Workshop on a "Drug Discovery" Approach to Breakthroughs in Batteries

Introduction

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Purdue University
(Core expertise – heterogeneous catalysis)

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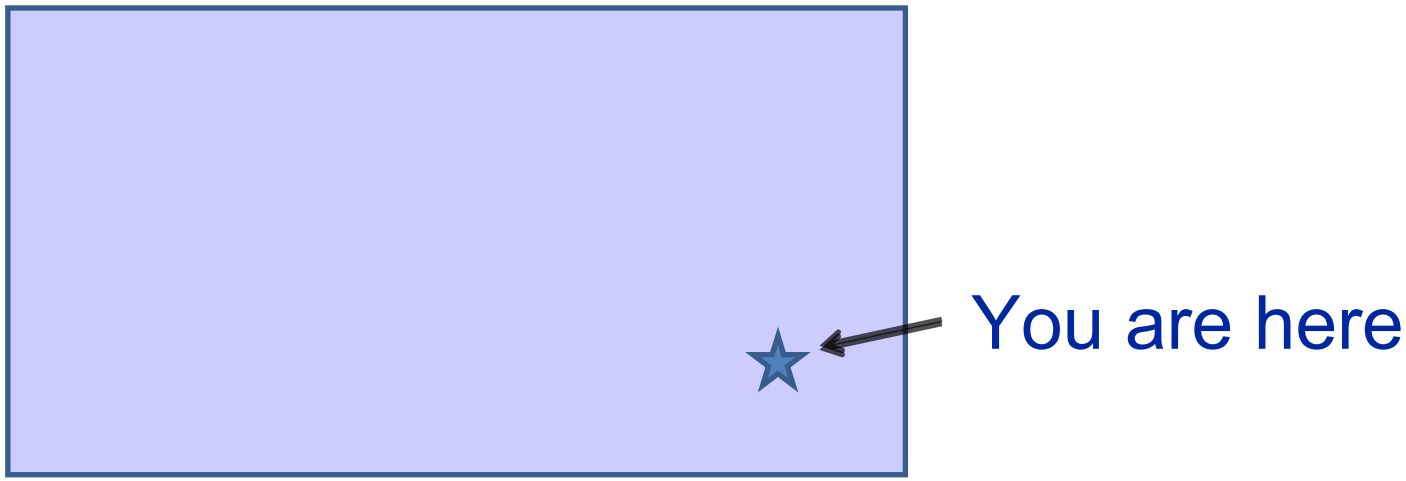
The Problem with Discovery

- **NOT business as usual**
- **Descriptor (search) space is huge – 10^6 – 10^{18}**
  e.g. elements of the periodic table 4 at a time



- **NOT only traditional scientific method**
- **Breakthrough means NOT an extrapolation from where you are. Need new approach.**

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Navigating Descriptor Space

- **Designed broad search – statistical analysis**
  Fast, helps identify descriptors
- **Model-based search – incorporate knowledge,**
  including fundamental
- **"Only" need better, not best, performance**
- **Intelligent search is an absolute necessity**
- **Need a lot of data (information)**

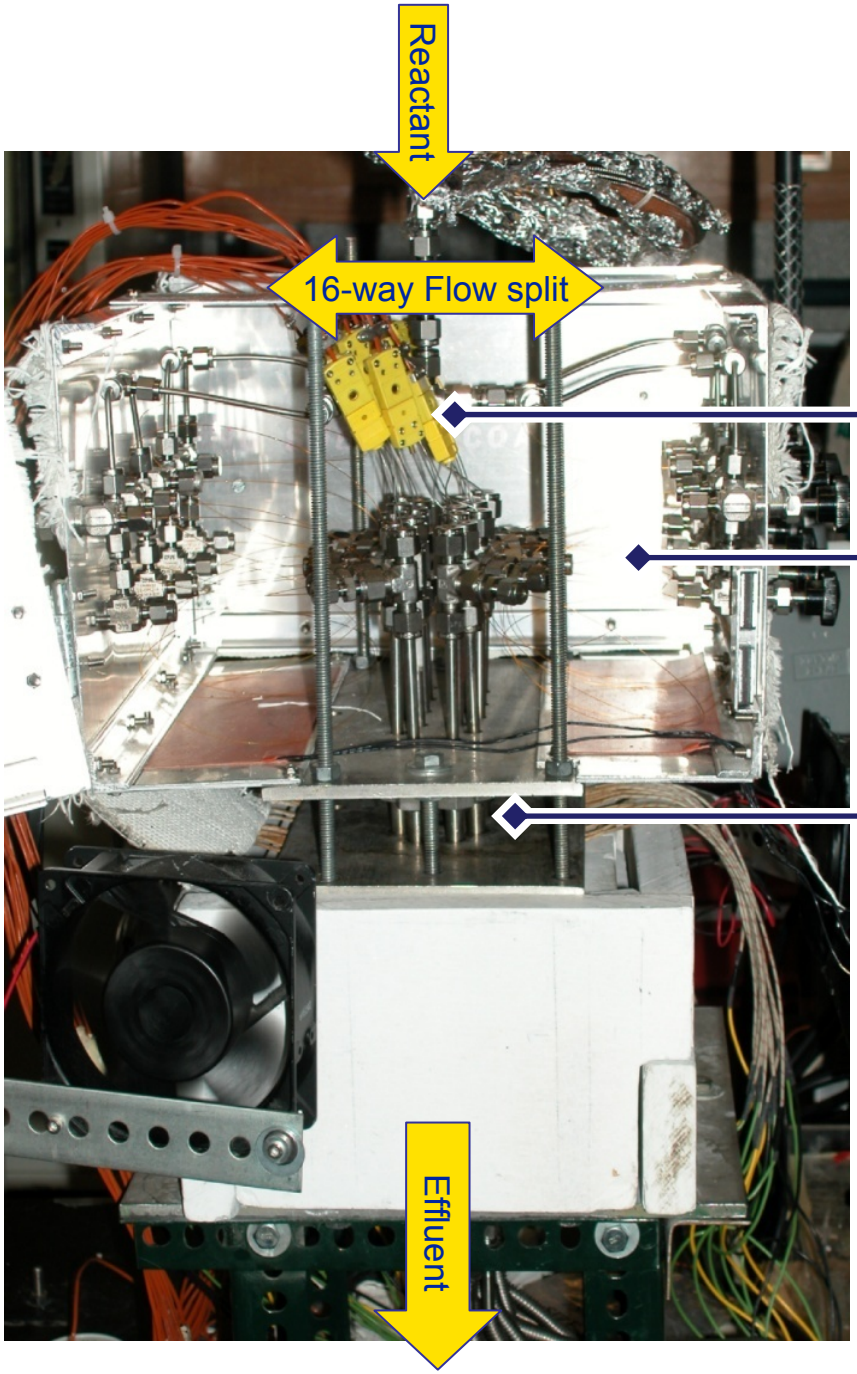
Navigating Descriptor Space

- **Experimental Data (parallel) - synthesis, performance, and materials characterization**
  - ***Primary*** **(high throughput, 1or 2 parameters)**
  - ***Secondary*****(lower data rate, more parameters)**
  - ***Tertiary*** **(lowest data rate, real conditions)**
- **Theory –**
  Guide or drive models, calculate descriptors, cover space not accessible to experiments
- **Informatics – Handling and using data**
  Searching, sharing, and archiving
  Tools for knowledge extraction, model building
- **TEAMS – Success requires all of the above**

Example
Search for a new catalyst

W. Pryz, R. Vijay, J. Binz, Jochen Lauterbach, and D.J. Buttrey, "Characterization of K-Promoted Ru Catalysts for Ammonia Decomposition Discovered Using High-Throughput Experimentation", *Topics in Catalysis*, 2008, online

