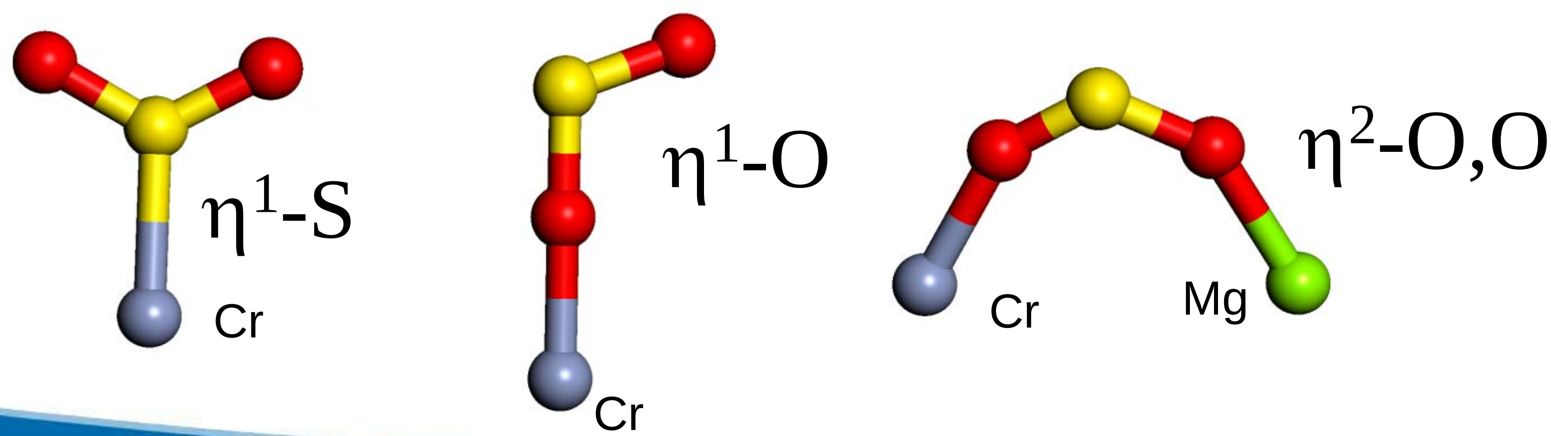


- Why is $Cr_{0.06}Mg_{0.94}O$ so active?
- What metal could be used to replace Cr?
  - Health hazard, environmental impact, cost

Calculation of SO_2 Adsorption on Surfaces

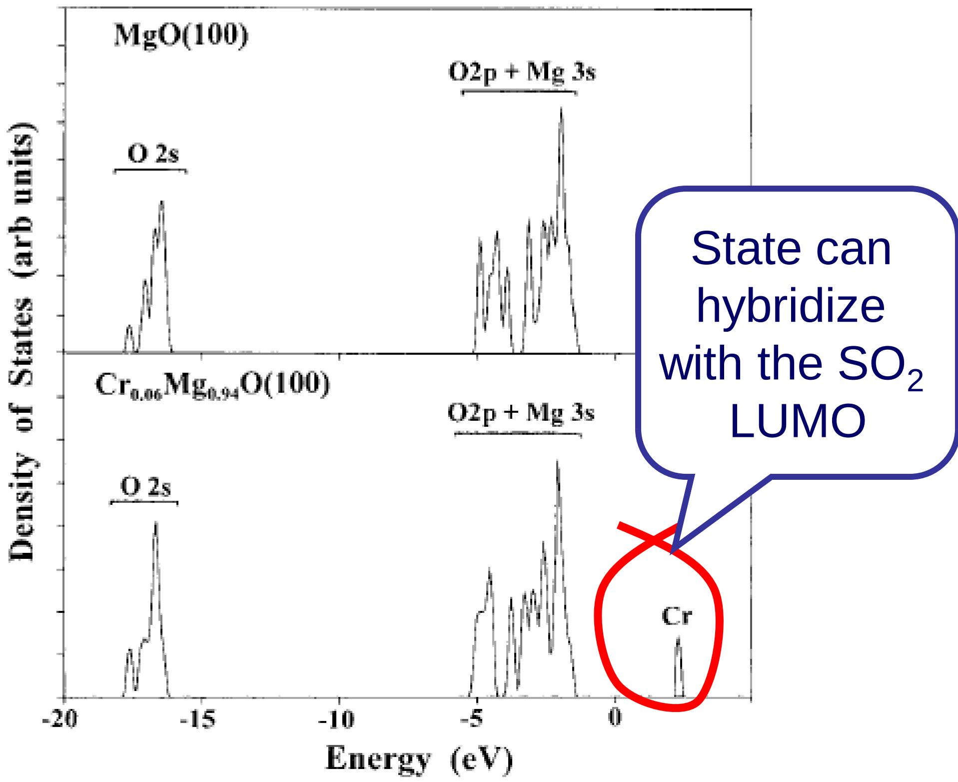
	bond lengths (Å)			ads energy
	metal–O[b]	metal–S[b]	S–O	(kcal/mol)[c]
free SO_2			1.43	
on MgO(100)				
η^1-S	not bound to this surface			
η^1-O	2.40		1.44(1.43)	
η^2-O,O bridge	2.41		1.45	
on $Cr_{0.06}Mg_{0.94}O(100)$				
η^1-S		2.27	1.48	
η^1-O	2.08		1.53(1.46)	
η^2-O,O bridge	2.03		1.54(1.48)	

