Multiscale Modeling and its Application to Catalyst Design and Portable Power Generation

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Outline

- Decentralized, future energy production
- Miniaturization differs from scaling up
- Multiscale modeling
- Application of multiscale modeling to
  - Development of detailed reaction mechanisms
  - Microreactor design
  - Process optimization
  - Catalyst design
  - Experiment design

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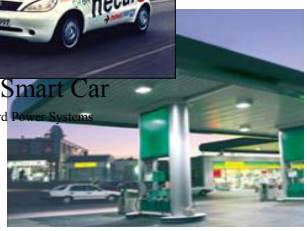
Down-scaling for future energy needs

- Distributed energy
  - On-board H_2 production
  - Electric reliability
  - Local solutions, e.g., farms based on biomass

Smart Car



Courtesy: Ballard Power Systems

- Portable energy (electronics)

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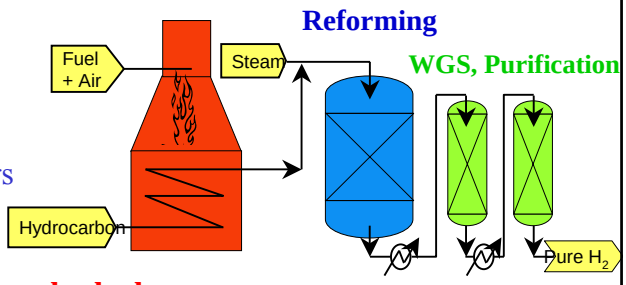
Large scale H_2 production is industrially mature

- Steady state operation
- Reforming: endothermic, heat transfer controlled
  - Fixed bed catalytic reactors with Ni catalyst for syngas



- **Large scale flames supply the heat**
  - **Half of NG is burned to CO_2 and H_2O**
- Complex downstream processing WGS and PROX or membrane separation/PSA
- Slow (τ~1s); bulky

SR: $CH_4 + H_2O = CO + 3H_2$ + 206 kJ/mol
WGS: $CO + H_2O = CO_2 + H_2$ - 41 kJ/mol

Steam reforming is a bulky process

Sehested, *Cat. Today* 111 (2006) 103

First example of on-board reforming

- GM unveiled the world's first gasoline fuel processor for fuel cell propulsion at the annual automotive management conference in Traverse City, Mich.
- The Gen III processor, packaged in a Chevrolet S-10 pickup, reforms 'clean' gasoline onboard, extracting a stream of hydrogen to send to the fuel cell stack.

Microsystems for transportation and portable applications

- Advantages
  - Process intensification
    - High heat and mass transfer coefficients
    - Multifunctionality
  - Compactness
  - Inherently safe
- Scale out is feasible for portable (small scale) devices

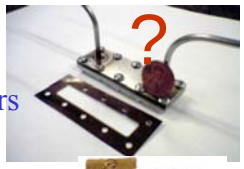
Smart Car

Courtesy: Ballard Power Syste

Microscales impose challenges and offer opportunities[1]

- Laminar flows - mixing?
- Small systems - enough catalyst?
- Reactors shake - no moveable parts
- Need small pressure drops

Monolithic type reactors



- Transient operation very common
  - Fast startup and shutdown require active catalyst and fast heat transfer
  - Catalyst deactivation can become a major issue

Dynamics

New chemistry and catalysts

- Fast chemistry
- Different systems' engineering[2]

Flowsheets/Optimization

[1] Norton *et al.*, "Downsizing chemical processes for portable hydrogen production", in *Microreactor Techn. Process Intensification*, ACS Symp. Series 914, 179 (2005)
[2] Mitsos *et al.*, IECR 43, 74 (2004)