High-Throughput - Reactor



Side view of Reactor
16 sample capacity

Individual temperature monitoring

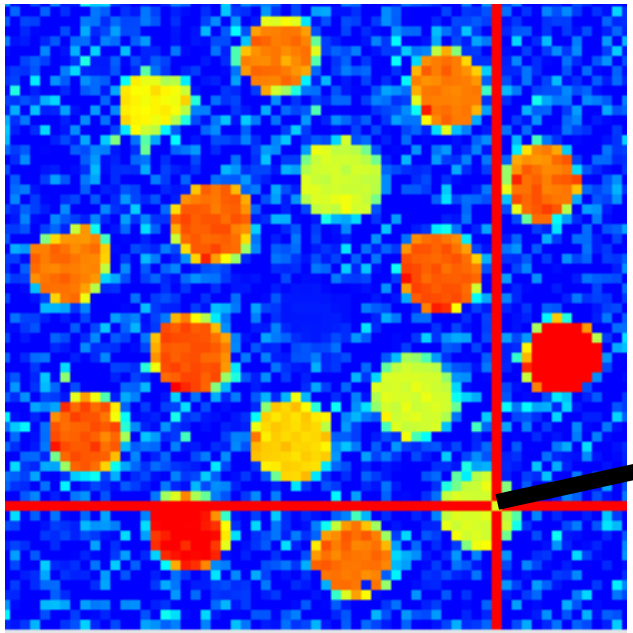
Capillaries

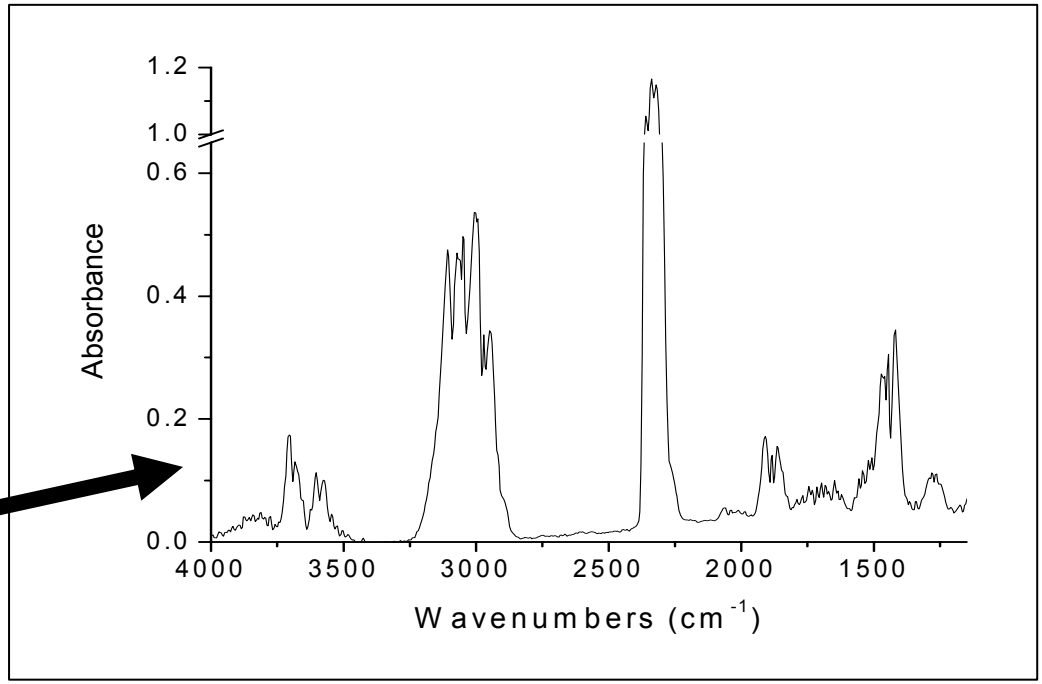
16 stainless steel reactor tubes

RJ Hendershot, et al, *Applied Catalysis A* (2003)