Activation of S-O bonds



Origins of SO_2 Activation

- $Cr_{0.06}Mg_{0.94}O$ is a good catalyst for the reduction of SO_2 by CO because
  - Occupied electronic states appear well above the valence band edge of MgO
  - The Cr atoms in $Cr_{0.06}Mg_{0.94}O$ are in a lower oxidation state than the atoms in Cr_2O_3



Design rule that can now be applied to look for alternative dopants to chromium!

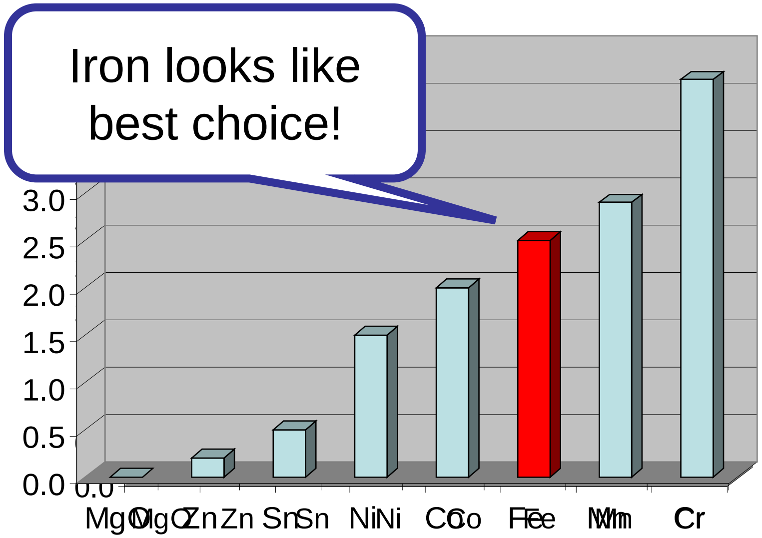
How can Cr be replaced?

- Candidates to replace Cr: Mn, Fe, Co, Ni, Zn & Sn
- INMATEL rank according to non-chemical factors

