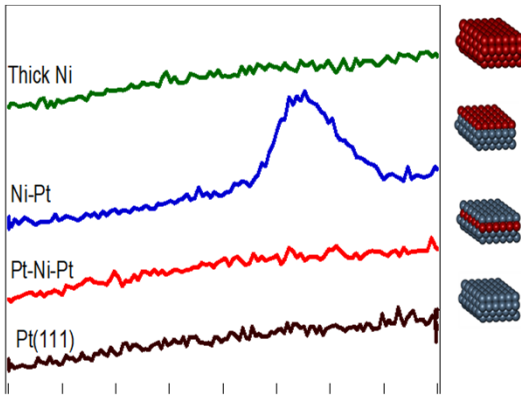
CATALYSIS CENTER FOR ENERGY INNOVATION
AN ENERGY FRONTIER RESEARCH CENTER

RAPID Transforming Process Industries

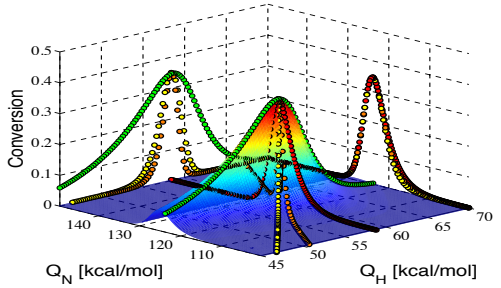
Delaware Energy Institute

In Silico Prediction of Materials for Energy Applications

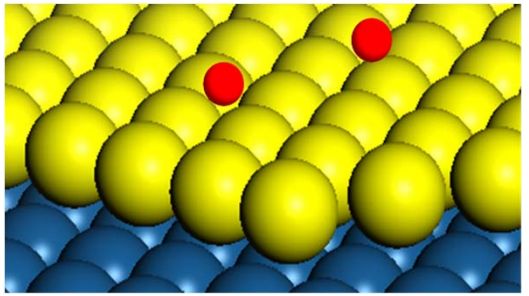


Dion Vlachos

June 27, 2018



University of Delaware
Department of Chemical and Biomolecular Engineering
Catalysis Center for Energy Innovation (CCEI),
an Energy Frontier Research Center



CCEI is an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Basic Sciences


ΚΑΛΗΜΕΡΑ
Kalimera good morning
ΚΑΛΗΣΠΕΡΑ
KALISPERA GOOD AFTERNOON
ΕΥΧΑΡΙΣΤΩ
EFHARISTO THANK YOU
ΠΑΡΑΚΑΛΩ
PARAKALO YOU ARE WELCOME
Σ' ΑΓΑΠΩ
I LOVE YOU SAGAPO
ΕΙΝΑΙ
INE OREO
ΩΡΑΙΟ
IT'S NICE
ΑΝΤΙΟ
ADIO BYE BYE
ΚΑΛΗΝΥΧΤΑ
KALINIHTA GOOD NIGHT
ΓΕΙΑ
GIASOU
ΣΟΥ
HELLO
ΕΙΣΑΙ
ISE KOYKLA
ΚΟΥΚΛΑ
YOU ARE BEAUTIFUL

Outline

- Energy, sustainability, and technological needs
- Grand computational challenges
- Topics
  - Catalyst prediction
  - Uncertainty
  - Design of active site
  - Materials gap
- Outlook

CATALYSIS

Synthesis,

multiscale modeling and

***in situ* characterization**

form the pillars of modern

catalytic science

Outline

- Energy, sustainability, and technological needs
- Grand computational challenges
- Topics
  - Catalyst prediction
  - Uncertainty
  - Design of active site
  - Materials gap
- Outlook

CATALYSIS

Synthesis,

multiscale modeling and

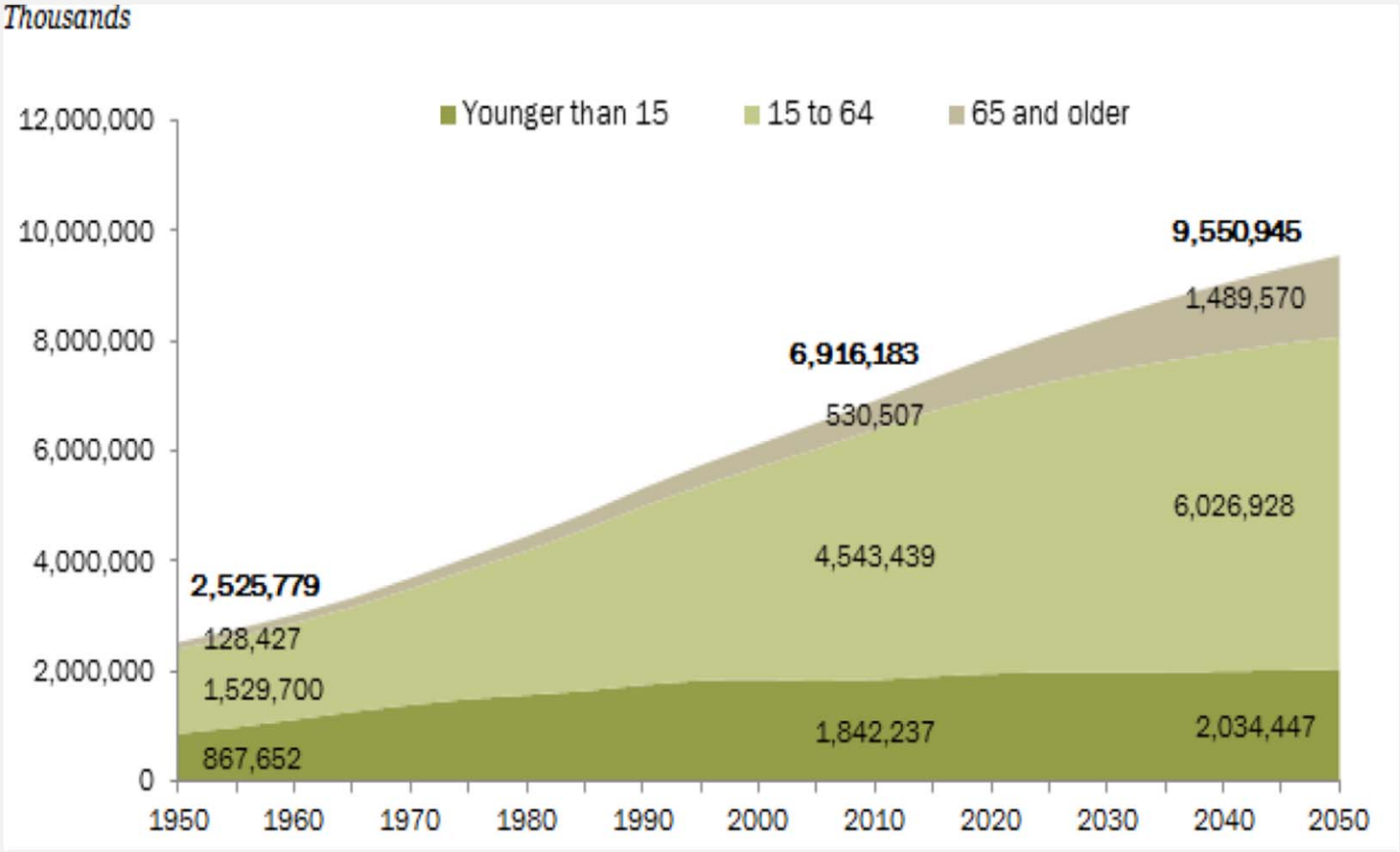
***in situ* characterization**

form the pillars of modern

catalytic science

Societal Challenges

Growing and Aging Population



Human needs

- Medicine
- Food
- Energy
- Water

The nexus of food-energy-water requires **more** *and* **cleaner** energy and chemicals

CATALYSIS CENTER FOR ENERGY INNOVATION
AN ENERGY FRONTIER RESEARCH CENTER

RAPID Transforming Process Industries

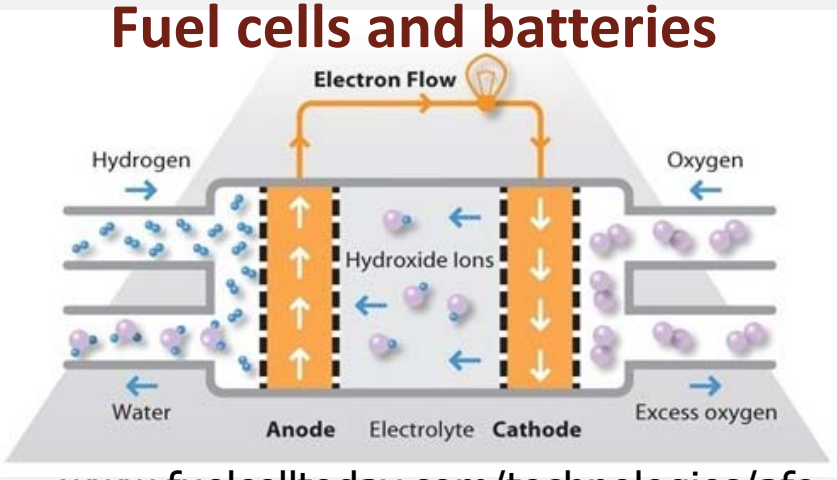
Delaware Energy Institute

Meeting Tomorrow's Renewable Energy and Sustainability Challenges

CO_2, CH_4 activation/RAPID

Efficiency/RAPID

Fuel cells and batteries



www.fuelcelltoday.com/technologies/afc

Renewables

Review: Vlachos & Caratzoulas, *Chem. Eng. Sci.* **65**, 18 (2010)

Meeting Tomorrow's Renewable Energy and Sustainability Challenges Requires

- New materials (catalysts, adsorbents, membranes)
- Emerging feedstocks: shale gas, biomass, biogas, food waste, CO_2, water,…
- Modular manufacturing – portable and distributed processing
- Clean energy, e.g., from solar or wind, beyond electricity
  - ✓ Efficient electrification of chemical plants (H_2 production, purposely tuned processes, localized heating, bond activation)

- Diversified and distributed feedstocks and renewable energy drive a paradigm shift

Review: Vlachos & Caratzoulas, *Chem. Eng. Sci.* **65**, 18 (2010)

Outline

- Energy, sustainability, and technological needs
- Grand computational challenges
- Topics
  - Catalyst prediction
  - Uncertainty
  - Design of active site
  - Materials gap
- Outlook