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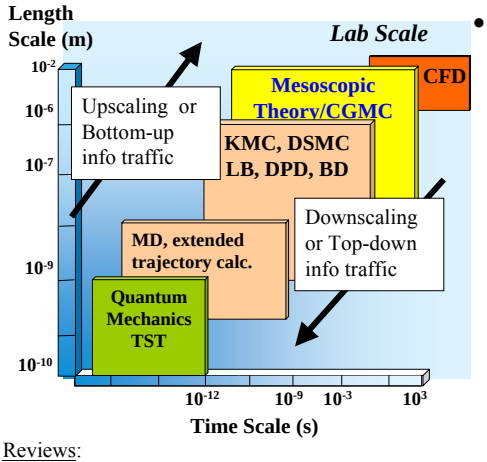
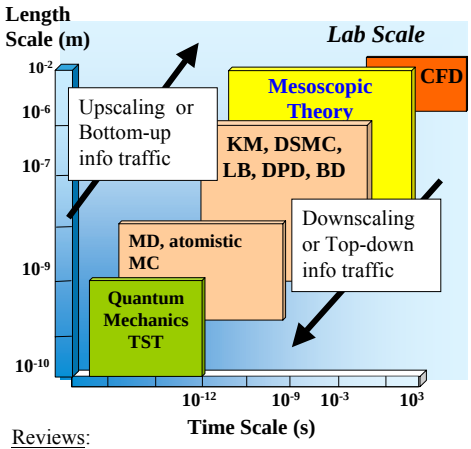
The multiscale simulation paradigm: A bottom-up ladder



Reviews:
Raimondeau and Vlachos, *Chem. Eng. J.* **90**, 3 (2002);
Chatterjee et al., *Chem. Eng. Sci., ISCRE Issue* (2004);
Vlachos, *Adv. Chem. Eng.* . **30**, 1 (2005)

- Previous work
  - focused usually on a single scale and one way of information passing
  - developed structure-properties relations (molecular descriptors) without attention to processing

The Multiscale Simulation Paradigm: Predict macroscopic performance from first principles



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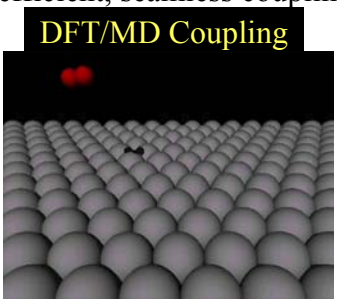
Vlachos, *Adv. Chem. Eng.* **30**, 1 (2005)

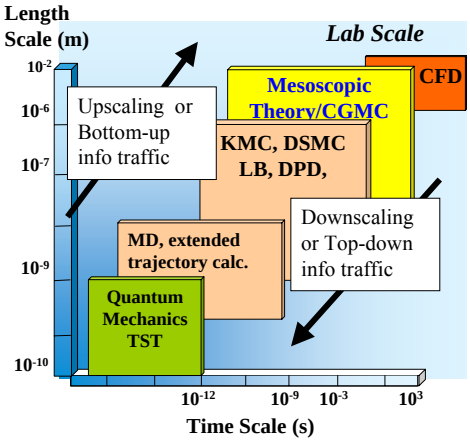
* For noise control in hybrid siml, see work by groups of Braatz, Christofides, Vlachos

- Challenges
  - Phenomena and models are strongly coupled
  - Develop bridges between models of various scales to enable accurate, robust, efficient, seamless coupling*



Ludwig and Vlachos, Mol. Simul. (2004)

The multiscale simulation paradigm: A bottom-up ladder



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- **Direct multiscale simulation (hybrid, coarse graining) is possible for systems of moderate complexity**
- **It is plagued by computational cost for complex systems, such as chemical reactors**
- **Are all scales and phenomena important?**

Hierarchical, multiscale model development

- Lower Level Theory
- Microkinetic model chemistry parameters
  - Semi-empirical techniques (BOC), TST
- Catalyst model
  - Mean field approximation
- Fluid flow/Transport
  - Simple reactor models (PFR, CSTR, transp. correlations)