Mn < Ni < Co < Sn < Zn < Fe

Worst Best

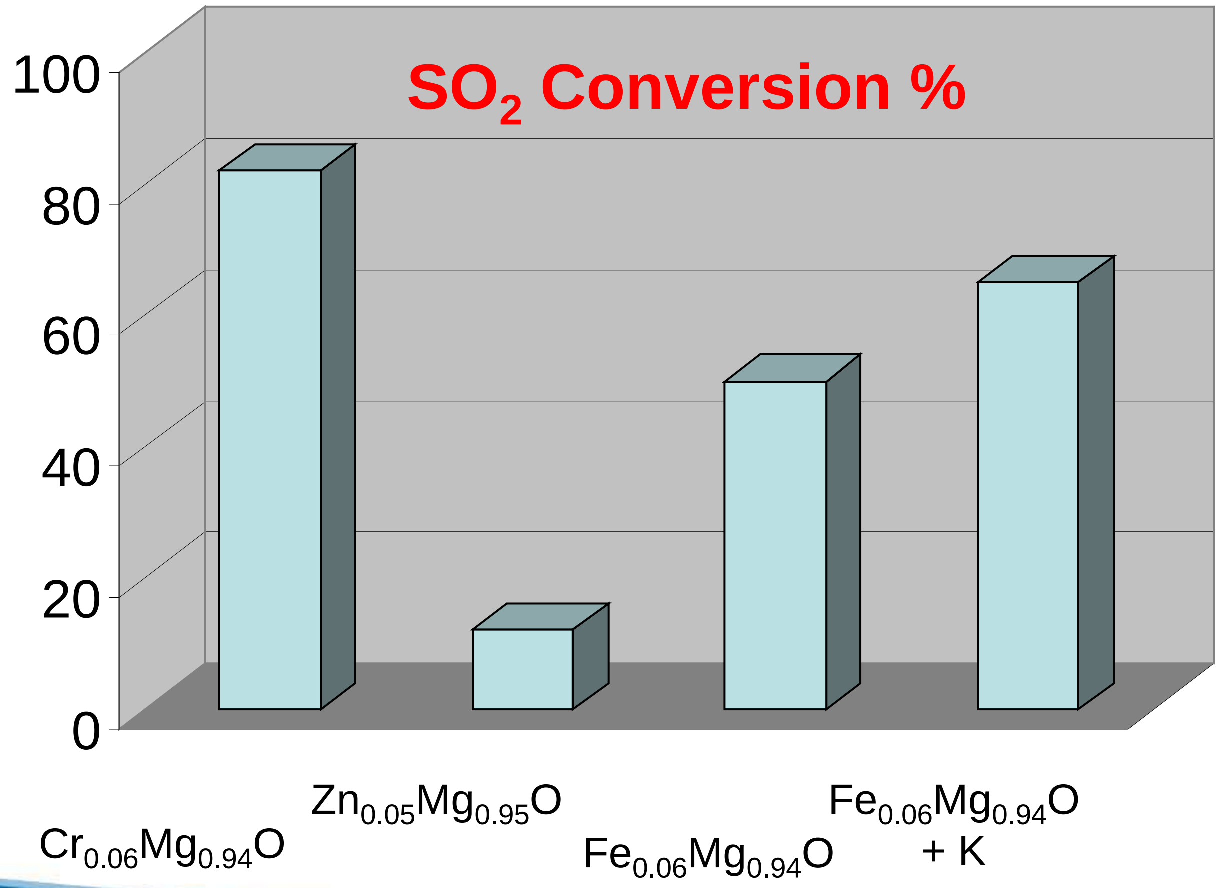
- Approach: compute electronic structure and measure dopant level position above Valence Band (VB) edge



Dopant position above VB edge in eV

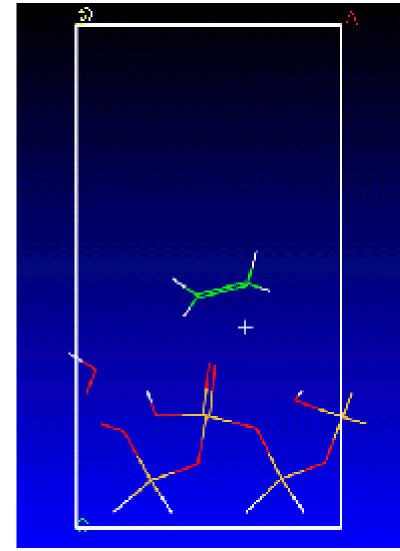
Catalyst Test at INMATEL

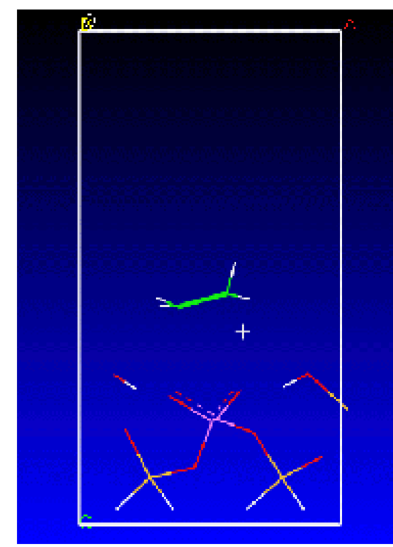
$SO_2 + 2CO \rightarrow 2C_2O + S_{solid}$ at 500 C