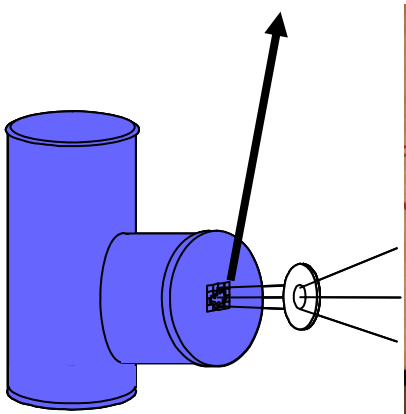
Truly Parallel Screening

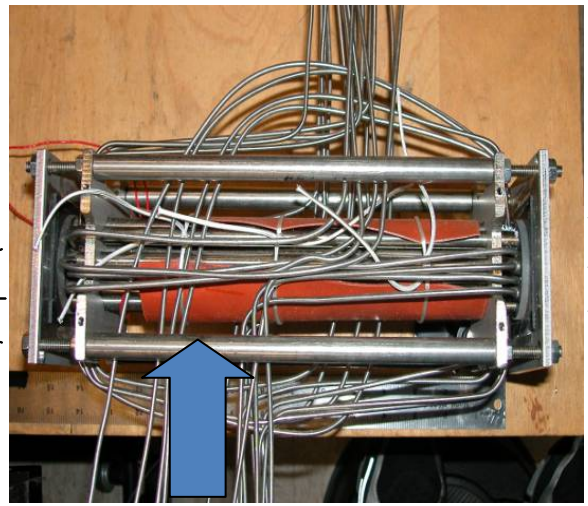
128 pixels



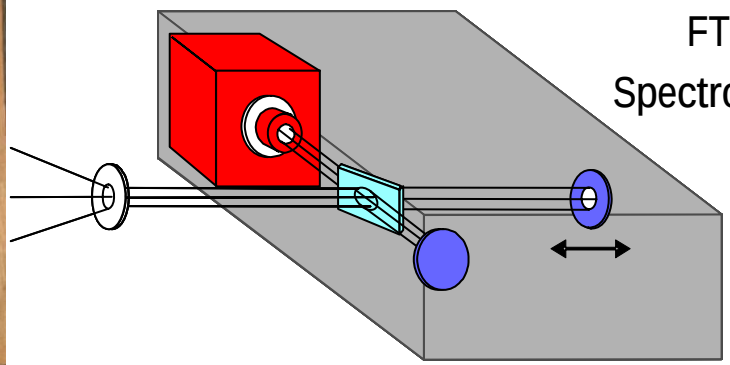


MCT FPA



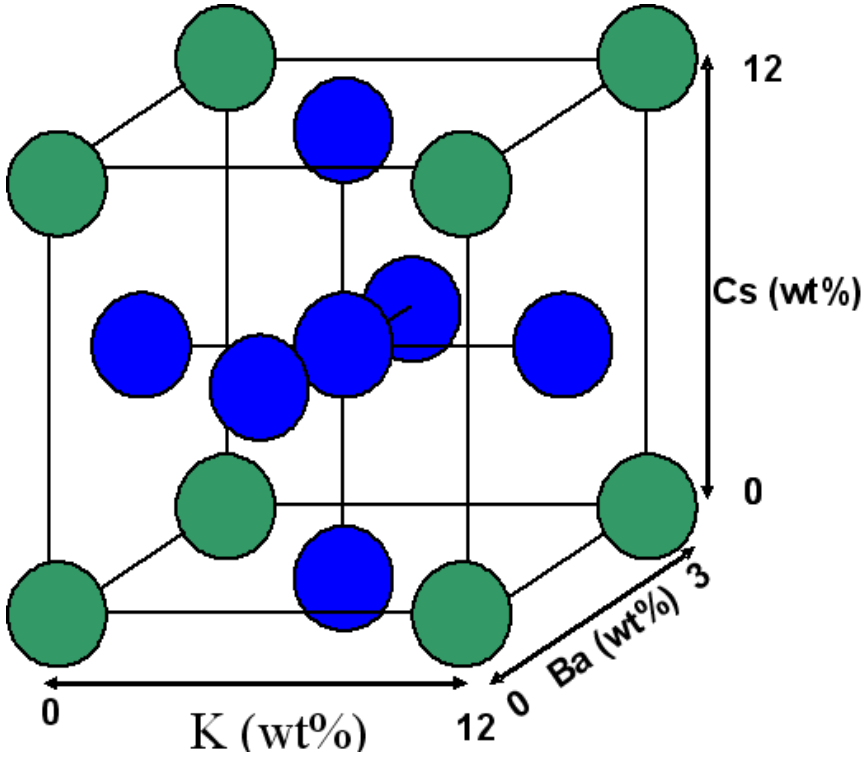


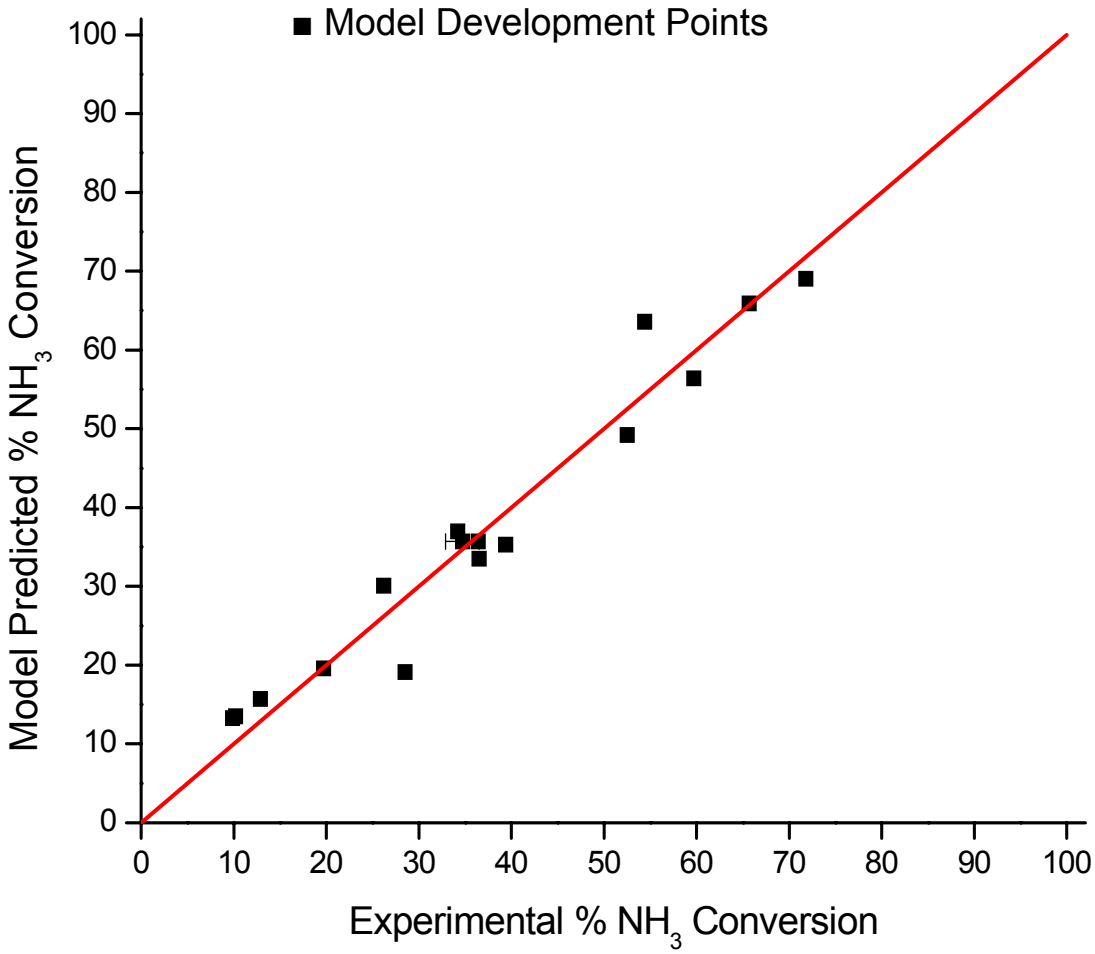
FTIR Spectrometer



C.M. Snively, G. Oskarsdottir, and J. Lauterbach, Angewandte Chemie, 40(2001)
Snively, C.M. and J. Lauterbach *Applied Spectroscopy* 59 (2005)
R. Hendershot, P. Fanson, C.M. Snively, and J. Lauterbach, Angewandte Chemie, 42(10); (2003).

The Next Step: Promotion of $Ru/\gamma\text{-}Al_2O_3$ Catalysts

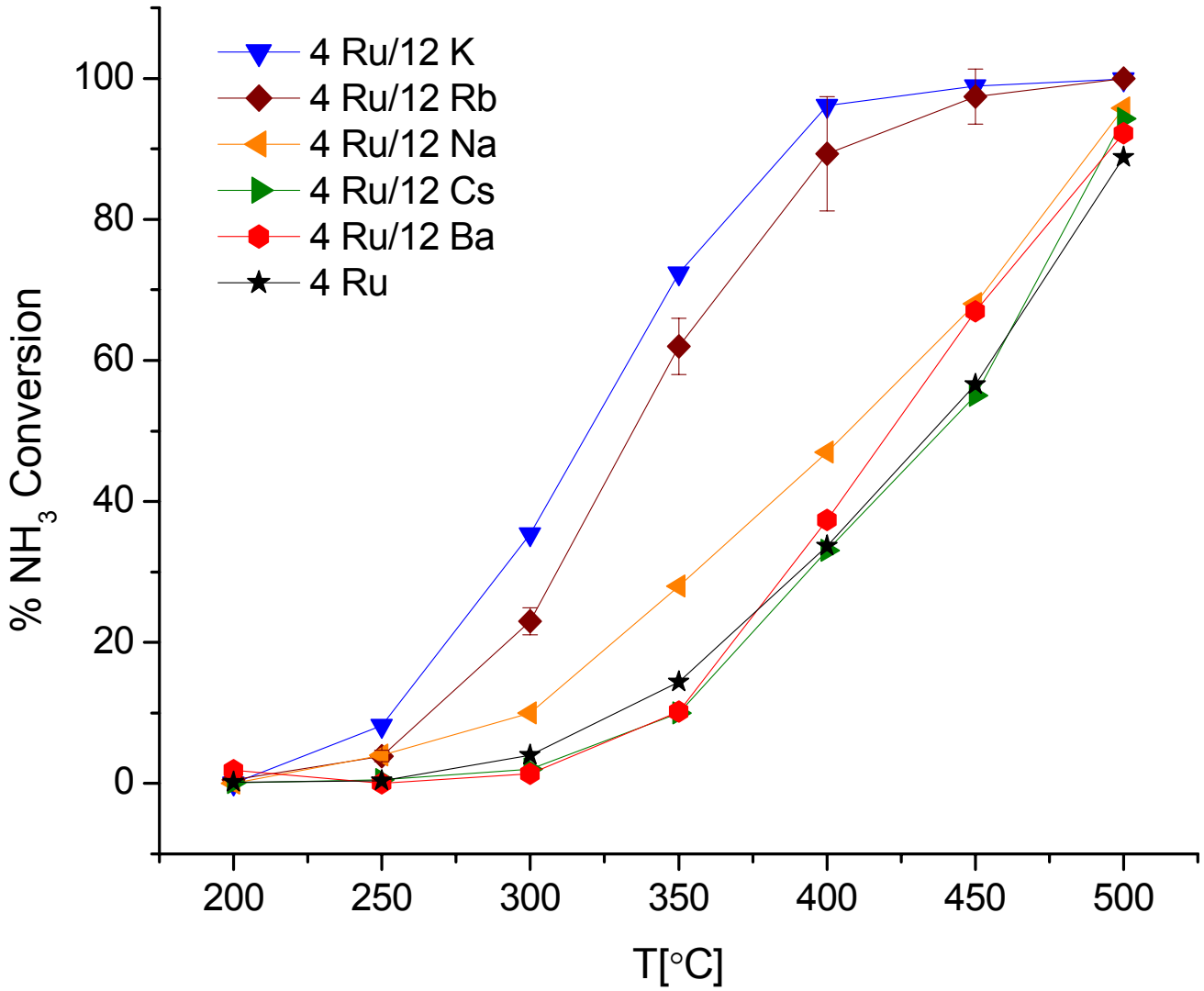




Term	Coefficients
Constant	35.7
Ba	-1.8
K	22.3
Cs	-2.6
Ba*Ba	-0.5
K*K	5.6
Cs*Cs	-3.0
Ba*K	-0.9
Ba*Cs	-1.0
K*Cs	-4.7

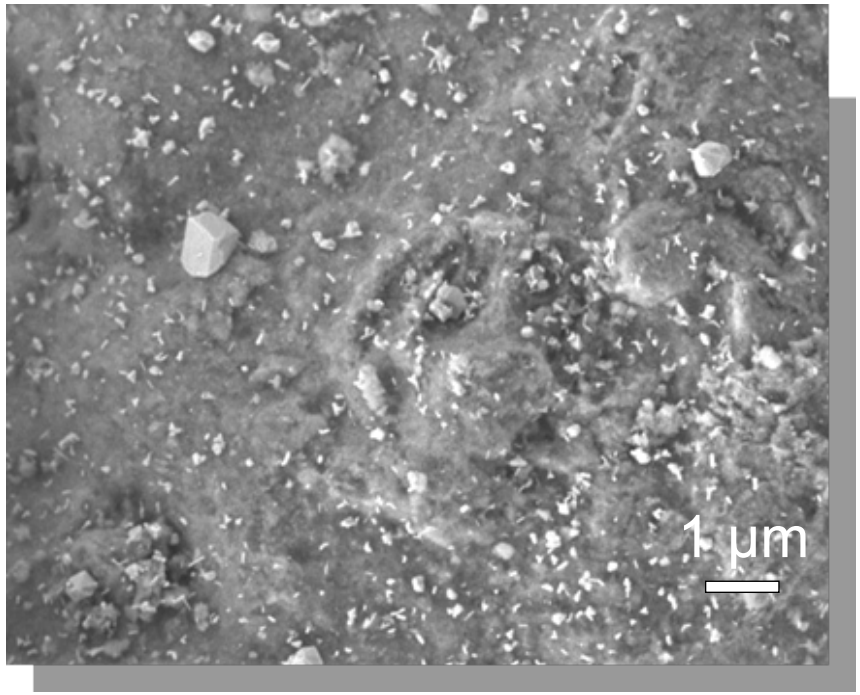
$$R = C + \alpha_1(Ba) + \alpha_2(K) + \alpha_3(Cs) \ldots\ldots + \beta_1(Ba)^2 + \beta_2(K)^2 \ldots\ldots + \lambda_1(Ba*K) + \lambda_2(Ba*Cs) \ldots\ldots$$