Hierarchical, multiscale model development

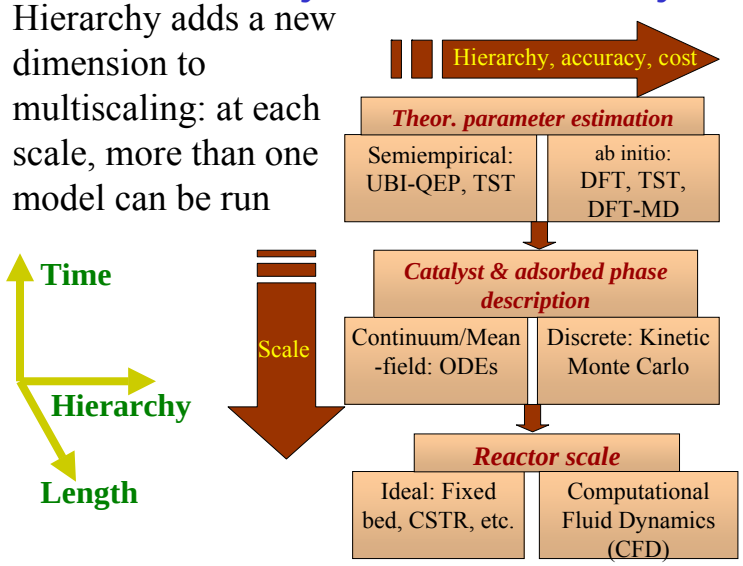
- Last theoretical level:

  Engineering models are needed for reactor optimization and control and for model-based catalyst design

- Feature identification toolbox enables hierarchical model development and reduction

Hierarchy enables rapid screening of chemistry, fuels, and catalysts

- Hierarchy adds a new dimension to multiscaling: at each scale, more than one model can be run



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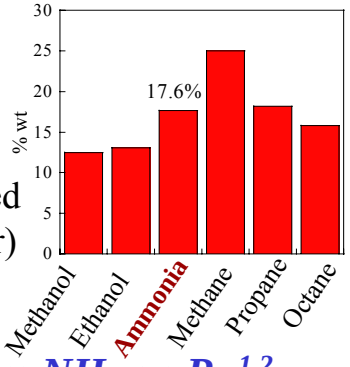
NH_3 cracking for H_2 production

- ***Good hydrogen carrier***
  - High energy density
  - Stored as a liquid (at 25 ^oC, 8 atm)
  - One of the most widely produced chemicals (>100 metric tones/yr)
    - Haber-Bosch Process
    - Infrastructure is already set up



- ***Catalytic decomposition of pure NH_3 on Ru[1,2]***

$$2\,NH_3 \rightarrow N_2 + 3\,H_2 + 46\ kJ/mol$$

  – Slightly endothermic

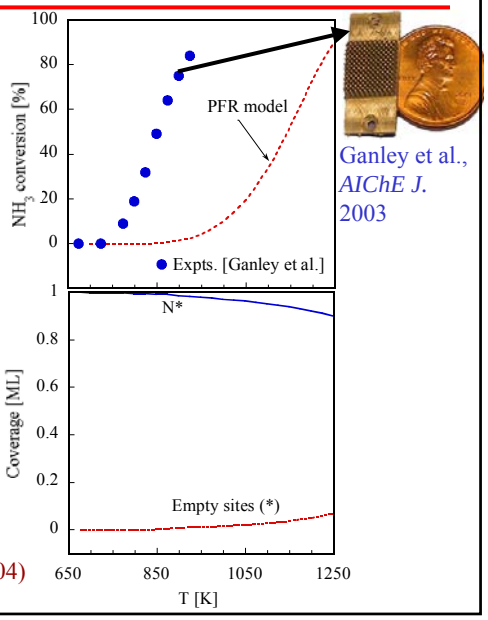
  – Minimal downstream processing

[1] Deshmukh et al., Ind. Eng. Chem. Res. (2004)
[2] Ganley et al., AIChE J. (2004)

NH_3 decomposition on Ru: $2NH_3 = N_2 + 3H_2$

- NH_3 as a storage medium
- 'Pure' H_2 – No CO_x
- A microkinetic model is build using BOC and TST
- Our microkinetic model captures the trend
- High N* coverages

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

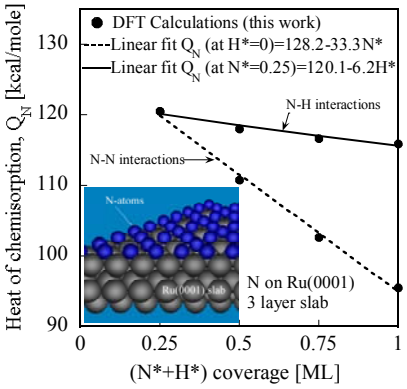


Ganley et al., *AIChE J.* 2003

Mhadeshwar et al., *Cat. Letters* **96**, 13-22 (2004)