CATALYSIS

Synthesis,

multiscale modeling and

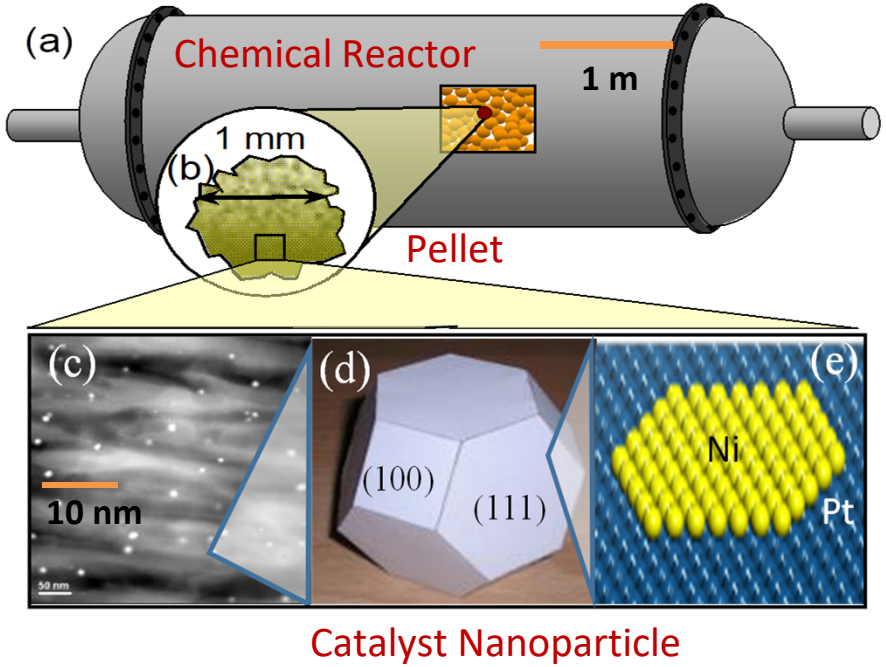
***in situ* characterization**

form the pillars of modern

catalytic science

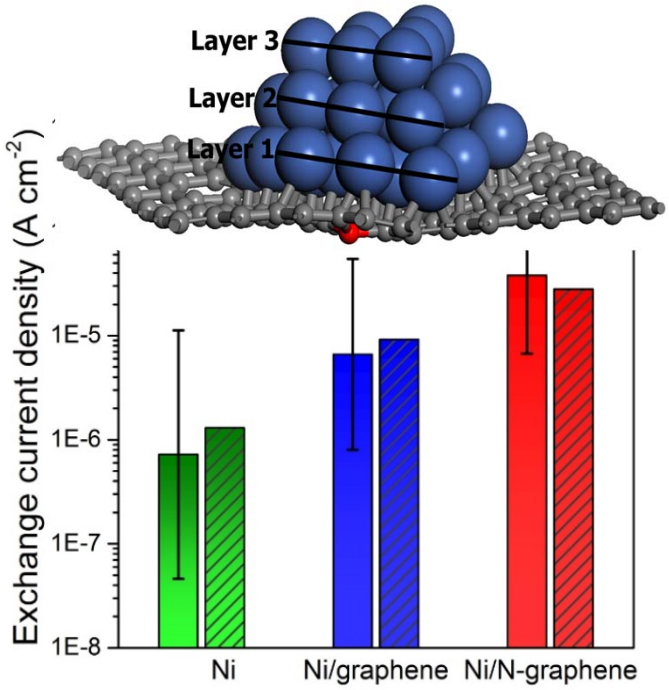
Multiscaling

The Multiscale Challenge^



9 orders disparity in scales
Quantum modeling inadequate

The Mesoscale Challenge*

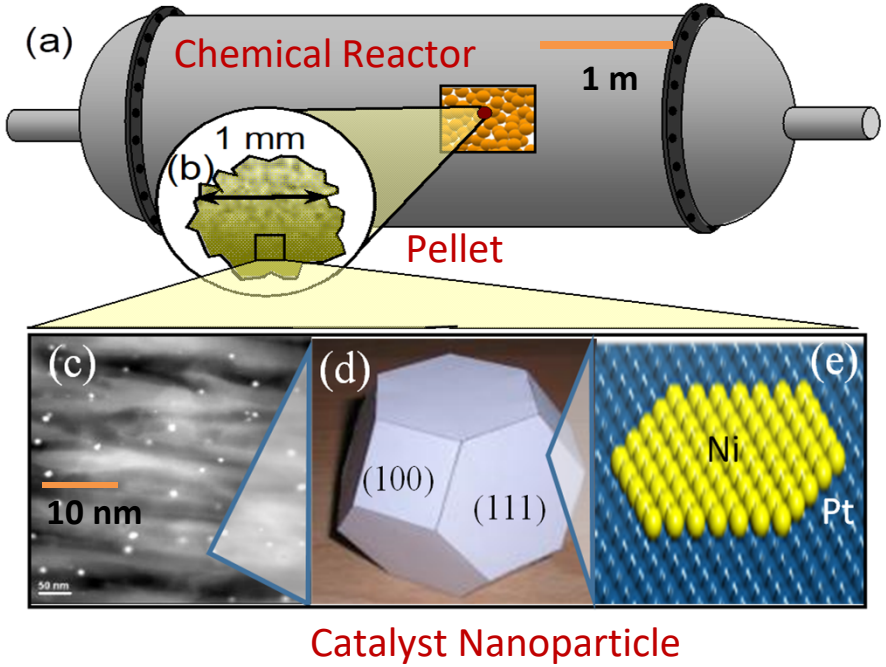


1.5 orders performance enhancement
Support and dopant effects important

^Vlachos, *Adv. Chem. Eng.* **30**, 1 (2005);
*Zhuang et al., *Nature Comm.* **7** (2016); 10.1038/ncomms10141

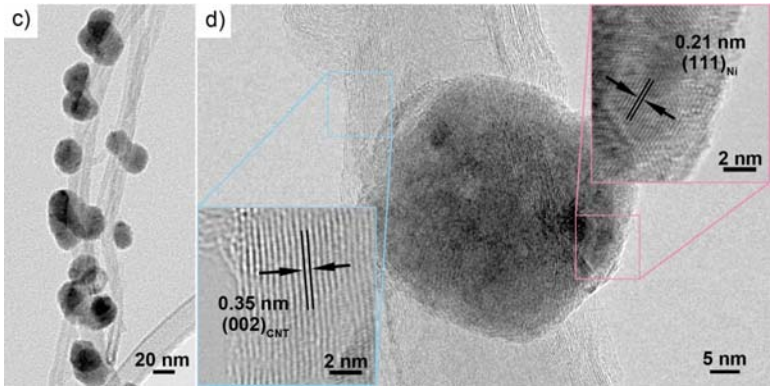
Multiscaling

The Multiscale Challenge^



9 orders disparity in scales
Quantum modeling inadequate

The Mesoscale Challenge*

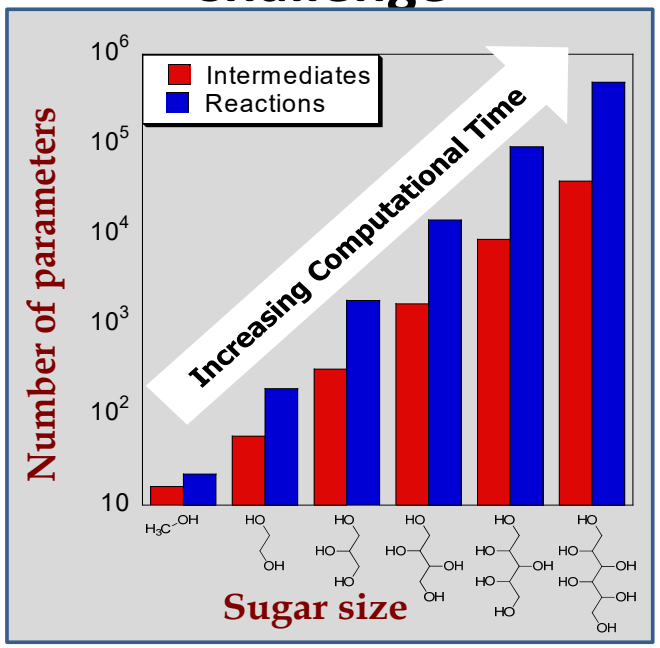


1.5 orders performance enhancement
Support and dopant effects important

^Vlachos, *Adv. Chem. Eng.* **30**, 1 (2005);
*Zhuang et al., *Nature Comm.* **7** (2016); 10.1038/ncomms10141

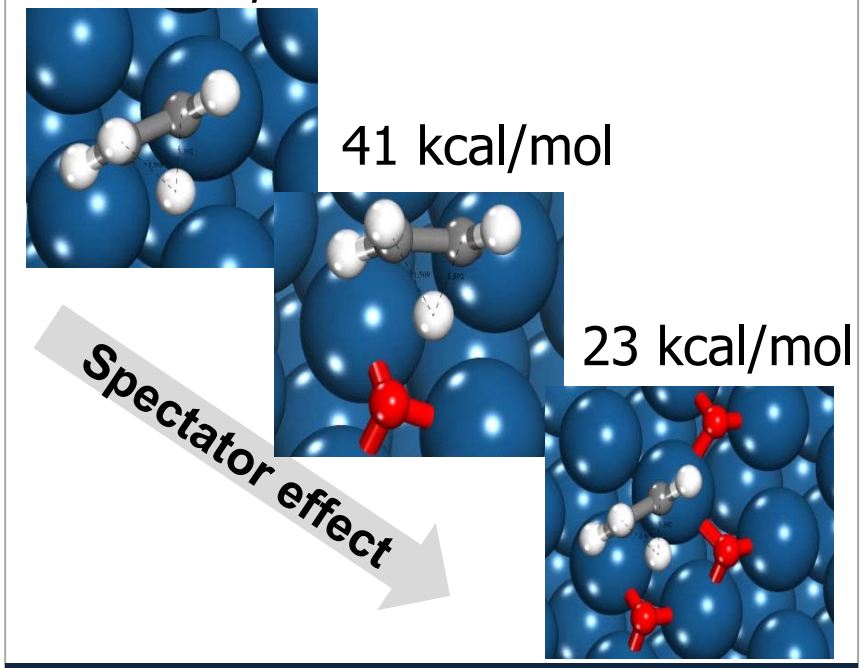
Parametric Complexity

Explosion in Parameters Challenge



1 million chemical reactions
Quantum calculations infeasible

Coverage-Effect Challenge



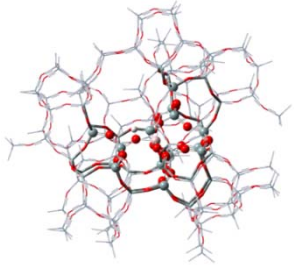
Combinatorial no. of configurations
Quantum calculations infeasible

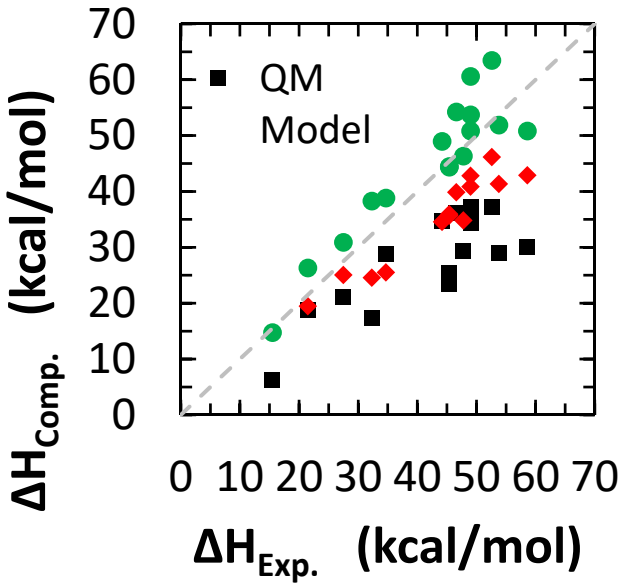
Vlachos, *AIChE J.* **58**, 1314 (2012) *Perspective.*

The Predictive Ability of Models Is Unclear

Parametric Uncertainty

The DFT-Error Challenge^

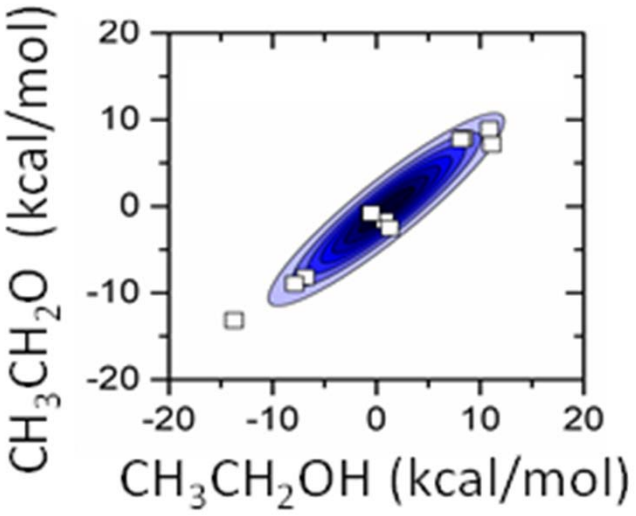




Adsorption in H-MFI zeolite

DFT errors are not well understood
How good are our models?

The Correlative Data and Uncertainty Challenge*



Energies in ethanol mechanism

DFT data is correlated
What's the role in predictions?

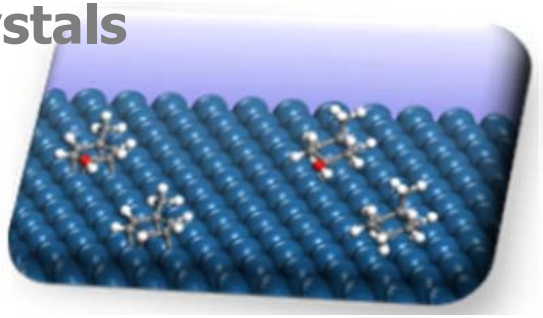
^Patet, Caratzoulas, and Vlachos, *Phys. Chem. Chem. Phys.* **18**(37), 26094 (2016).
*Sutton, Guo, Katsoulakis, and Vlachos, *Nat. Chem*. **8**(4), 331 (2016).