Promotion of Ru Catalyst

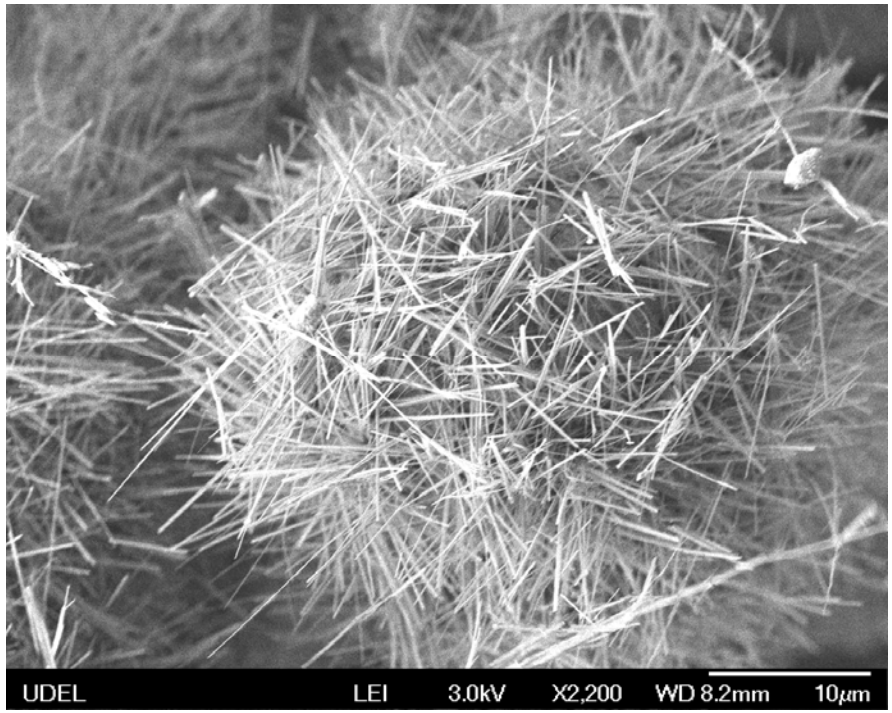


K-Promotion: Effect on Morphology

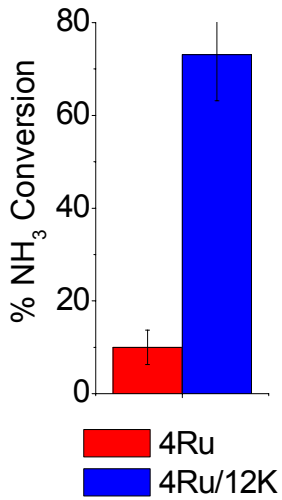
4Ru / γ-Al_2O_3



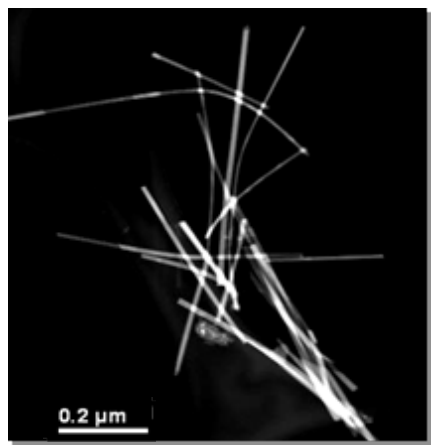
4Ru-12K / γ-Al_2O_3

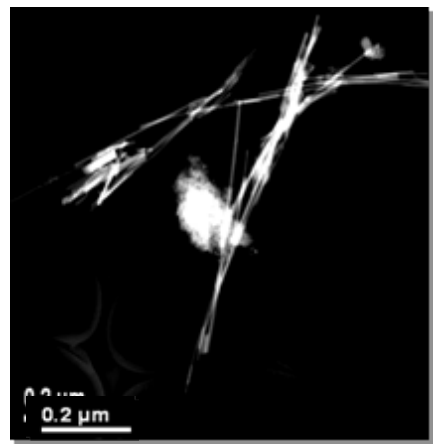


T = 350°C



KRu_4O_8



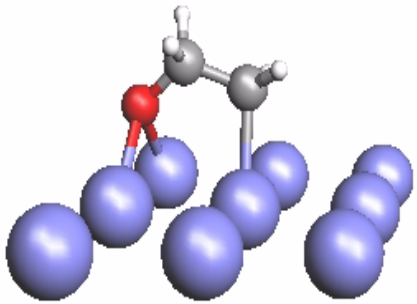


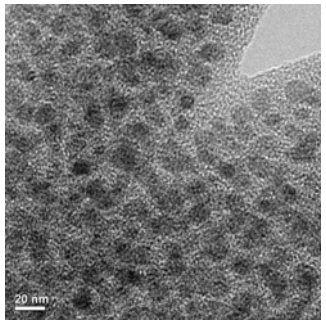
W. Pyrz, R. Vijay, J. Binz, J. Lauterbach, and D. Buttrey, *Topics in Catalysis*

Our Research Philosophy - HT Catalytic Science

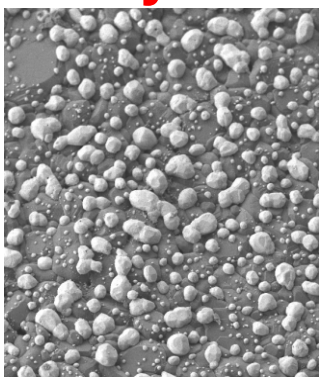
R. J. Hendershot, C.M. Snively, and J. Lauterbach, Chemistry – A European Journal, 11; 806-814, 2005

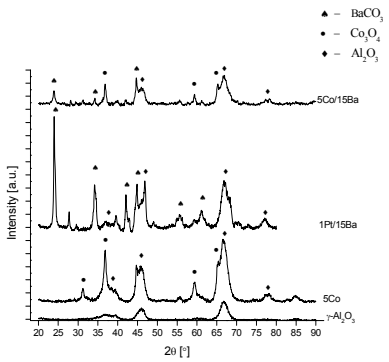
Modeling + UHV + Spectroscopy + Synthesis