Effect of Surface P on ODH Over SiO_2
Predicting behavior of new materials

- ODH offers low-energy alternative to C_2H_4 production
  - $2\ C_2H_6 + O_2$ à $2C_2H_4 + 2H_2O$
- SiO_2 is a model catalyst for ODH
- Insertion or substitution of P increases %conversion
- Theory provides
  - First principle prediction of this
  - Complete reaction mechanism
  - Understanding of the role of penta-valent P
- Once mechanism is established, performing “what if” tests is easy!





A. Maiti, et al., *J. Chem. Phys.* **117**, 8080 (2002)

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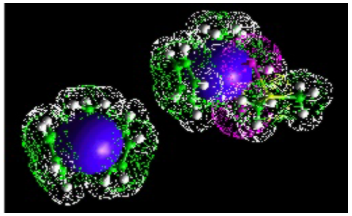
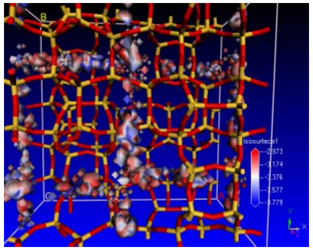


Heterogeneous: Zeolites



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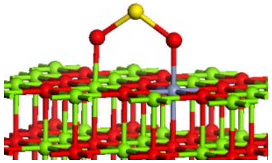

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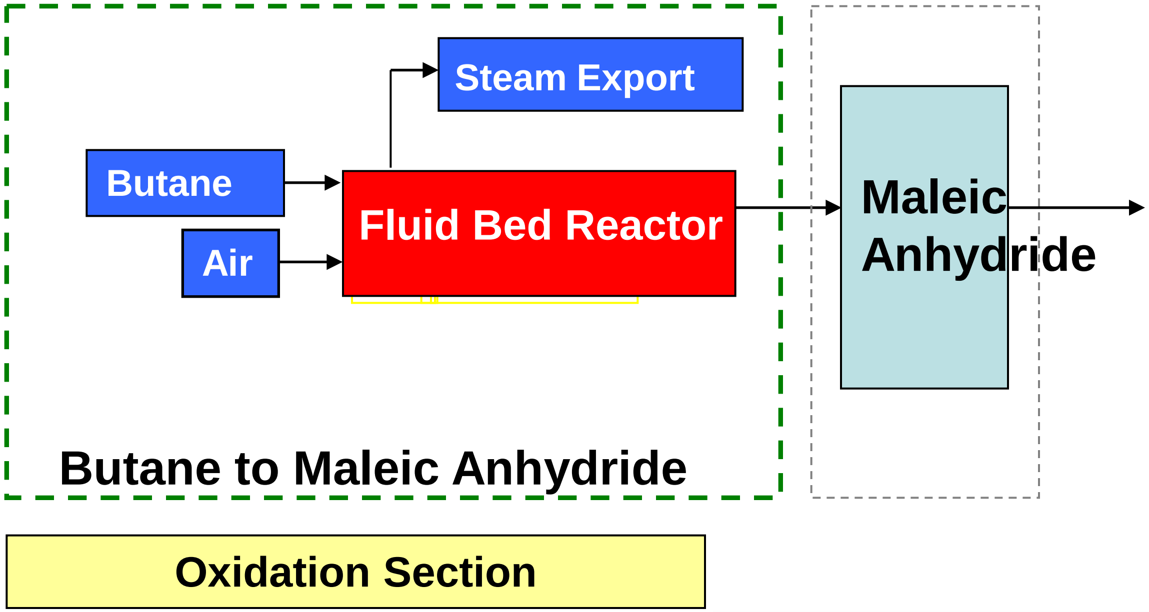
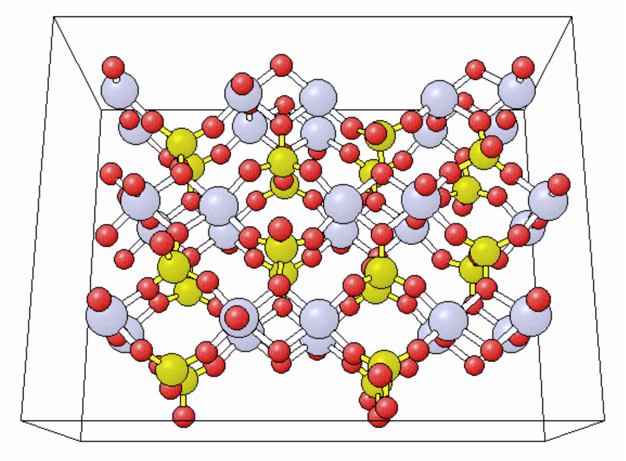
Learning More from UV-Visible Spectroscopy & The Role of Defects in Selective Propane Ammoxidation: **Modeling Defects in Vanadyl Pyrophosphate**