Materials Gap

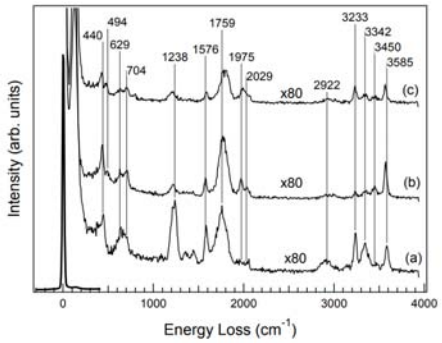
Model Form Uncertainty

Models Catalysts

Single Crystals



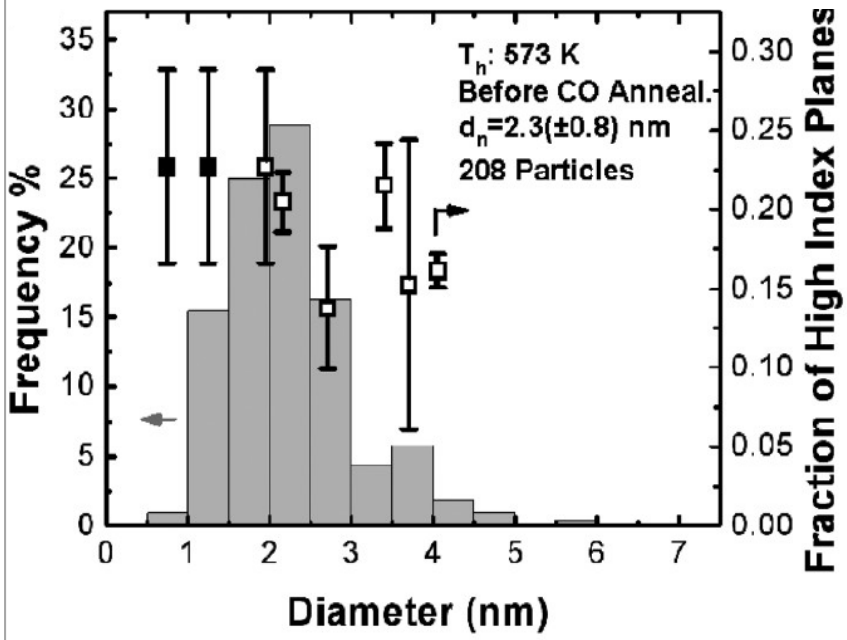
UHV
STM
TPD
HREELS



Model studies on ideal catalysts and far from realistic conditions

Real Catalysts Are Complex

Lee et al., J. Am. Chem. Soc. **131**, 15669 (2009)



Multicomponent, heterogeneous, unobserved, multi-oxidation states

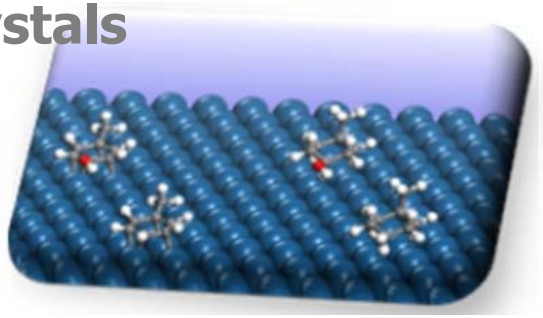
Ni/Pt: Tupy et al., *ACS Catal.* **2**, 2290 (2012); Ru/RuO_x: Jae et al., *ChemSusChem* **6**, 1158 (2013); Pt/WO_x: Wang et al., *Catal. Lett.* **148**, 1047 (2018); Pt SAC/TiO_2: In preparation.

Materials Gap

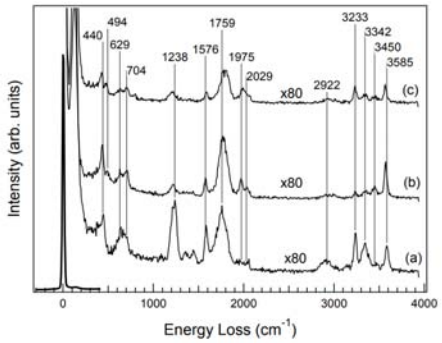
Model Form Uncertainty

Models Catalysts

Single Crystals

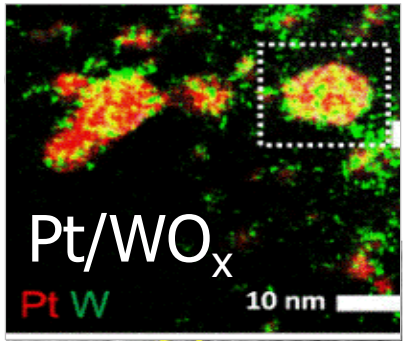


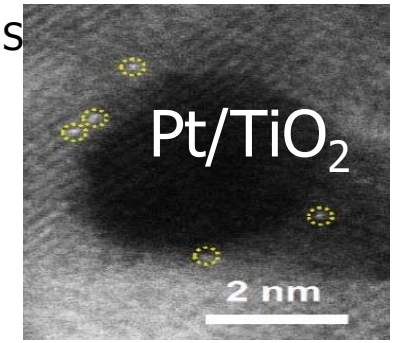
UHV
STM
TPD
HREELS

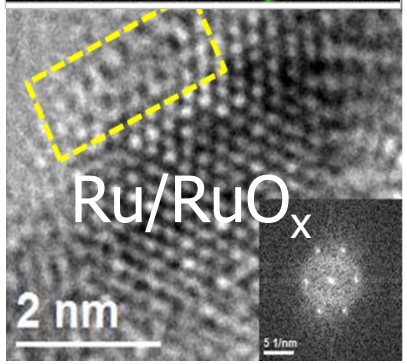


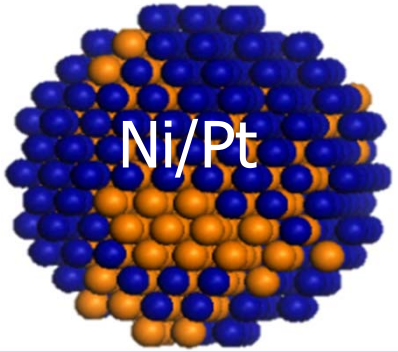
Model studies on ideal catalysts and far from realistic conditions

Real Catalysts Are Complex









Multicomponent, heterogeneous, unobserved, multi-oxidation states

Ni/Pt: Tupy et al., *ACS Catal.* **2**, 2290 (2012); Ru/RuO$_x$: Jae et al., *ChemSusChem* **6**, 1158 (2013); Pt/WO$_x$: Wang et al., *Catal. Lett.* **148**, 1047 (2018); Pt SAC/TiO$_2$: In preparation.

Outline

- Energy, sustainability, and technological needs
- Grand computational challenges
- Topics
  - Catalyst prediction
  - Uncertainty
  - Design of active site
  - Materials gap
- Outlook

CATALYSIS

Synthesis,

multiscale modeling and

***in situ* characterization**

form the pillars of modern

catalytic science

Predicting Novel Catalytic Materials

- First principles methods (DFT) promise to deliver strategies for rational catalyst design
- Current studies limited to cases when:
  - Thermodynamics (heat of adsorption) dominates[1,2]
  - Linear interpolation is employed[3]
  - Sabatier's principle optimizes catalyst activity (no selectivity)

Sabatier's Principle

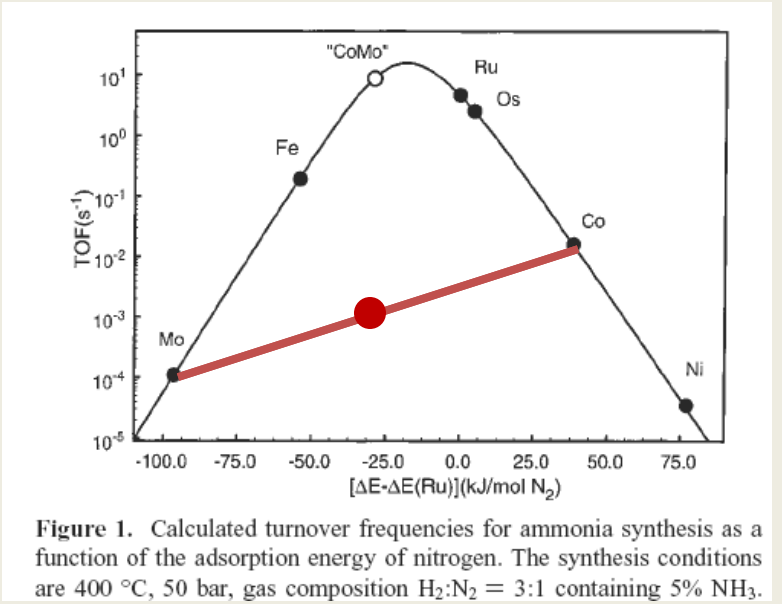
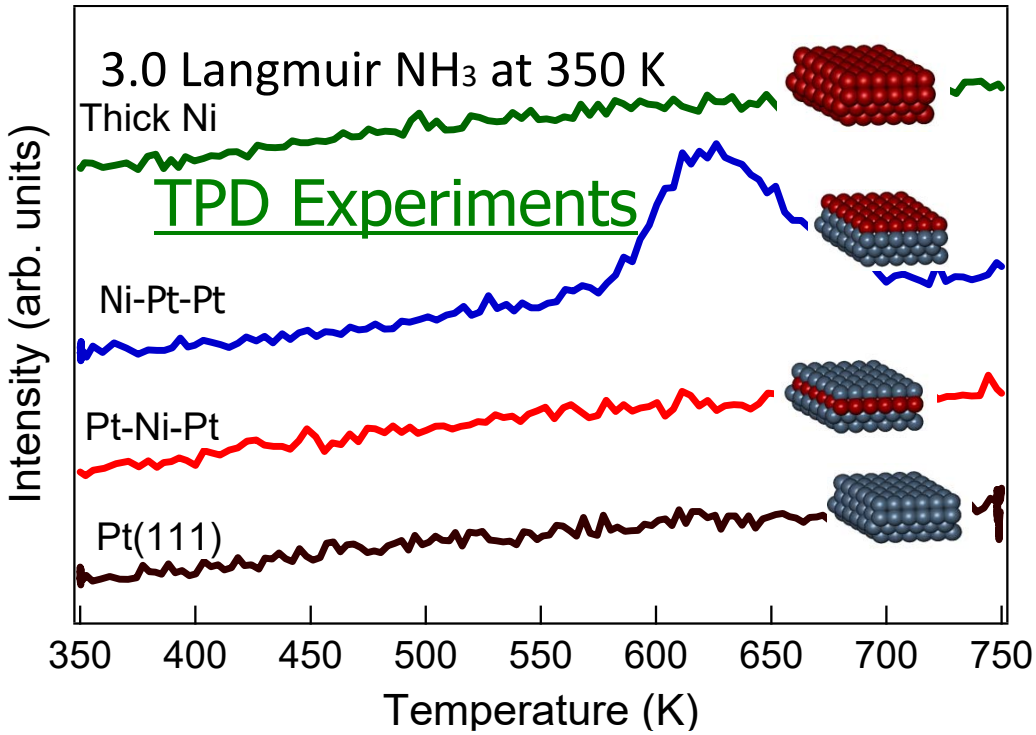


Figure 1. Calculated turnover frequencies for ammonia synthesis as a function of the adsorption energy of nitrogen. The synthesis conditions are 400 °C, 50 bar, gas composition H_2:N_2 = 3:1 containing 5% NH_3.

$$N_2 + 3H_2 \Rightarrow 2NH_3$$

[1] Strasser et al., *J. Phys. Chem. B* **107**(40), 11013 (2003)
[2] Greeley and Mavrikakis, *Nat. Materials* **3**(11), 810 (2004)
[3] Jacobsen et al., *J. Am. Chem. Soc.* **123**, 8404 (2001)

Bimetallics Exhibit Emergent Behavior



$$2NH_3 = N_2 + 3H_2$$

- **Ni-Pt-Pt is the most active single crystal catalyst known today!**
- **Interpolation principle is inadequate**
- **Core-shell bimetallics provide a *'new class of materials'* that *'expands the periodic table'***

ARTICLES
PUBLISHED ONLINE: 25 APRIL 2010 | DOI: 10.1038/NCHEM.626
nature chemistry

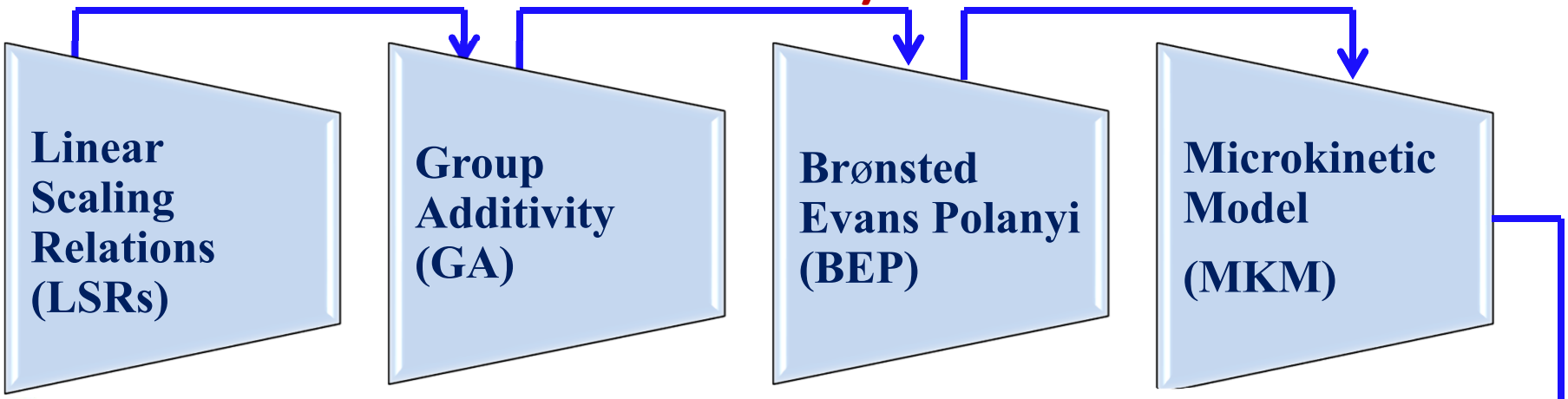
Using first principles to predict bimetallic catalysts for the ammonia decomposition reaction

Danielle A. Hansgen, Dionisios G. Vlachos* and Jingguang G. Chen*

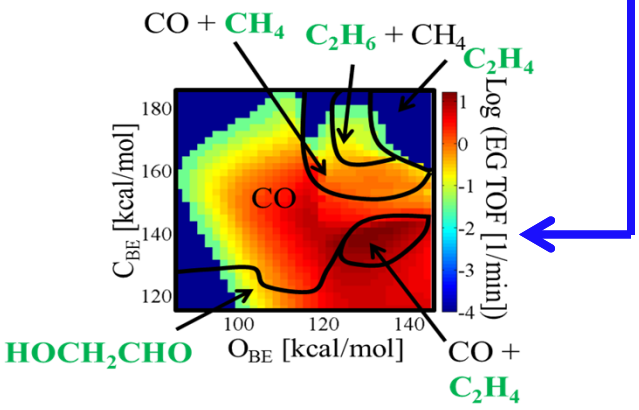
The facile decomposition of ammonia to produce hydrogen is critical to its use as a hydrogen storage medium in a hydrogen economy, and although ruthenium shows good activity for catalysing this process, its expense and scarcity are prohibitive to large-scale commercialization. The need to develop alternative catalysts has been addressed here, using microkinetic modelling combined with density functional studies to identify suitable monolayer bimetallic (surface or subsurface) catalysts based on nitrogen binding energies. The Ni-Pt-Pt(111) surface, with one monolayer of Ni atoms residing on a Pt(111) substrate, was predicted to be a catalytically active surface. This was verified using temperature-programmed desorption and high-resolution electron energy loss spectroscopy experiments. The results reported here provide a framework for complex catalyst discovery. They also demonstrate the critical importance of combining theoretical and experimental approaches for identifying desirable monolayer bimetallic systems when the surface properties are not a linear function of the parent metals.