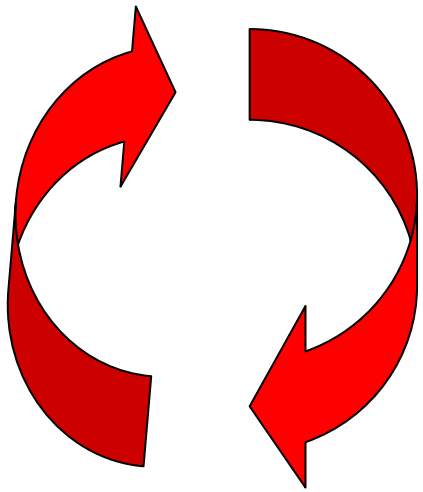




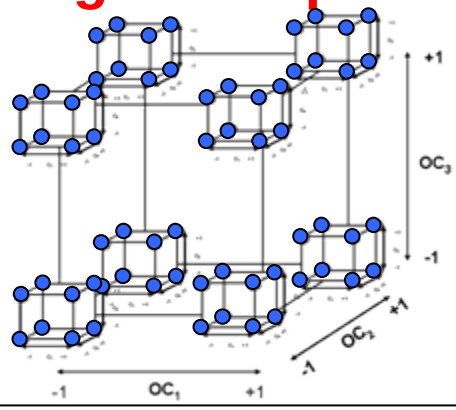
Catalyst Characterization



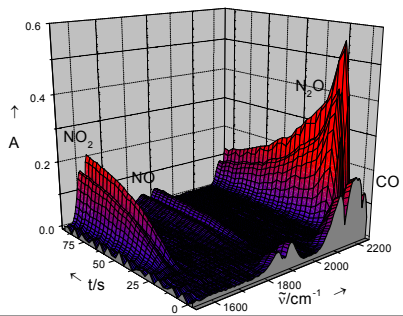


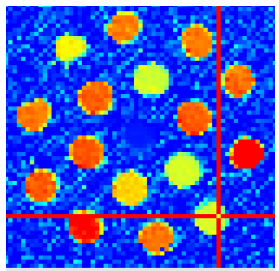


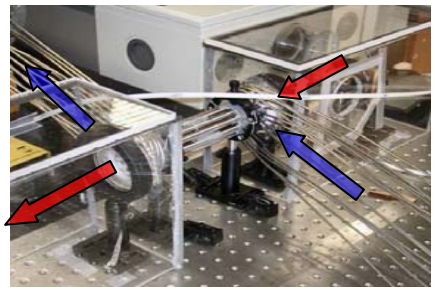
Design of Experiment



Reactor

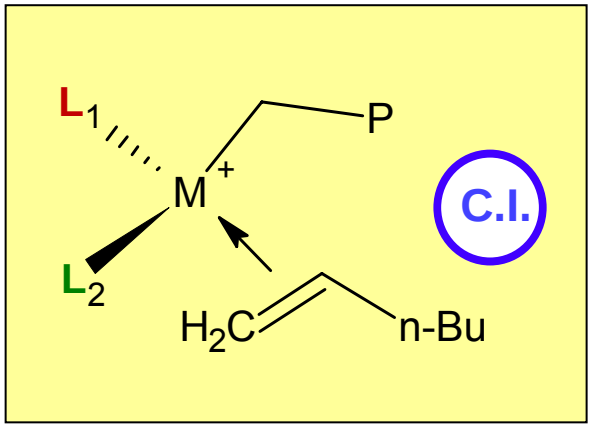






1- Hexene Polymerization by Titanium Catalysts with Phenoxy based ligands

A large number of available substituted phenols allow tunability of steric and electronic variation of the catalyst.

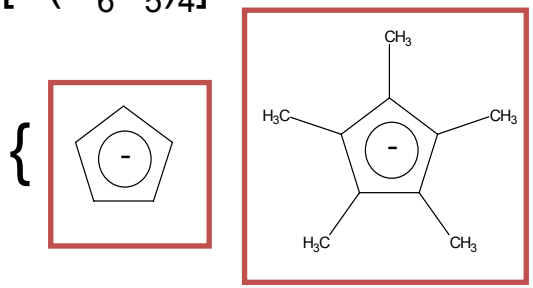


M = Ti, Zr, Hf

C.I. = $[MeB(C_6F_5)_3]^-$

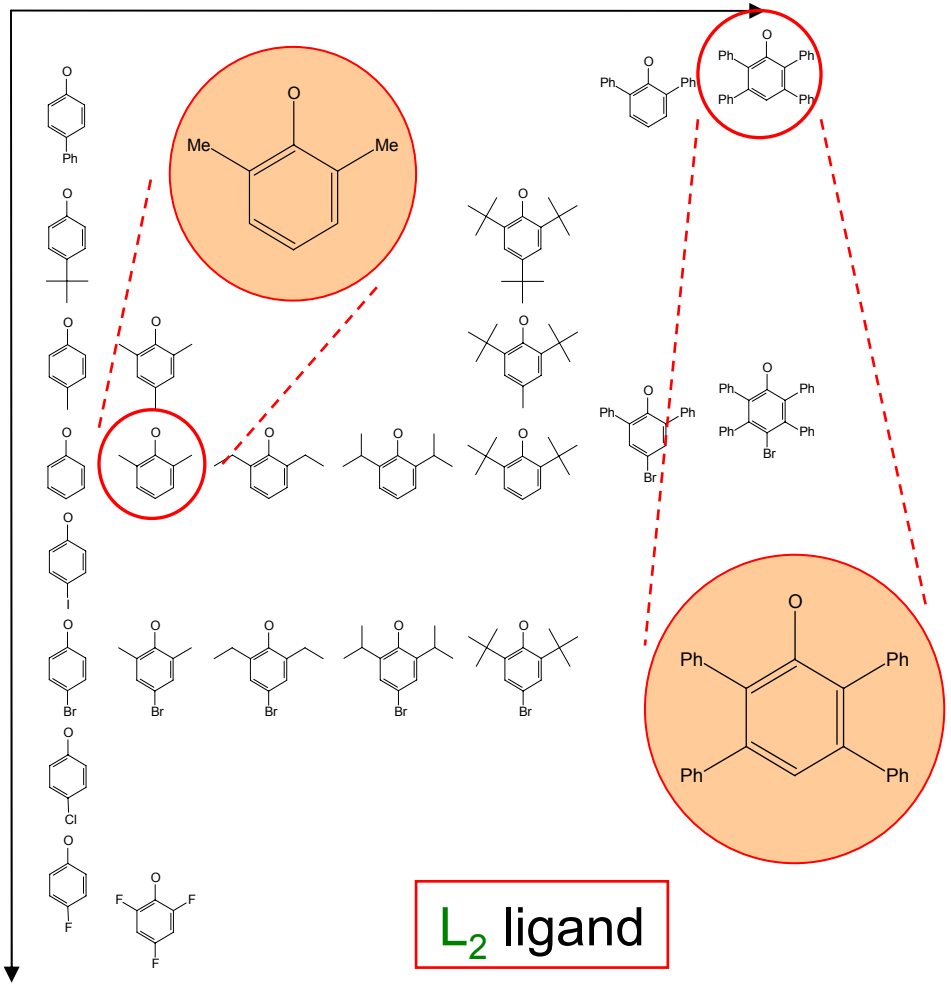
$[B(C_6F_5)_4]^-$

L_1 =



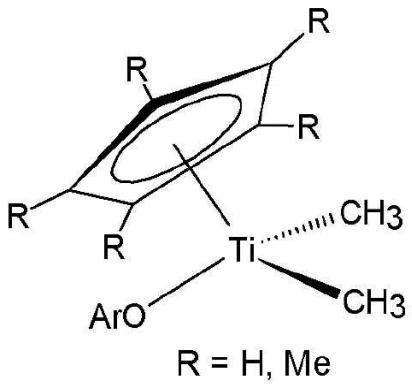
Steric

Electronic

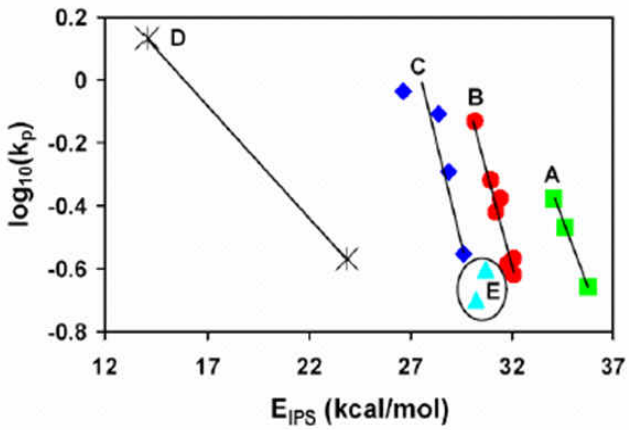


L_2 ligand

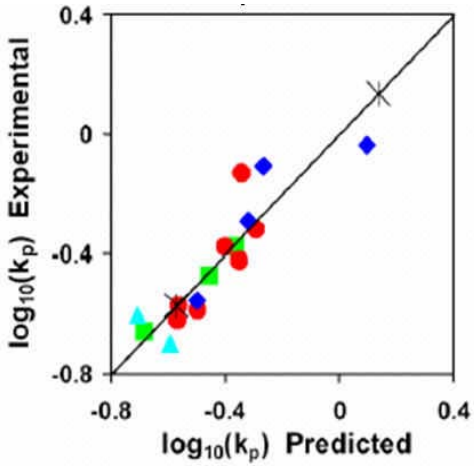
Structure-Activity Correlation in Single-Site, Aryl-Oxide, Olefin Polymerization Catalysts