DFT is used to estimate lateral interactions

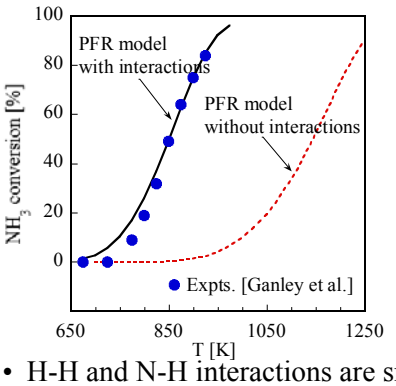
- DACAPO (solid-state electronic structure package by Hammer and coworkers*)
- 3-Layer slab of Ru(0001)
- 2 × 2 unit cell
- All layers are relaxed
- Plane wave cutoff = 350eV
- 18 k-points for surface Brillouin zone
- Generalized gradient approximation (PW-91)

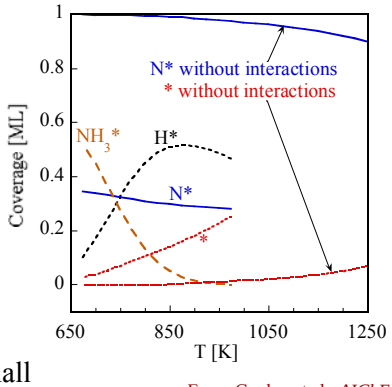


Deshmukh et al., *Int. J. Multiscale Comp. Eng.* **2**, 221-238 (2004)

* Hammer et al., DACAPO version 2.7 (CAMP, Technical University, Denmark)

DFT-retrained microkinetic model describes the experimental data well



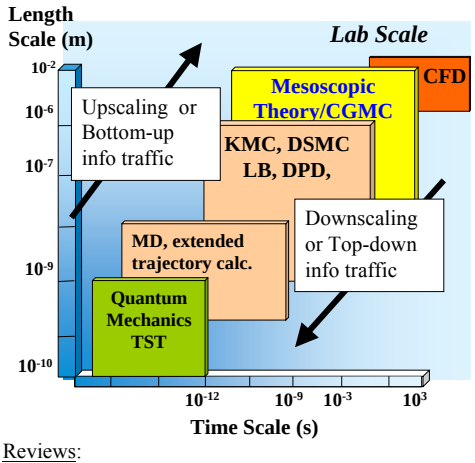


- H-H and N-H interactions are small
- N-N interactions completely change the chemistry
- **Extensive validation against UHV and high P data has been done**

Exps: Ganley et al., *AIChE J.* (2004)

Deshmukh et al., *Int. J. Multiscale Comp. Eng.* **2**, 221-238 (2004)

The multiscale simulation paradigm: A bottom-up ladder



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- **Typical objective**
  - Mechanistic understanding
  - Reconcile large differences in published data
  - Process optimization: **Process engineering**

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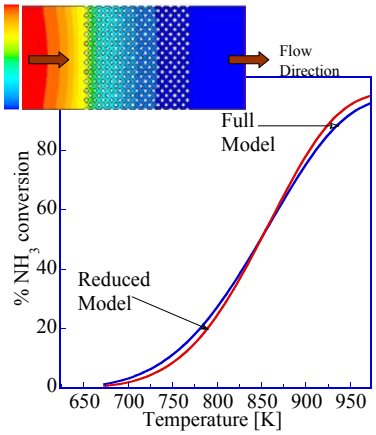
Computer-aided chemistry reduction

- Sensitivity and Principal Component Analyses
  - No *a priori* assumptions
  - Identification of important reactions and species
- Small parameter asymptotics on species balances and site conservation
  - Simple algebra to derive a rate expression



Mhadeshwar *et al.*, *Cat. Letters* **96,** 13 (2004)