Toward High-throughput Computing:

Extendibility (Periodic Table) and Scalability (Molecular & Network)



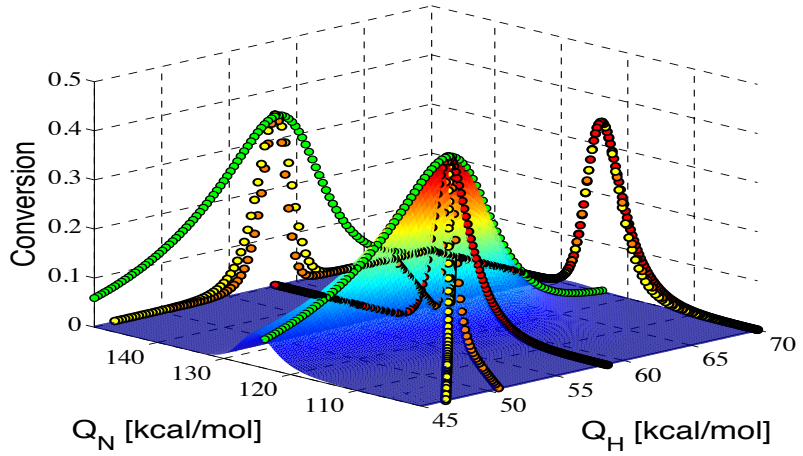
- **Hierarchical refinement** allows first-principles accuracy at minimal computationa
- **Machine learning** to develop **correlations** (surrogates) and **descriptor-based models**
- Descriptor-based modeling allows high throughput computing and solving the **inverse problem**



Review: Salciccioli et al., *Chem. Eng. Sci.* **66**, 4319 (2011);
Salciccioli et al., *J. Phys. Chem. C* **114**, 20155 (2010); *J. Phys. Chem. C* **116**, 1873 (2012); Sutton and Vlachos, *ACS Catal.* **2**, 1624 (2012); *J. Catal.* **297**, 202 (2013)

High-throughput Multiscale Model-based Optimization for Catalyst Discovery

350 °C
1 atm



NH_3 decomposition

$$NH_3 + * \Leftrightarrow NH_3 *$$
$$NH_3 * + * \Leftrightarrow NH_2 * + H *$$
$$NH_2 * + * \Leftrightarrow NH * + H *$$
$$NH * + * \Leftrightarrow N * + H *$$
$$2N * \Leftrightarrow N_2 + 2 *$$
$$2H * \Leftrightarrow H_2 + 2 *$$

- Search is done on atomic descriptors while running the full chemistry and reactor models
- Optimal catalyst properties are identified

Prasad et al., *Chem. Eng. Sci.* **65**, 240 (2010)

Toward Predictive Models

Errors, Correlations, Small Data,…

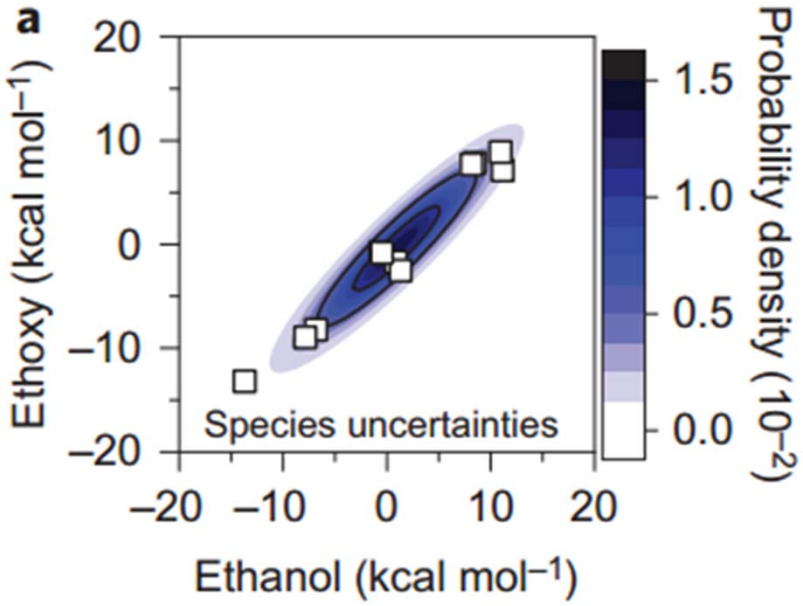
Correlative Global Uncertainty Quantification – Ethanol steam reforming

nature chemistry
ARTICLES
PUBLISHED ONLINE: 22 FEBRUARY 2016 | DOI: 10.1038/NCHEM.2454

Effects of correlated parameters and uncertainty in electronic-structure-based chemical kinetic modelling

Jonathan E. Sutton[1], Wei Guo[1,2], Markos A. Katsoulakis[3] and Dionisios G. Vlachos[1]*

Kinetic models based on first principles are becoming common place in heterogeneous catalysis because of their ability to interpret experimental data, identify the rate-controlling step, guide experiments and predict novel materials. To overcome the tremendous computational cost of estimating parameters of complex networks on metal catalysts, approximate quantum mechanical calculations are employed that render models potentially inaccurate. Here, by introducing correlative global sensitivity analysis and uncertainty quantification, we show that neglecting correlations in the energies of species and reactions can lead to an incorrect identification of influential parameters and key reaction intermediates and reactions. We rationalize why models often underpredict reaction rates and show that, despite the uncertainty being large, the method can, in conjunction with experimental data, identify influential missing reaction pathways and provide insights into the catalyst active site and the kinetic reliability of a model. The method is demonstrated in ethanol steam reforming for hydrogen production for fuel cells.

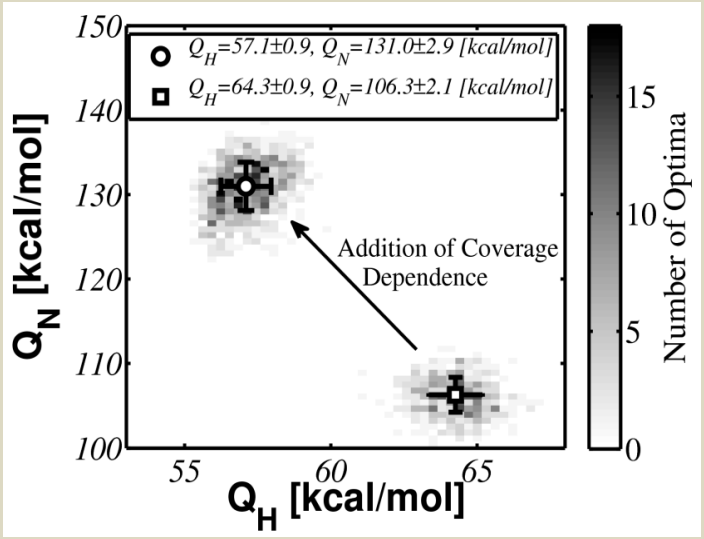


J. E. Sutton, W. Guo, M. A. Katsoulakis, D. G. Vlachos, *Nature Chem.* **2016**, *8*, 331-337

Identifying Bimetallic Catalysts: Uncertainty

- Predictions are robust!
- Adsorbate-adsorbate interactions are crucial

Activity (& Selectivity) Maps



Variation in pre-exponentials

Ulissi, Prasad and Vlachos, *J. Catal.* **281**, 339 (2011).

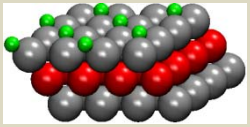
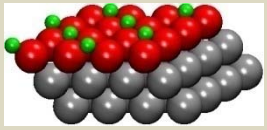
CATALYSIS CENTER FOR ENERGY INNOVATION
AN ENERGY FRONTIER RESEARCH CENTER

RAPID Transforming Process Industries

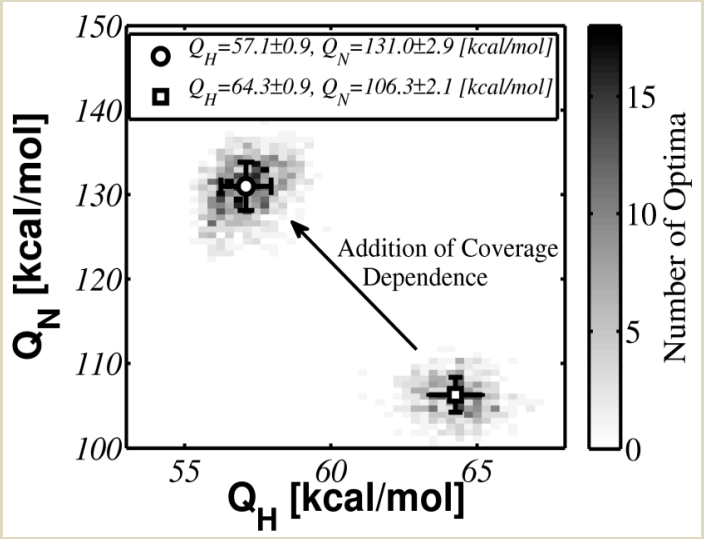
Delaware Energy Institute

Identifying Bimetallic Catalysts: Uncertainty & Informatics

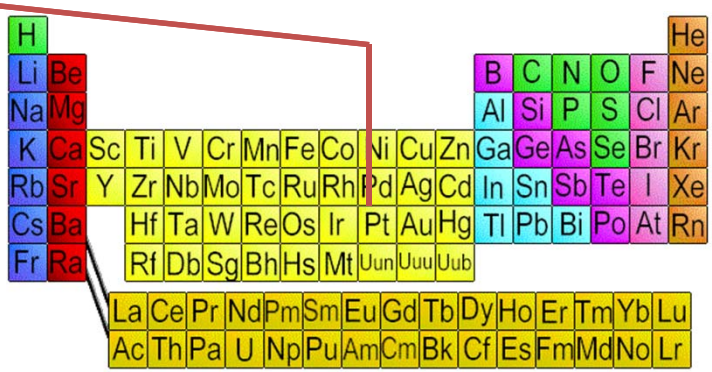
Informatics Databases

Structure	Metals	BE_N (kcal/mol)
Subsurface Core-shell-shell 	PtTiPt	56.5
	PtVPt	59.5
	PtCrPt	72.6
	PtMnPt	84.9
	PtFePt	83.9
	PtCoPt	87.0
	PtNiPt	89.8
Surface Core-shell 	CoPtPt	127.8
	NiPtPt	130.5
	FePtPt	137.7
	MnPtPt	162.2
	CrPtPt	166.5
	VPtPt	184.1
	TiPtPt	191.5

Activity (& Selectivity) Maps



Variation in pre-exponentials



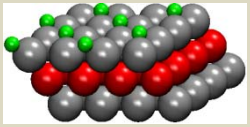
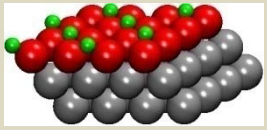
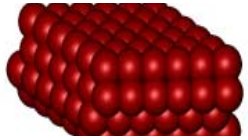
CATALYSIS CENTER FOR ENERGY INNOVATION
AN ENERGY FRONTIER RESEARCH CENTER