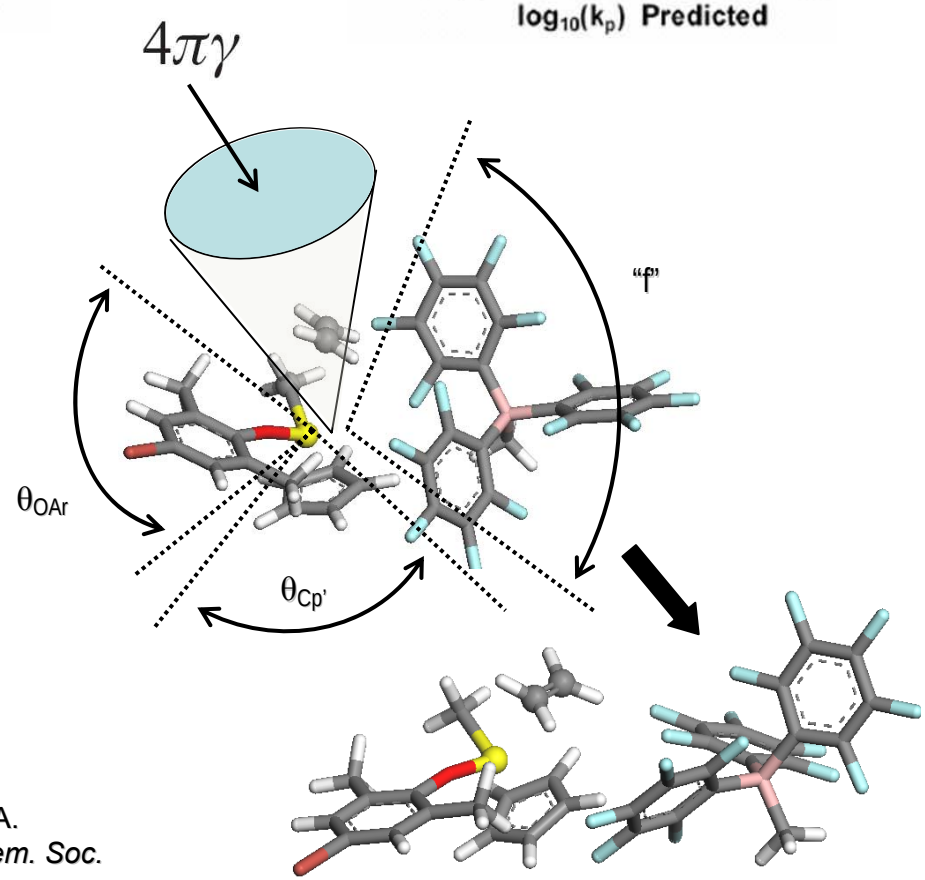
R = H, Me



Universal correlation



Family-dependent correlation of propagation rate versus E_{IPS}



DFT-Based Structure Model: The solid-angle available for monomer approach ($4\pi\gamma$) to Ti-center is related to the OAr- and Cp'-ligand exclusion cone-angles (θ) and a steric factor (f) related to the counter-anion exclusion.

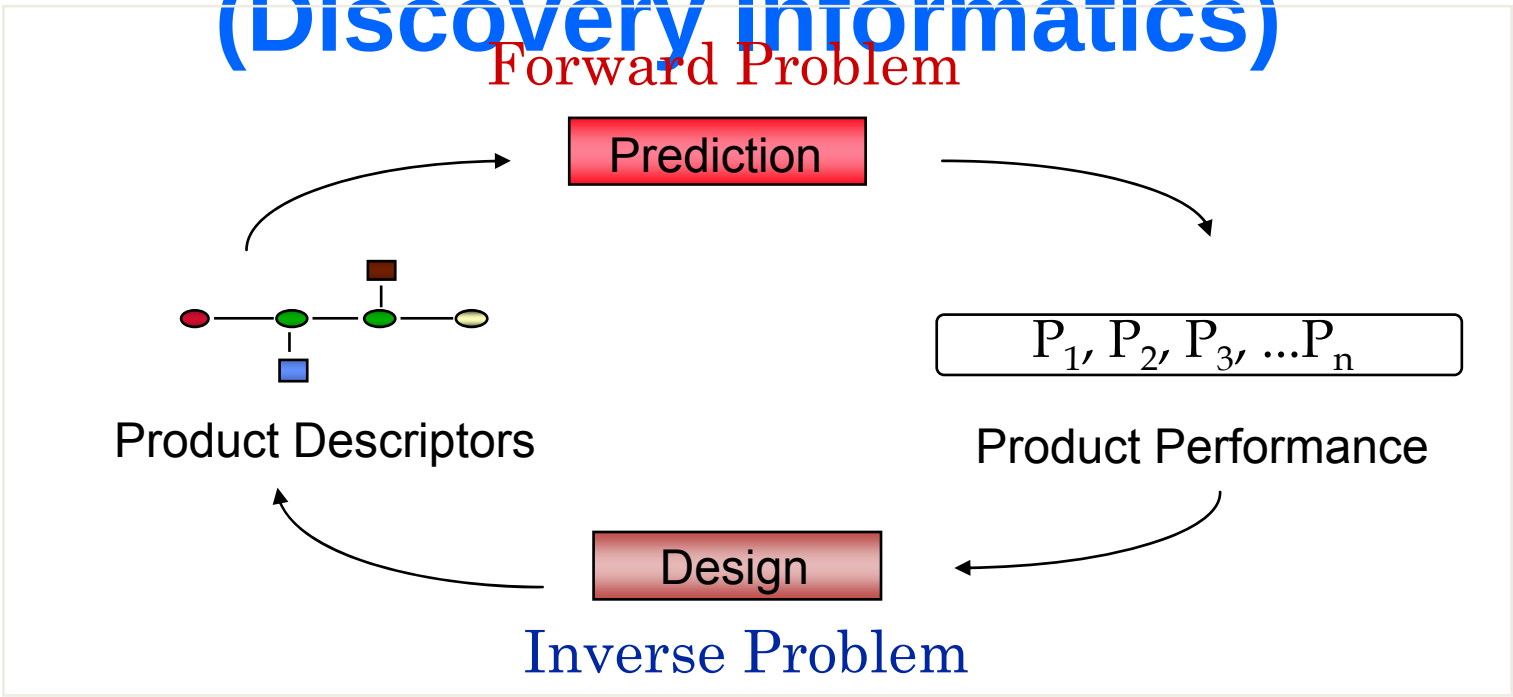
$$\gamma = 1 - \sin^2(\theta_{Cp'}/4) - \sin^2(\theta_{OAr}/4) - f$$

The propagation rate constant correlates with ion-pair separation energy (E_{IPS}) in a univeral manner:

$$k_{pred} = k_0 e^{-E_a/RT} = \gamma a_0 e^{-E_0/RT} e^{-\alpha E_{IPS}/RT}$$

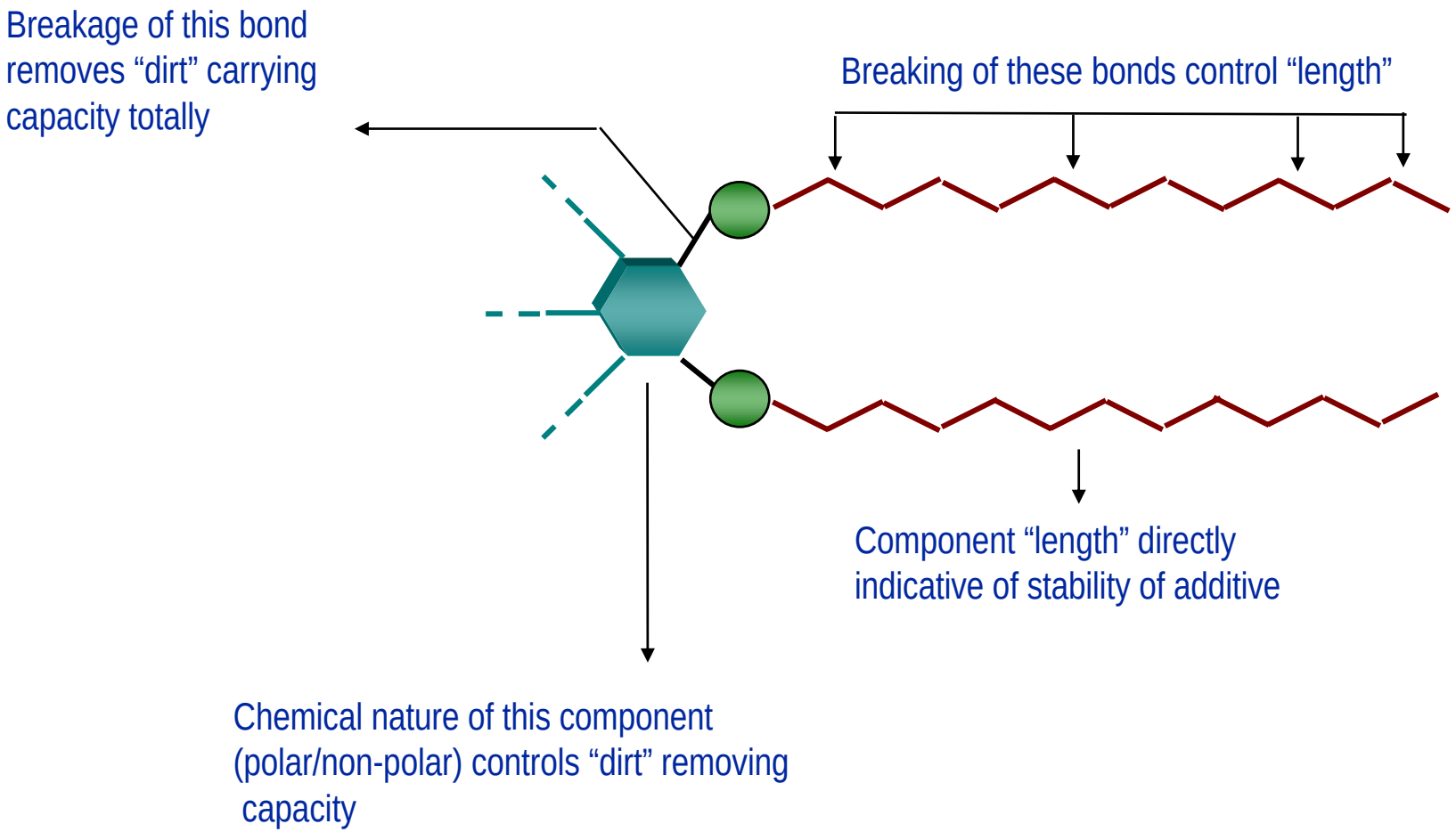
T.A. Manz, K. Phomphrai, G. Medvedev, B.B. Krishnamurthy, S. Sharma, J. Haq, K.A. Novstrup, K.T. Thomson, W.N. Delgass, J.M. Caruthers, M.M Abu-Omar, *J. Am. Chem. Soc. 2007, 129, 3776.*

Computer-aided Product Formulation/Design (Discovery Informatics)



- Forward Problem: Prediction
  - Estimate Product Performance from Descriptors
    - Quantitative forward model
- Inverse Problem: Design
  - Determine a set of products that satisfy desired performance criteria
    - Guided stochastic search (e.g. genetic algorithm)

Search for New Surfactant Molecules
Forward model: First-Principles Model of Additive Degradation + neural net model of engine performance



The first-principle model tracks the structural distribution of fuel-additive with time due to reactive degradation

Results of GA Inverse Search

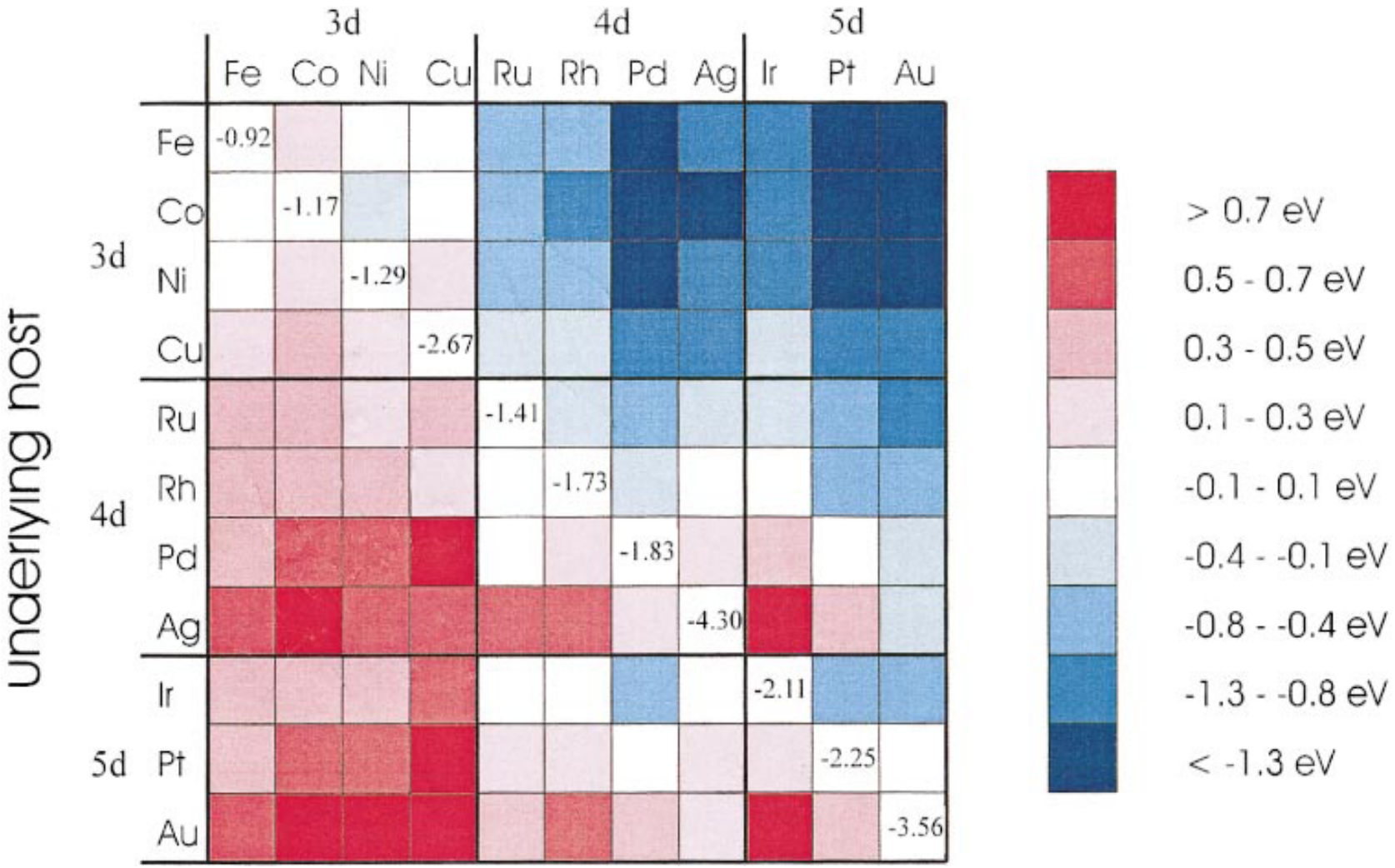
Objective:

Determine a structure with IVD < 10 mg

Population Size: 25; Generations: 25

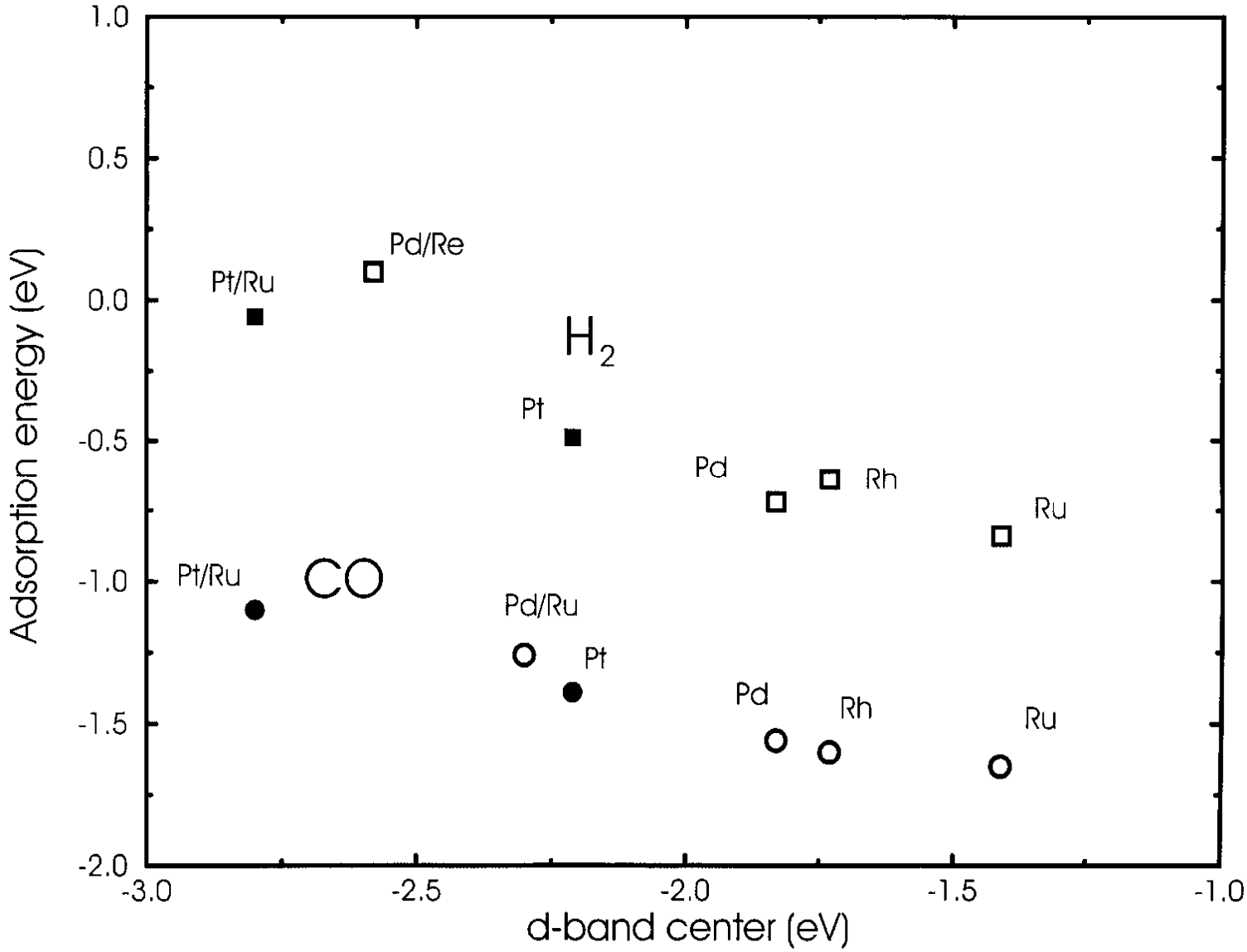
Run	Rank/Identifier	Fitness	Predicted IVD (PLS-NN Model)	Structural Description
I	*1, I-1*	0.997	11.4 mg	Novel Structure. Infrequently used linker.
	2, I-2	0.996	11.5 mg	Novel Structure. Same tails as best structure, different heads and linkers
	6, I-6	0.993	12.0 mg	Variant of structure found in the BMW database. Same head and linkers, different tails
II	*1, II-1*	0.999	10.1 mg	Novel Structure. Different from *I-1* . Infrequently used linker component.
	2, II-2	0.989	12.6 mg	Slight variant of additive structure found in BMW and HONDA databases. Different tails but same head and linker
	4, II-4	0.983	13.2 mg	Minor variation of structure *II-2* above. Slight modification of the head
III	*1, III-1*	1.00	8.9 mg	Novel Structure. Different from *I-1* and *II-1* . Commonly used components
	2, III-2	0.994	11.9 mg	Variant of *III-1* . One linker and tail modified.
	3, III-3	0.993	12.1 mg	Variant of structure *II-2* above. Slight modification of head. A linker and tail inserted.

Norskov d-band Center Descriptor (DFT)



E. Christoffersen, P. Liu, A. Ruban, H.L. Skiver, and J. K. Norskov, "Amode Materials for Low-Temperature Fuel Cells: A Density Functional Theory Study". *J. Catal.*, **199,** 123-131 (2001).

Correlation of ΔH_{ads} with d-Band Center



E. Christoffersen, P. Liu, A. Ruban, H.L. Skiver, and J. K. Norskov, "Amode Materials for Low-Temperature Fuel Cells: A Density Functional Theory Study". *J. Catal.*, **199,** 123-131 (2001).

Drug Discovery Approach to Breakthroughs in Batteries

Informatics in Drug Discovery Ernst R. Dow, Eli Lilly

Electrochemical energy storage and extended-range electric vehicles Mark Verbrugge, GM

Data handling and informatics tools for model-based discovery James Caruthers, Purdue

New High Energy/Power Devices Ralph J. Brodd, Broddarp

High-throughput ab-initio computing and data mining methods for the prediction of crystal structure Gerbrand Ceder, MIT

Materials Informatics: An "omics" approach to materials based design for battery technology Krishna Rajan, Iowa State

Discussion at dinner tonight

Breakout Groups (Tuesday)

- **Two discussion sessions**
- **One writing session**

Objective

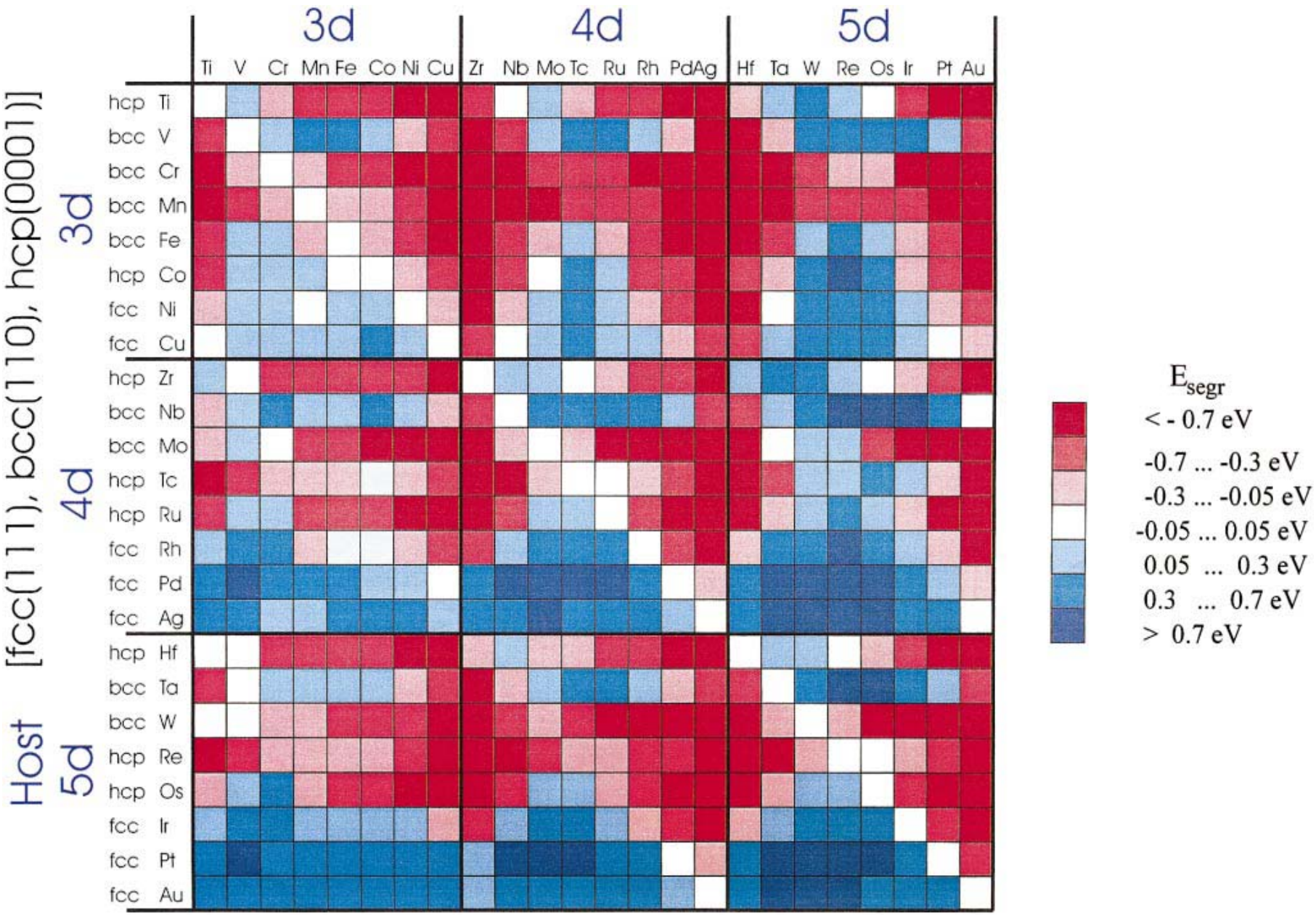
- **Report:**

  Define and justify opportunities for significant advancement in battery technology.

  Suggest guidelines for program structure

- **Website: Maintain as a resource for the community. Start by uploading slides of talks**

Computed surface segregation energies



E. Christoffersen, P. Liu, A. Ruban, H.L. Skiver, and J. K. Norskov, "Amode Materials for Low-Temperature Fuel Cells: A Density Functional Theory Study". *J. Catal.*, **199,** 123-131 (2001).