Reduced Model

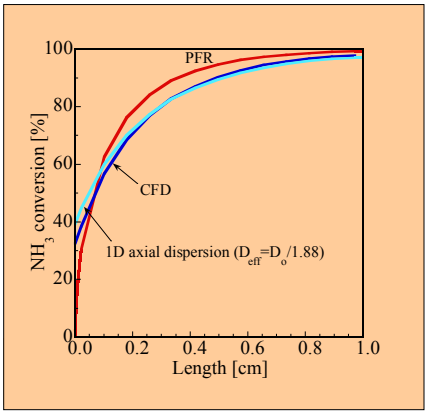
$$\sigma_{N_2} = k_4\theta_{N^*}^2 - k_3 P_{N_2}\theta_*^2$$

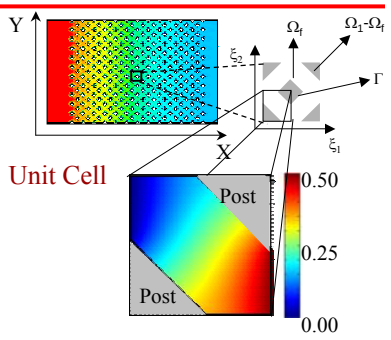
$$\sigma_{H_2} = 3\sigma_{N_2} \text{ and } \sigma_{NH_3} = -2\sigma_{N_2}$$

$$\theta_* = \frac{1}{1+\frac{k_{11}}{k_{12}}P_{NH_3}+\sqrt{\frac{k_1}{k_2}P_{H_2}}+\sqrt{\frac{k_3}{k_4}P_{N_2}}+\sqrt{\frac{k_2}{k_1}}\frac{k_7 k_9 k_{11}}{2k_4 k_{10} k_{12}}P_{NH_3}P_{H_2}^{-0.5}}$$

μReactor is close to axial dispersion model
D_{eff} vs. Geometric characteristics

- The method of homogenization is used that is based on separation of length scales $\varepsilon = \frac{\ell}{L} << 1$