RAPID Transforming Process Industries

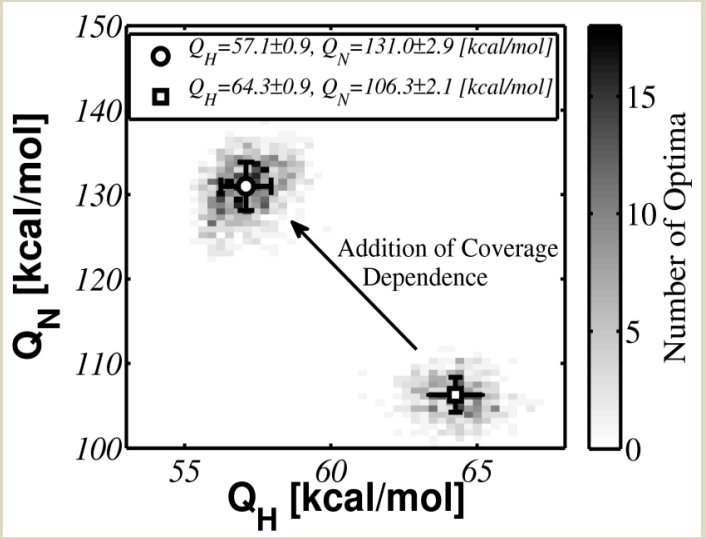
Delaware Energy Institute

Identifying Bimetallic Catalysts: Uncertainty & Informatics

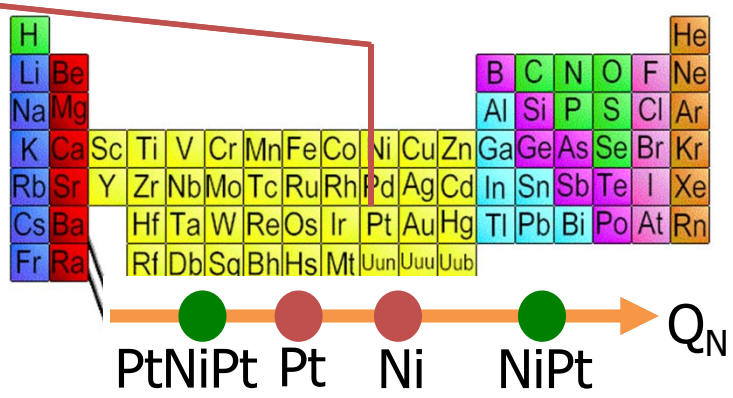
Informatics Databases

Structure	Metals	BE_N (kcal/mol)
Subsurface Core-shell-shell 	PtTiPt	56.5
	PtVPt	59.5
	PtCrPt	72.6
	PtMnPt	84.9
	PtFePt	83.9
	PtCoPt	87.0
	PtNiPt	**89.8**
Surface Core-shell 	CoPtPt	127.8
	NiPtPt	**130.5**
	FePtPt	137.7
	MnPtPt	162.2
	CrPtPt	166.5
	VPtPt	184.1
	TiPtPt	191.5
	**Pt**	**102.1**
	Ni	**113.8**

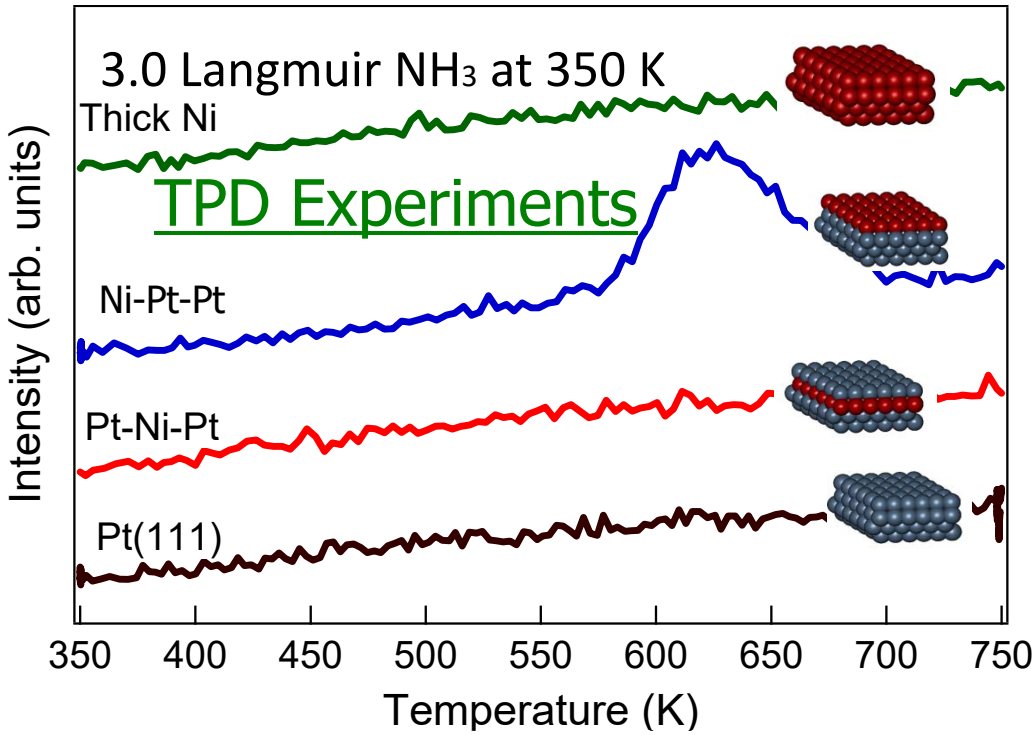
Activity (& Selectivity) Maps



Variation in pre-exponentials



Emergent Behavior



$$2NH_3 = N_2 + 3H_2$$

- **Ni-Pt-Pt is the most active single crystal catalyst known today!**
- **Interpolation principle is inadequate**
- **Core-shell bimetallics provide a *'new class of materials'* that *'expands the periodic table'***

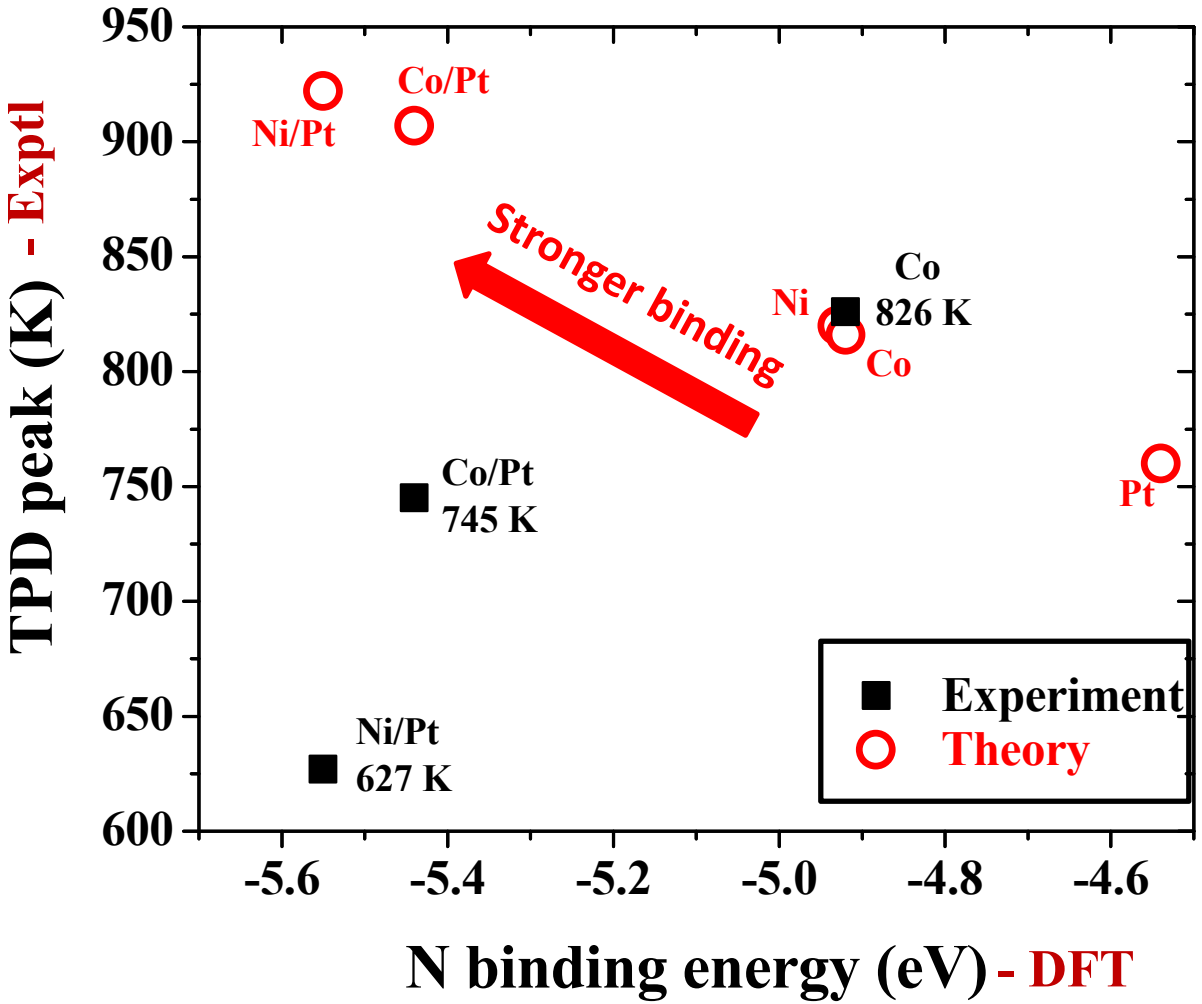
ARTICLES
PUBLISHED ONLINE: 25 APRIL 2010 | DOI: 10.1038/NCHEM.626
nature chemistry

Using first principles to predict bimetallic catalysts for the ammonia decomposition reaction

Danielle A. Hansgen, Dionisios G. Vlachos* and Jingguang G. Chen*

The facile decomposition of ammonia to produce hydrogen is critical to its use as a hydrogen storage medium in a hydrogen economy, and although ruthenium shows good activity for catalysing this process, its expense and scarcity are prohibitive to large-scale commercialization. The need to develop alternative catalysts has been addressed here, using microkinetic modelling combined with density functional studies to identify suitable monolayer bimetallic (surface or subsurface) catalysts based on nitrogen binding energies. The Ni-Pt-Pt(111) surface, with one monolayer of Ni atoms residing on a Pt(111) substrate, was predicted to be a catalytically active surface. This was verified using temperature-programmed desorption and high-resolution electron energy loss spectroscopy experiments. The results reported here provide a framework for complex catalyst discovery. They also demonstrate the critical importance of combining theoretical and experimental approaches for identifying desirable monolayer bimetallic systems when the surface properties are not a linear function of the parent metals.

Typical Descriptor Fails to Describe Experiments



$$-\frac{d\theta_N}{dT} = \frac{k_0}{\beta_H}\theta_N{}^2 \exp(-E_a(\theta_N)/(k_B T))$$

- **Binding energy** on terrace sites is **not a good descriptor**, especially for bimetallic surfaces

Hansgen, D. A. *et al. J. Chem. Phys.* **2011,** 134, (18), 184701.