Gerry Zajac, Innovene USA LLC, Naperville, IL 60563

BP's Maleic Anhydride Technology



- Fluid-Bed Catalyst
- Single Phase Material
- No Added Hardening Agent
- 100 % Vanadyl Pyrophosphate (VO)2P2O7



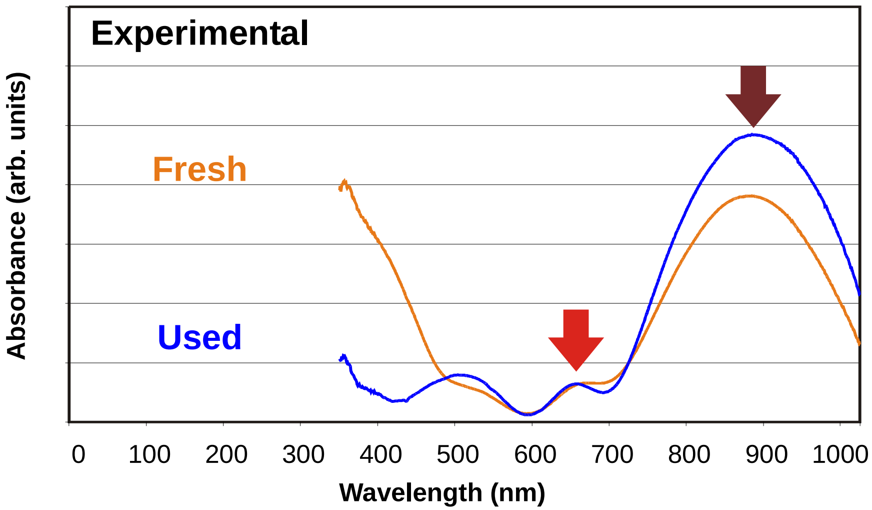
$(VO)_2P_2O_7$ is key to Maleic Anhydride Manufacture

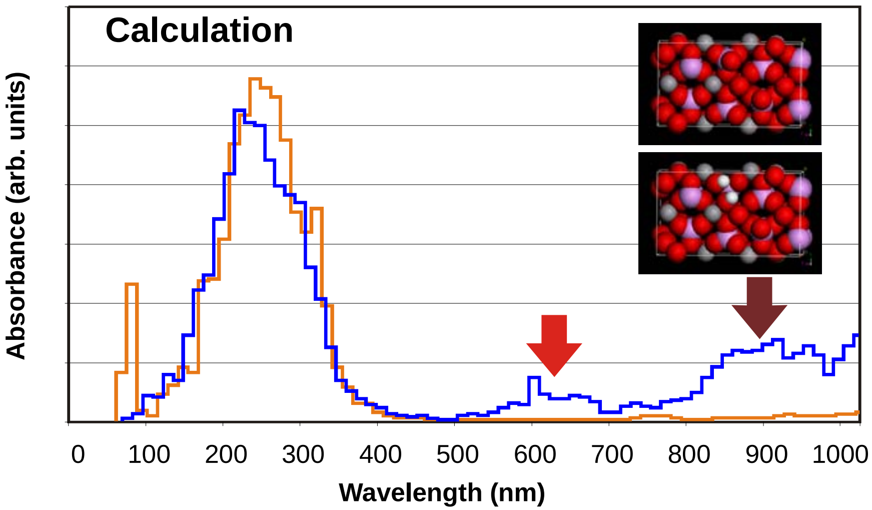
- Catalyst Activation is well understood:

  $2\ VOHPO_4 \rightarrow (VO)_2P_2O_7 + H_2O$

- What happens during Catalyst Deactivation?
  - Known that Phosphorous is lost
  - Analytical measurements show changes in XPS, UV
  - But structure of deactivated catalyst, deactivation mechanism are not known
- What is the structure of deactivated Vanadyl Pyrophosphate?

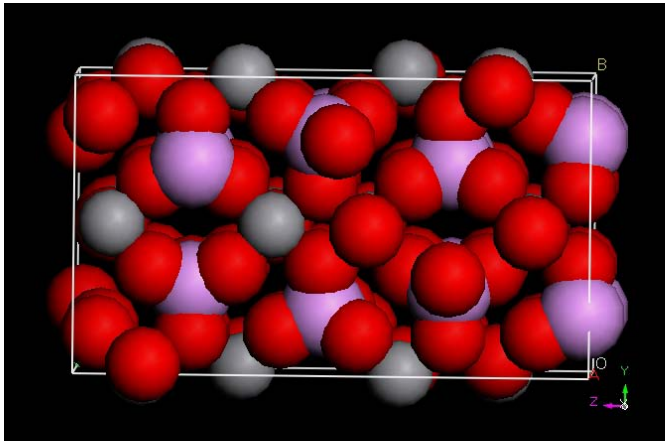
UV-VIS Absorption $(VO)_2P_2O_7$



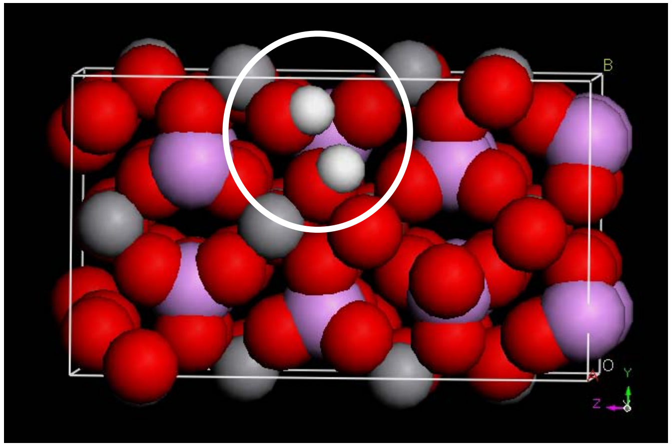


- Spectrum provides a fingerprint of active vs. deactivated catalyst
- Compute spectrum for several hypothetical deactivated structures
- Continue until match between computation & experiment
- Not blind guessing:
  - Loss of P is know from elemental analysis
  - Shift of XPS to lower energy O_{2s} energy implies loss of PO_2