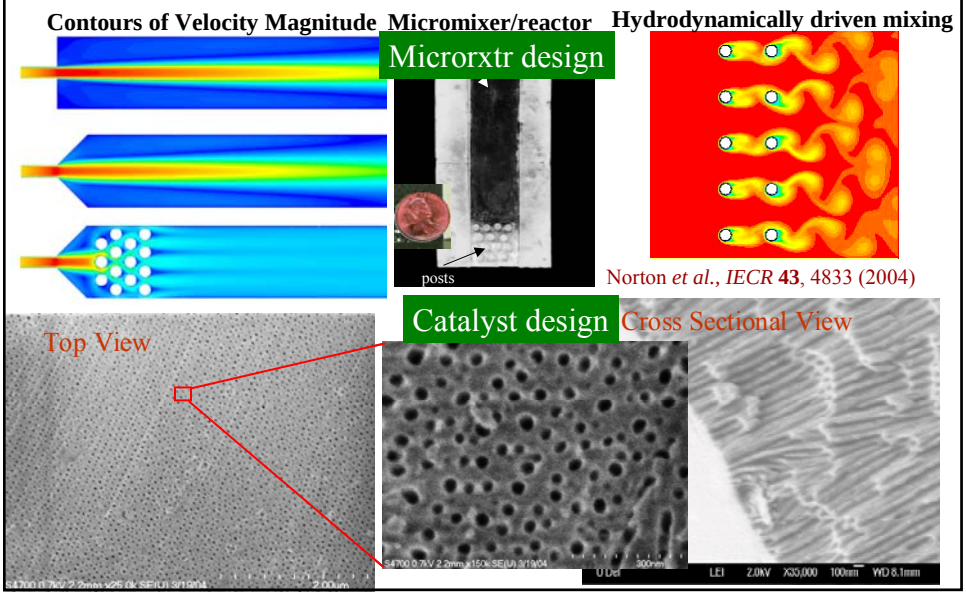




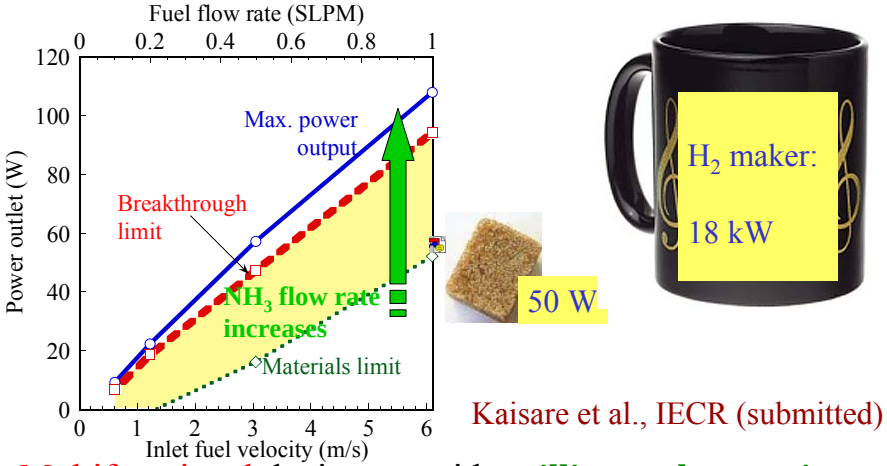
Multiscale simulation allows us to explore cheaply the effect of post shape, size, and density on microreactor performance by solving simple unit cell problems

Deshmukh et al., *Int. J. Multiscale Comp. Eng.* **2**, 221-238 (2004)

Design and fab of microchemical systems via multiscale modeling



Attainable regions in multifunctional microdevices



Kaisare et al., IECR (submitted)

- Multifunctional devices provide **millisecond operation**
- Adjustment of flow rates can provide **variable power**
- Scaling out can supply transportation power levels

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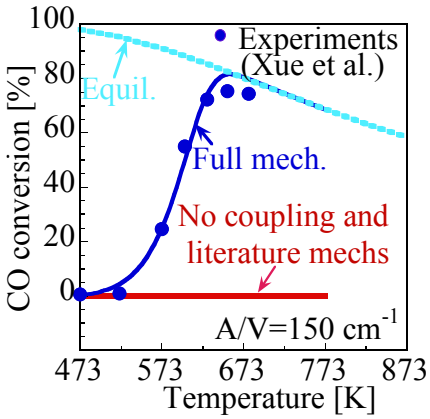
Water-gas shift reaction on Pt: $CO+H_2O=CO_2+H_2$

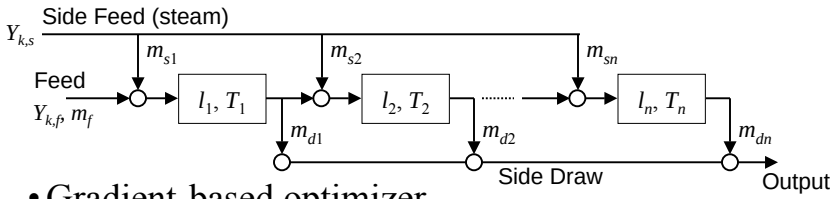


Thermodynamics[1] is important **but** not sufficient: **kinetics** 'corrects' the WGS speed

[1]Mhadeshwar et al., *J. Phys. Chem. B* (2003)

Reactor Superstructure Optimization

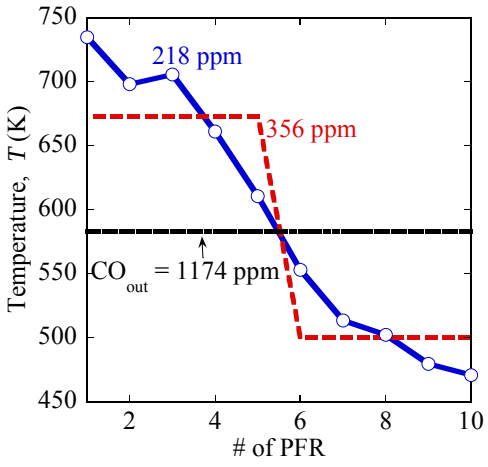
- Modeled as *n* PFRs in series
- Side feed and side draw from each reactor
- Each PFR: same length and different temperature