Outline

- Energy, sustainability, and technological needs
- Grand computational challenges
- Topics
  - Catalyst prediction
  - Uncertainty
  - Design of active site
  - Materials gap
- Outlook

CATALYSIS

Synthesis,

multiscale modeling and

***in situ* characterization**

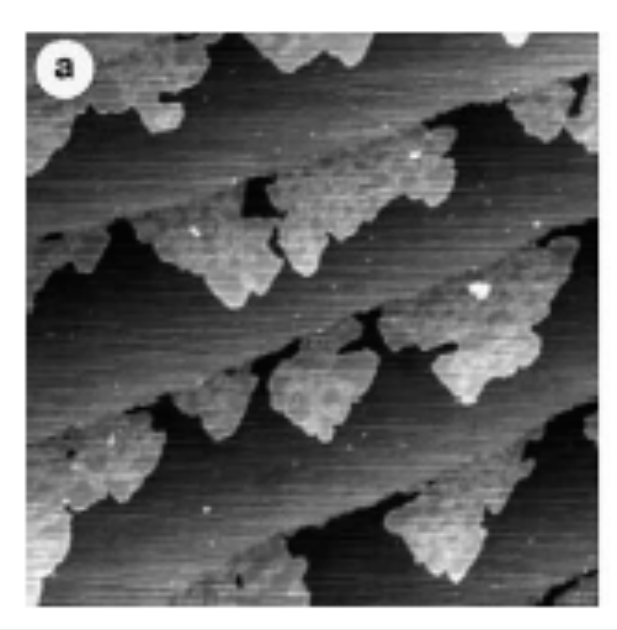
form the pillars of modern

catalytic science

Microstructure of Core-Shell Catalysts

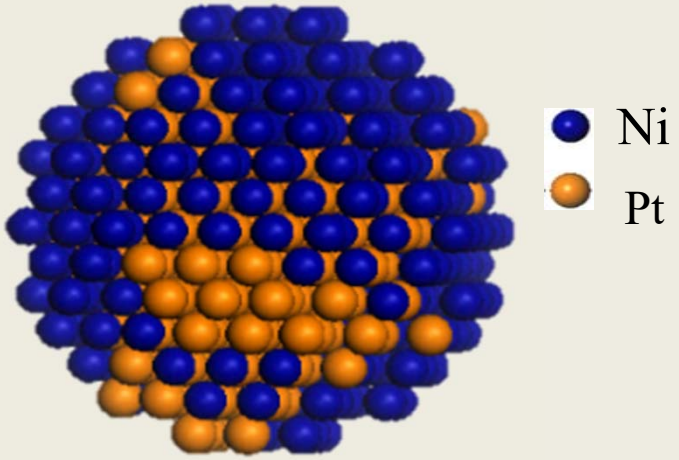
- **Microstructure** consists of a defected monolayer

STM image



Kitchin et al., *Surf. Sci.* **544**, 295, (2003)

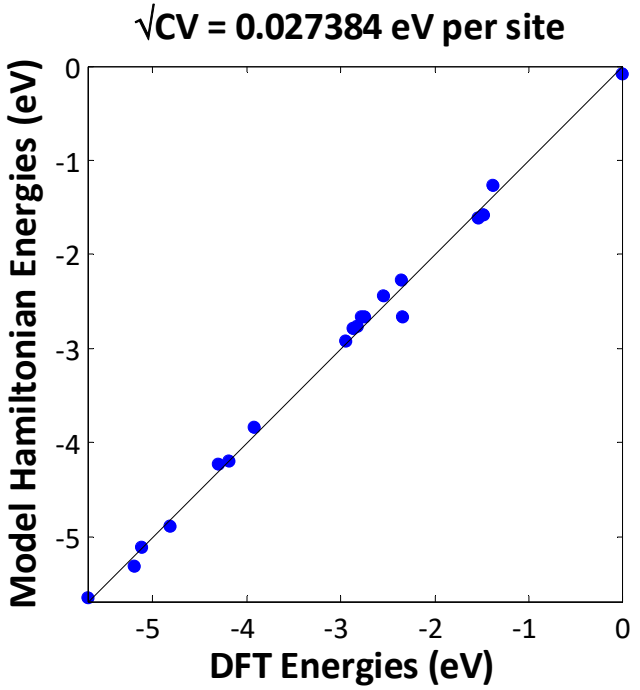
Reconstruction (in situ EXAFS data)

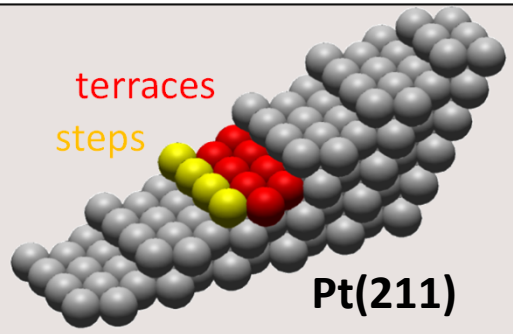


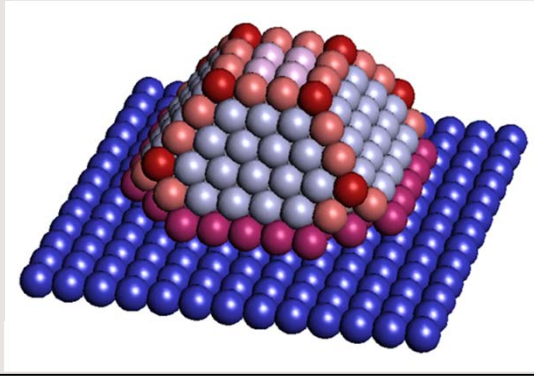
Tupy et al., *ACS Catal.* **2**, 2290 (2012)

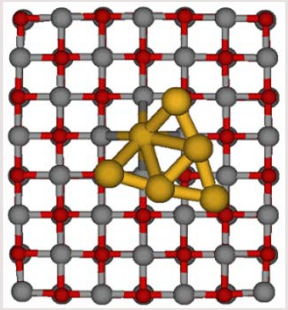
Features of Graph-Theoretical KMC

- Complex chemistries
- Accurate lateral interactions – Cluster expansion
- **Microscopic reversibility and thermodynamic consistency**
- **Fast algorithms**
- **Multiple facets, nanoparticles, clusters, multifunctional materials**

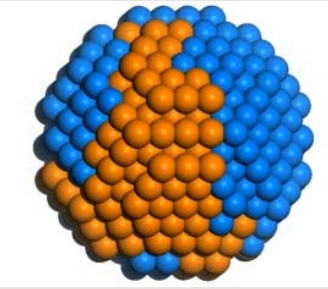








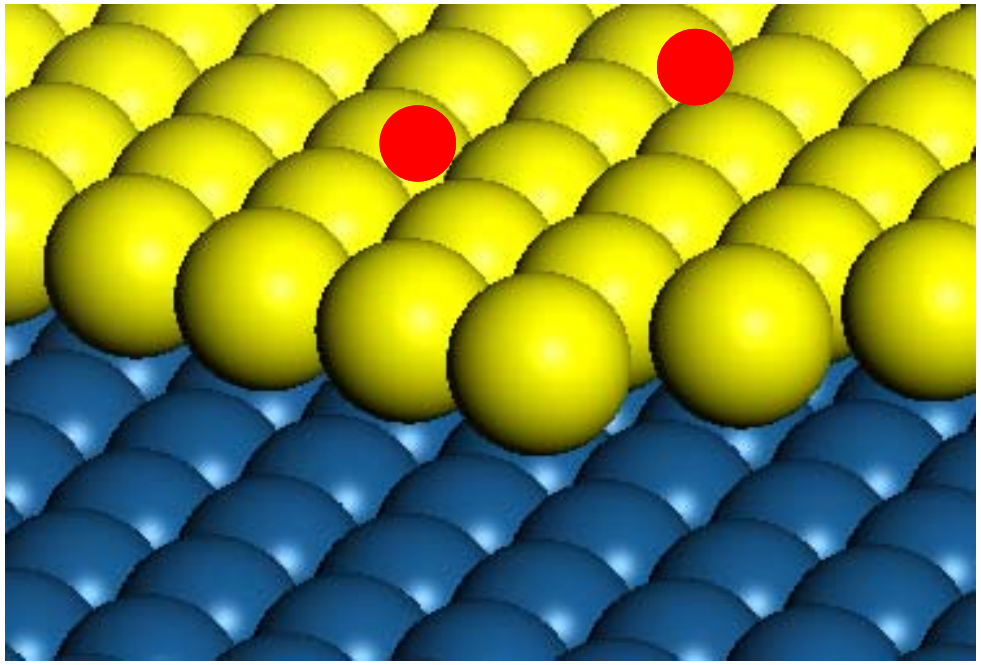
Au_6^{-1}/MgO



Ni/Pt - EXAFS

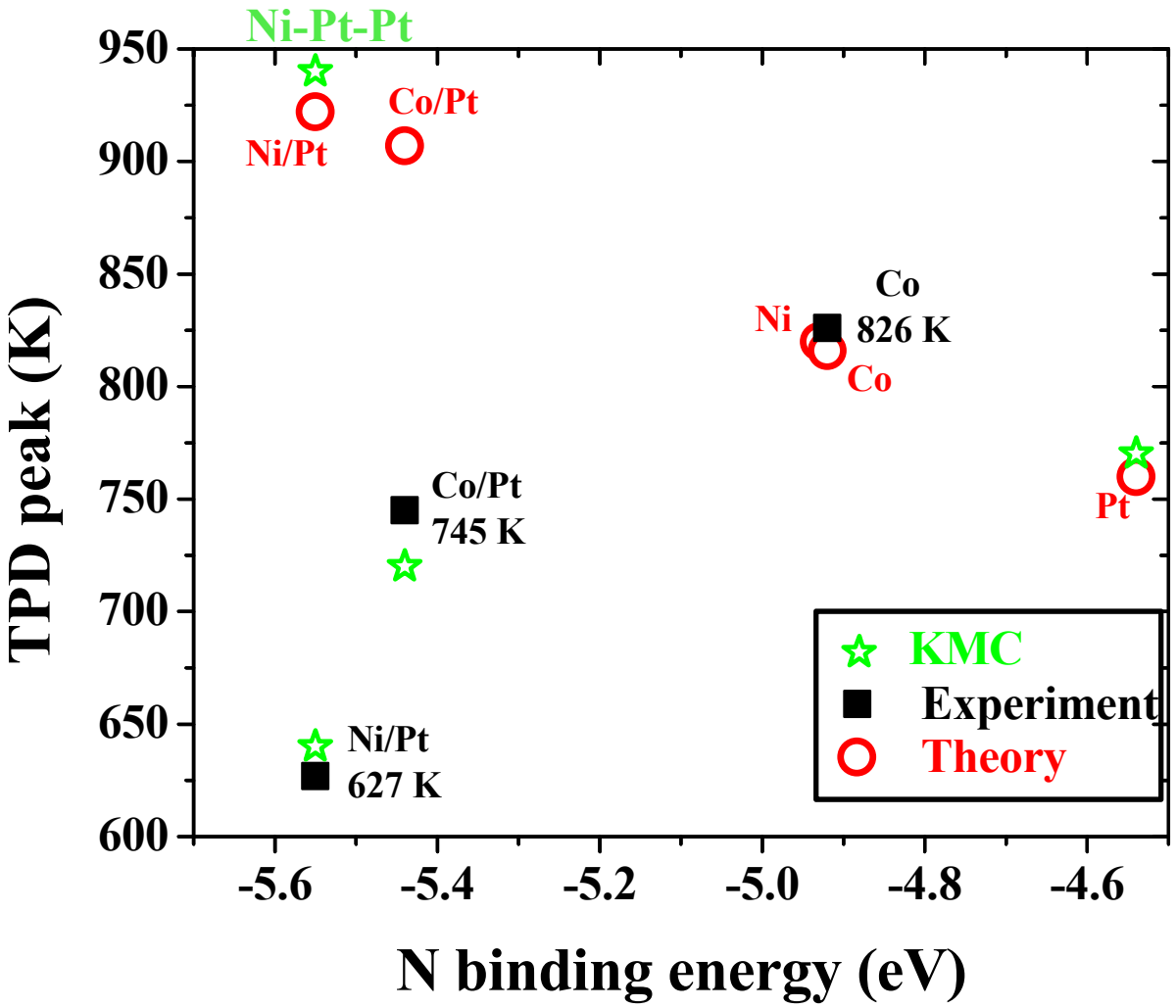
Reviews: Chatterjee and Vlachos, *J. Comp.-Aided Mat. Design* **14**, 253 (2007); Stamatakis and Vlachos, *ACS Catal.* **2**, 2648 (2012).

A Minimum Energy Path: Defected Bimetallics



- Ni/Pt serves as a reservoir of N due to strong binding
- N diffuses at interfacial sites invoking steps and Pt terraces and associates and desorbs from there

First-Principles KMC Resolves Structure Sensitivity



- Flat surfaces: strong N binding results in high desorption temperature, well described by Redhead theory
- Steps are responsible for the low N_2 desorption temperature on Ni/Pt and Co/Pt surfaces