Vanadyl Pyrophosphate Unit Cells



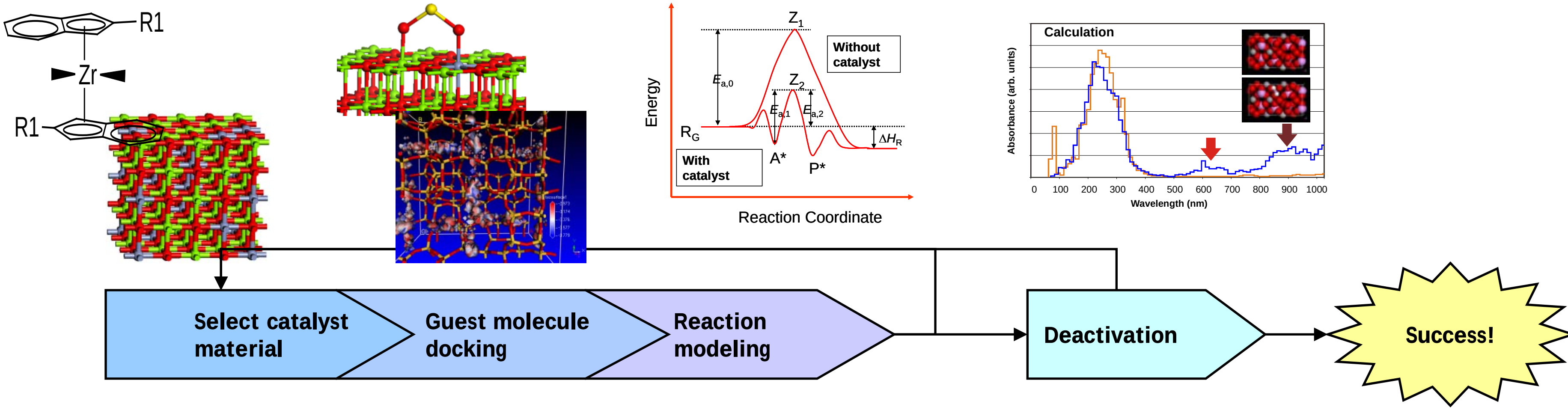
Vanadyl Pyrophosphate Unit Cell



Vacancy Model - Loss of PO_2^+

- Deactivation of $(VO)_2P_2O_7$ corresponds to loss of PO_2^+
- Experimental evidence of these defects by XPS and UV-visible spectroscopy
- Computation can be used to verify detailed crystal structure of deactivated material
- Future: Can we determine the mechanism and how to prevent it?

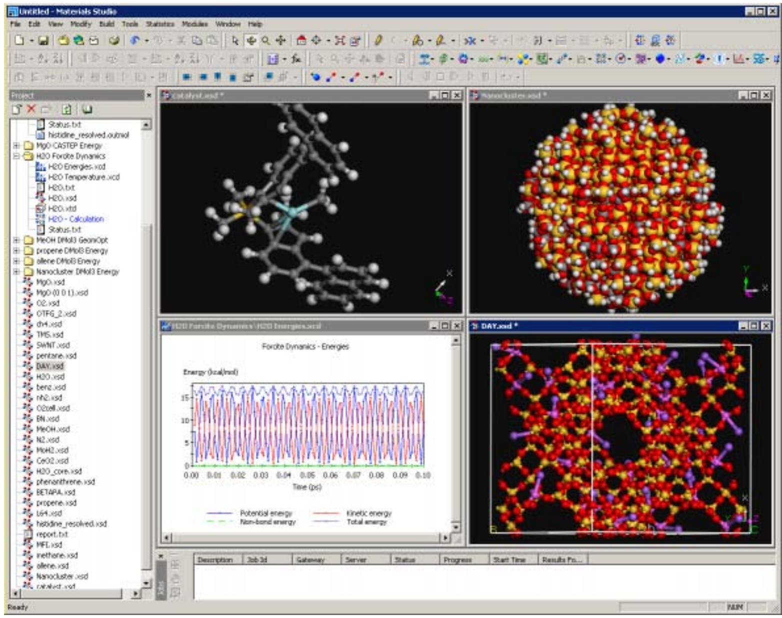
Iterate and Try Again



- Develop mechanistic understanding
- Create empirical model, e.g. QSAR
  - Create a function to predict properties in terms of “descriptors”, e.g., solubility, binding energy, molecular surface area
- Determine values of descriptors that yield optimum behavior, and use corresponding materials
- Refine the model as you test each new material

Software for Modeling

- Adsorption and docking of molecules
  - Use empirical force fields
  - Fast but approximate calculations
  - Typically require $\approx 10^6$ conformations
  - Programs: Forcite, COMPASS, Sorption
- Reactions, bond breaking
  - Require methods that use quantum mechanics
  - Accurate but time-consuming calculations
  - Programs: CASTEP, $DMol^3$
- Ease of use is essential: Materials Studio
- High-performance hardware is critical



Summary

- Modeling can be used to
  - Make prediction about catalyst performance
  - Understand reaction mechanisms
  - Provide information that lets you design better catalysts
- The examples here used modeling to
  - Model guest molecules in zeolites
  - Predict performance of a polymerization catalyst
  - Improving ODH performance with dopants
  - Find alternatives to using toxic Cr
  - Verify the structure of deactivated $(VO)_2P_2O_7$ catalyst