Microstructure Can Profoundly Impact Activity

nature COMMUNICATIONS

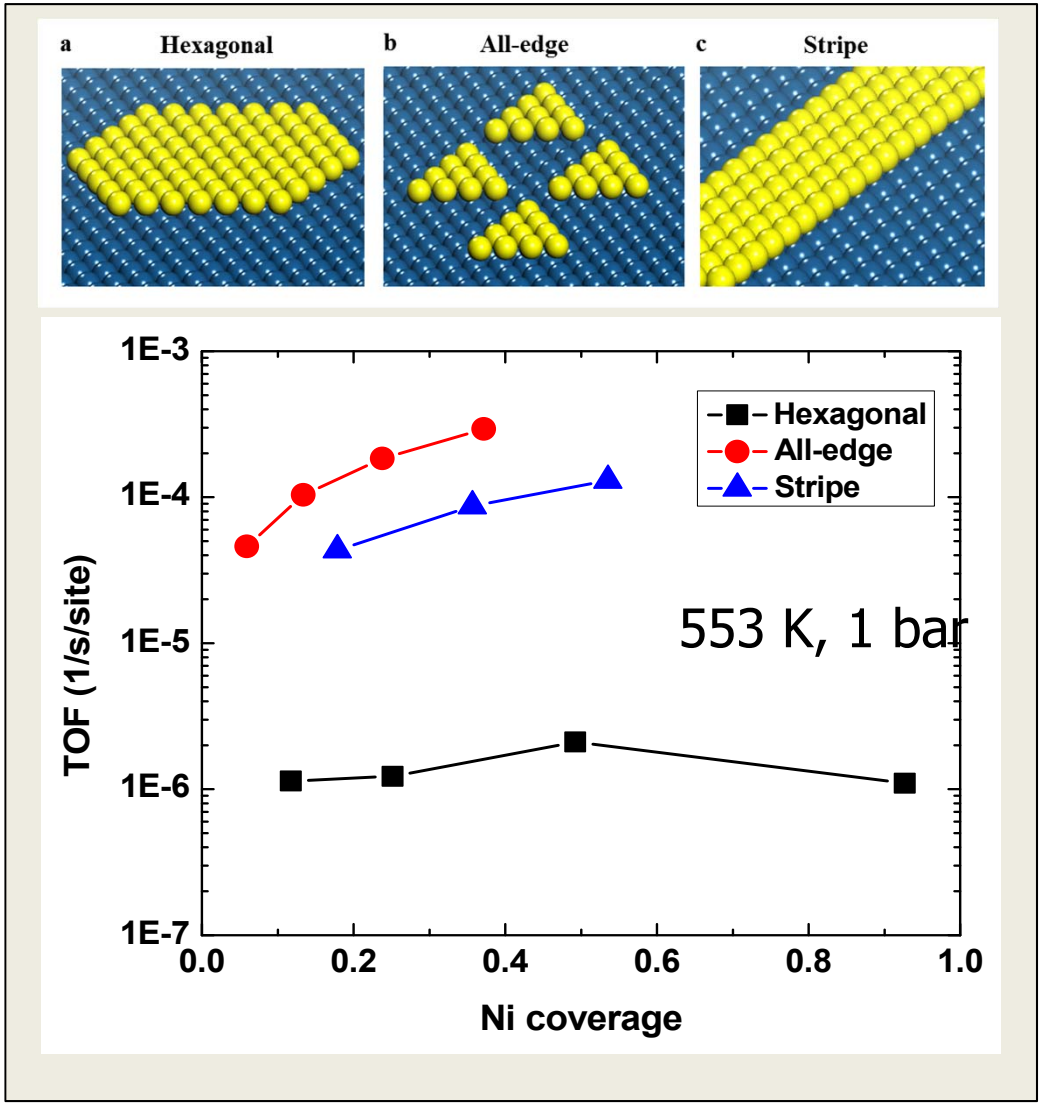
ARTICLE

Received 17 Jan 2015 | Accepted 12 Sep 2015 | Published 7 Oct 2015 DOI: 10.1038/ncomms9619 OPEN

Patched bimetallic surfaces are active catalysts for ammonia decomposition

Wei Guo[1,2,3] & Dionisios G. Vlachos[1]

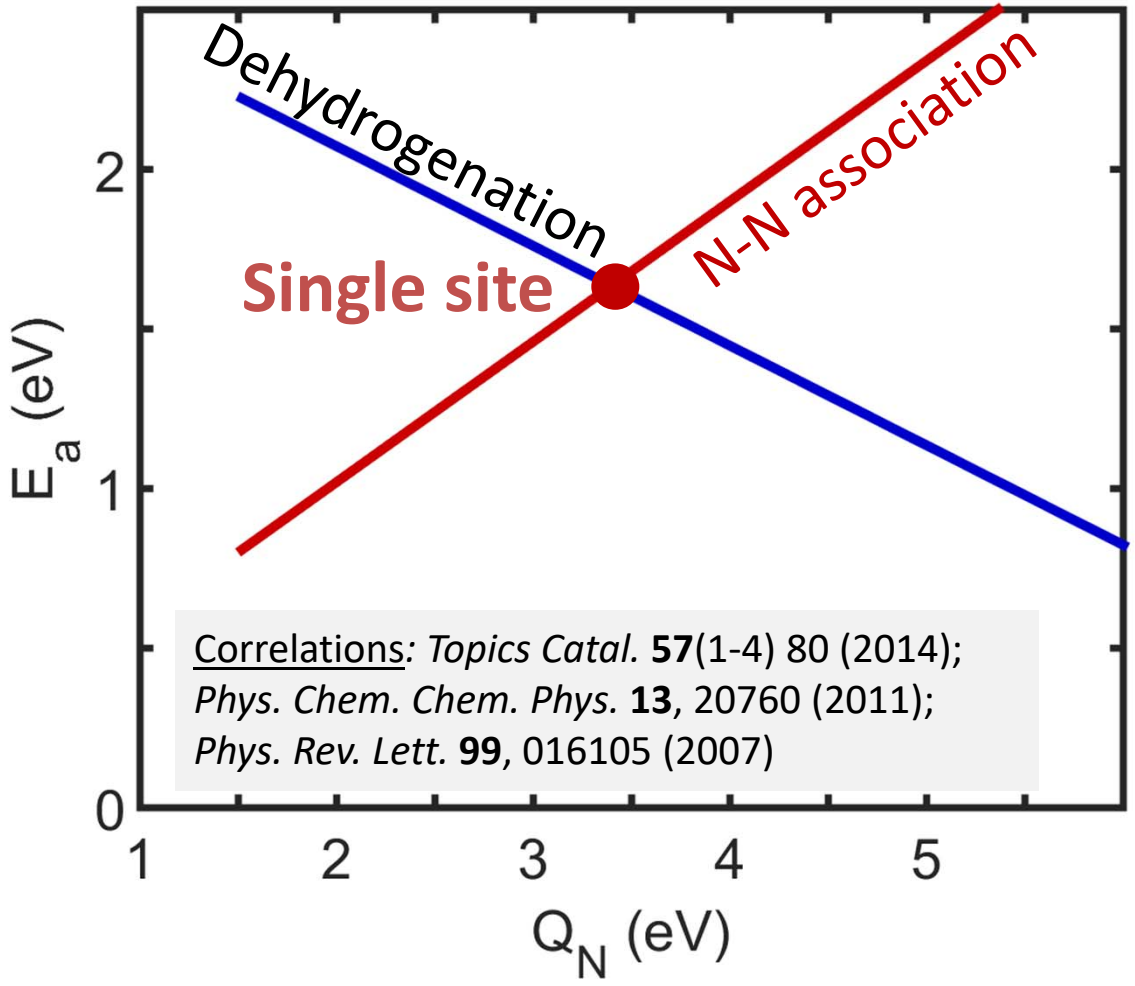
- How do we determine the active site?
- How do we find the optimal catalyst structure?
  - Shape, size, spatial arrangement in multifunctional materials



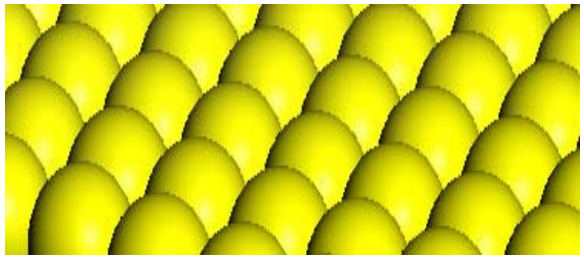
* Guo and Vlachos, *Nature Communications* **6**, No. 8619 (2015); doi:10.1038/ncomms9619

Controlling Multiple (Tandem) Reactions

Re-interpreting the Volcano curve



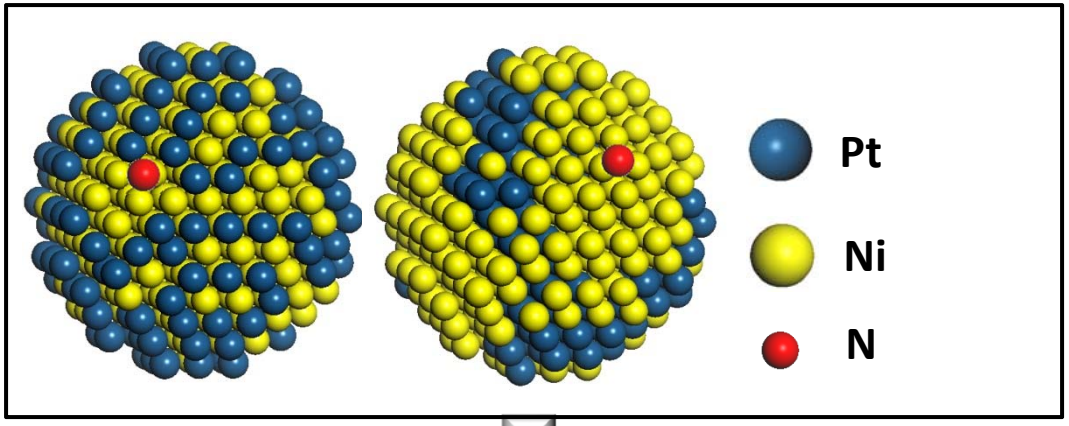
Correlations: *Topics Catal.* **57**(1-4) 80 (2014);
Phys. Chem. Chem. Phys. **13**, 20760 (2011);
Phys. Rev. Lett. **99**, 016105 (2007)



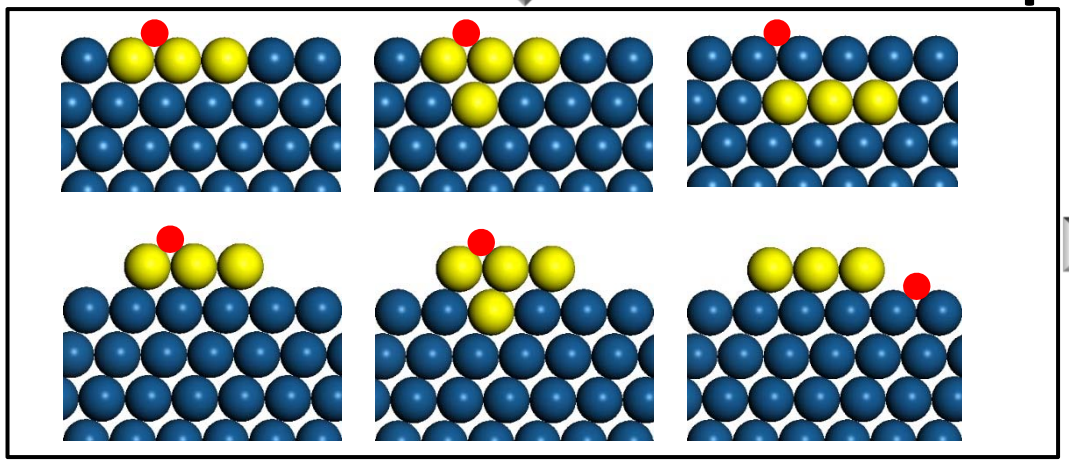
Single site leads to a volcano due to competing rate determining steps

Highest rate is controlled by thermodynamics and kinetics

Energetics of Complex Microstructures



Structure Sampling



DFT

Hamiltonian

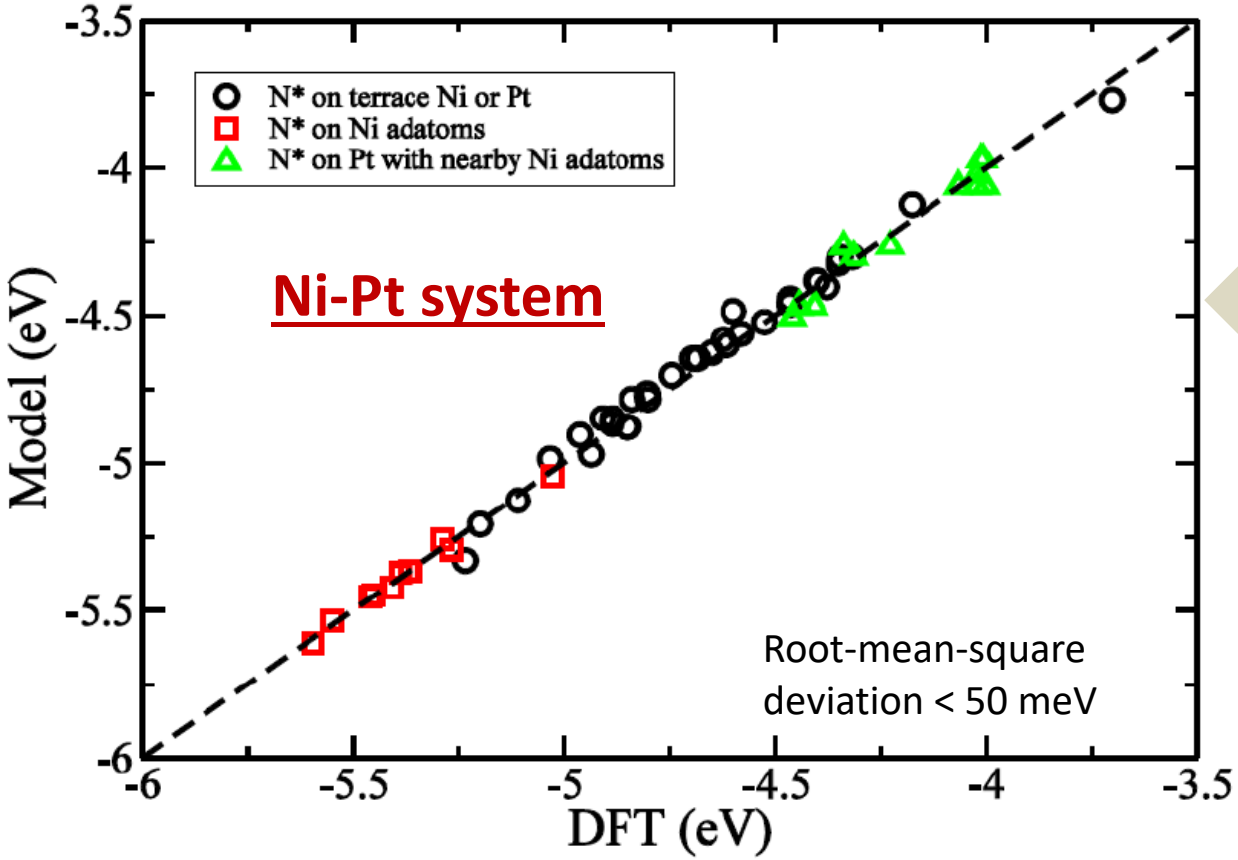
- Effect of Ni coordination
- Effect of lateral interactions

$$\Delta E(N^*) = \Delta E_{Pt}(N^*) + tr(\bar{\mathrm{E}} \cdot \overline{n_{Ni}})$$

$\overline{n_{Ni}}$ — # of i^{th} (i=1, 2, 3) Ni nearest neighbors around an N atom

- A bilinear model is postulated with respect to microstructure (Ni coordination) and N coverage

Designing Active Sites with Dialed-in Properties



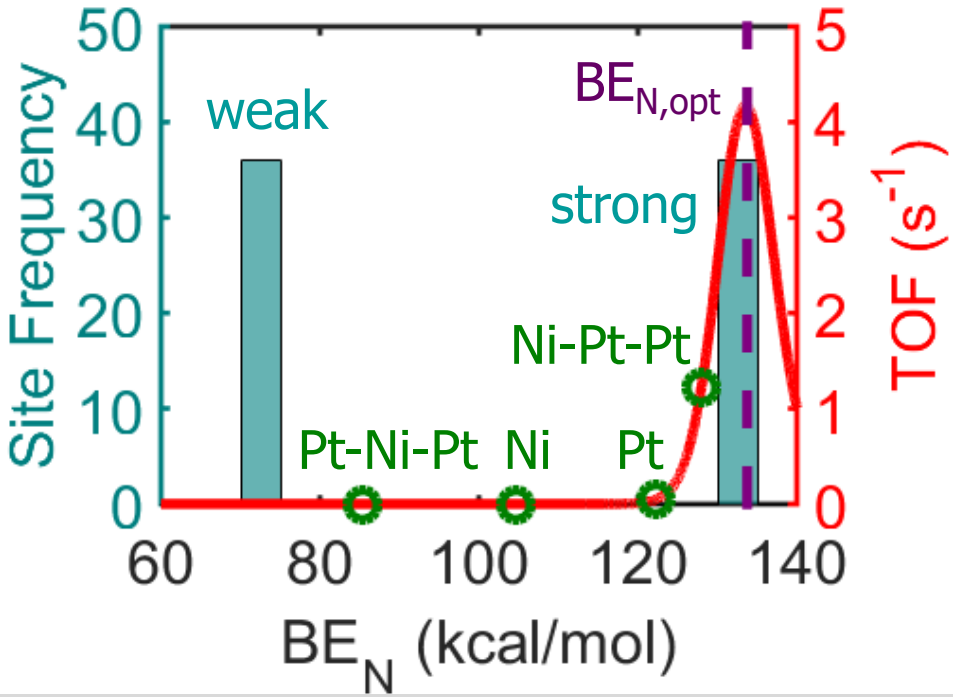
Hamiltonian Model describes energies well

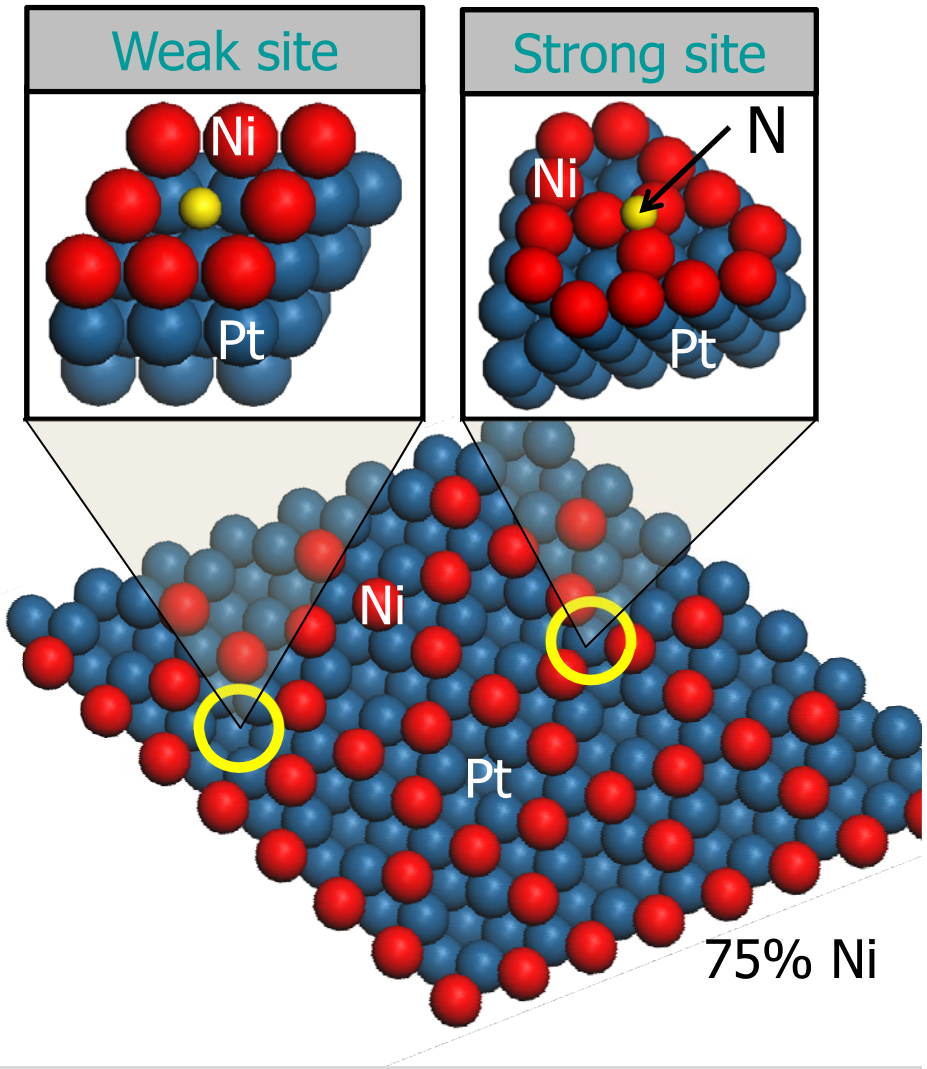
- **Energies can be tuned over a wide range of ~2 eV even for a single bimetallic** (loading and location dependent)
- **Multimetallics provide an uncharted territory**

Guo and Vlachos, *J. Chem. Phys.* **138**, No. 174702; 8 pgs. (2013).

Determining the Active Site(s)

- A genetic algorithm automatically identifies active site(s) with machine learning for rate





Nunez and Vlachos, In preparation.

Outline

- Energy, sustainability, and technological needs
- Grand computational challenges
- Topics
  - Catalyst prediction
  - Uncertainty
  - Design of active site
  - Materials gap
- Outlook

CATALYSIS

Synthesis,

multiscale modeling and

***in situ* characterization**

form the pillars of modern

catalytic science

CATALYSIS CENTER FOR ENERGY INNOVATION
AN ENERGY FRONTIER RESEARCH CENTER

RAPID Transforming Process Industries

Delaware Energy Institute

nature COMMUNICATIONS

Nat. Comm. 8, 1842 (2017)

Can vibrational signatures close the materials gap?

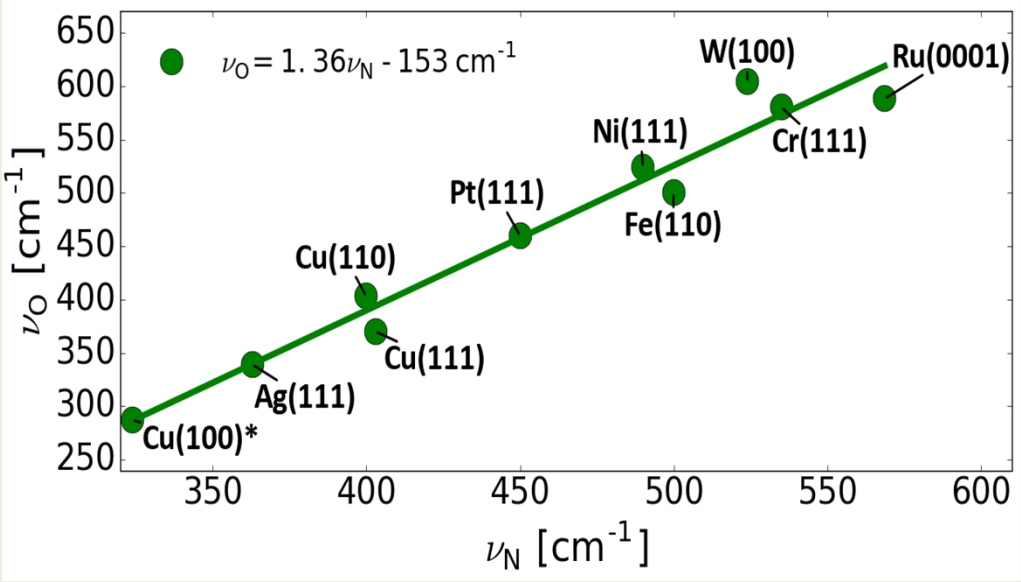
ARTICLE

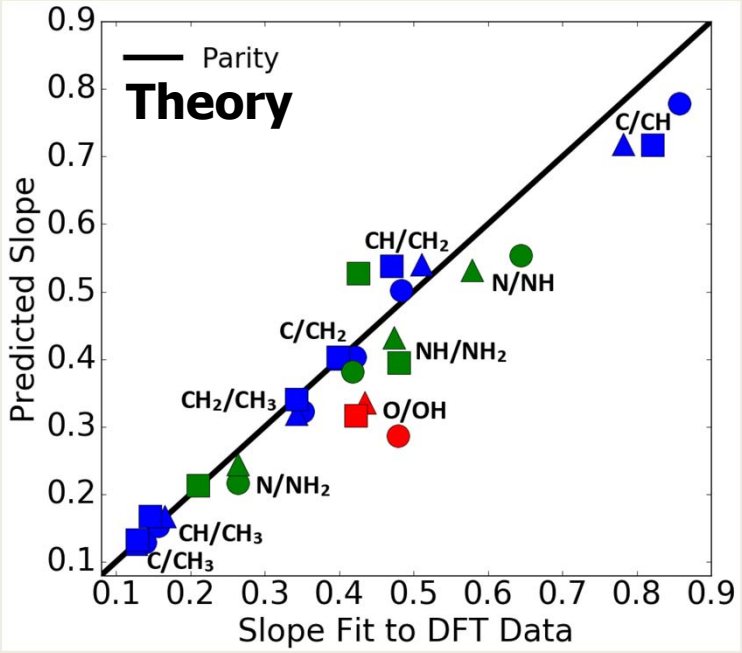
DOI: 10.1038/s41467-017-01983-6 OPEN

Scaling relationships and theory for vibrational frequencies of adsorbates on transition metal surfaces

Joshua L. Lansford[1], Alexander V. Mironenko[1,2] & Dionisios G. Vlachos[1,2]

Data from 40+ different HREEL studies





Outline

- Energy, sustainability, and technological needs
- Grand computational challenges
- Topics
  - Catalyst prediction
  - Uncertainty
  - Design of active site
  - Materials gap
- Outlook

CATALYSIS

Synthesis,

multiscale modeling and

***in situ* characterization**

form the pillars of modern

catalytic science

Summary and Outlook

Drivers & Current Status

- Sustainability and breakthroughs are necessary
- Materials are key to energy applications
- Tremendous advances in synthesis & operando characterization
- Models provide unprecedented opportunity for atom-by atom design of materials and for process design
- Models for *in silico* materials prediction are not currently adequate

Three Grand Challenges

- **Materials gap**: optimization of microstructure, synthesis, and stability
- **Predictive modeling**: Parametric and model form uncertainty
  - Can **data science** make models more predictive?
  - How do we design experiments?
- **Process and product design** vs. **materials/media design**
  - Should catalyst and media (solvent) around the active site be optimized simultaneously with process and product design?

Acknowledgements

- Students/Postdocs
  - **Danielle Hansgen**; Ying Chen; Mike Salciccioli; **Zach Ulissi**; **Wei Guo**; **Taylor Robie; Ioanna Fampiou; Marcel Nunez**
- Collaborators
  - **Jingguang Chen, Markos Katsoulakis**
- Funding
  - **NSF, CCEI/EFRC, DOE, DARPA**