- Gradient-based optimizer

Process optimization: Optimum temperature profile in the WGS reaction

- Total length: $\sum_i l_i = 2\,\text{cm}$
- Inlet: 40 sccm feed (dry basis), with 18% CO
- Steam: $\sum_i m_{s,i} \le 40\,\text{sccm}$
- Temperature constraints: $373\,\text{K} \le T_i \le 873\,\text{K}$
- All cases:
  - No split feed or side draw
  - All steam utilized
  - *T* constraints were inactive



Vlachos et al., Compt. Chem. Eng. (2006)

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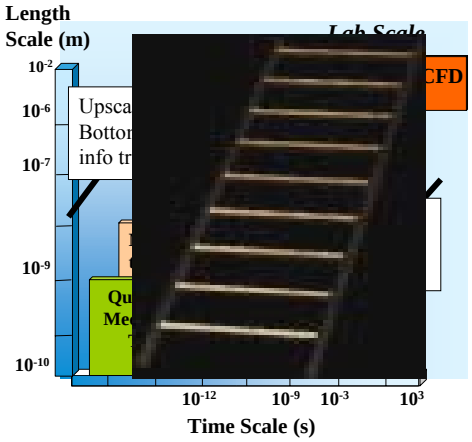
The multiscale simulation paradigm: A bottom up and top-down ladder



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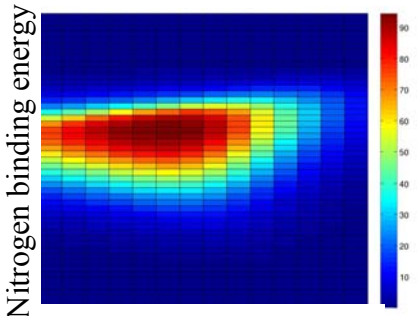
- **Typical objective**
  - Mechanistic understanding
  - Reconcile large differences in published data
  - Process optimization: **Process engineering**

- **Opportunity**
  - Given a macroscopic behavior, design materials and/or control nanoscale
  - **Product engineering**

An example of catalyst optimization: NH_3 decomposition

Ammonia conversion (%) at 380 °C



- Search is done on atomic descriptors while running the full chemistry model
- Libraries of computational information are created via DFT
- Models are built
- Potential catalyst candidates are identified

Ulissi et al.

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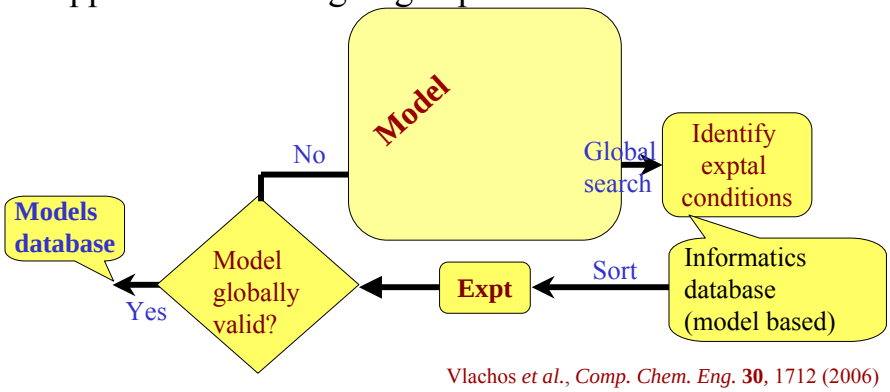
Maximizing information content of a model

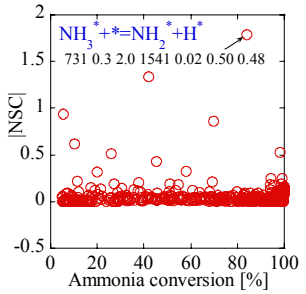
- Parameters are uncertain
- Often refined using statistically based experiments
- We need to bridge first-principles modeling with systems approaches in designing experiments



Vlachos *et al.*, *Comp. Chem. Eng.* **30**, 1712 (2006)

Model-based design of experiments: Ensuring global accuracy of models

- Global Monte Carlo search in **exptl parameter space** (τ, P, T, compos., A/V)
- Local sensitivity analysis
  - Only **a few model parameters are important** and can be **extracted**, **but change** in manipulated parameter space
- Sort by max NSC, RDS, MARI,…



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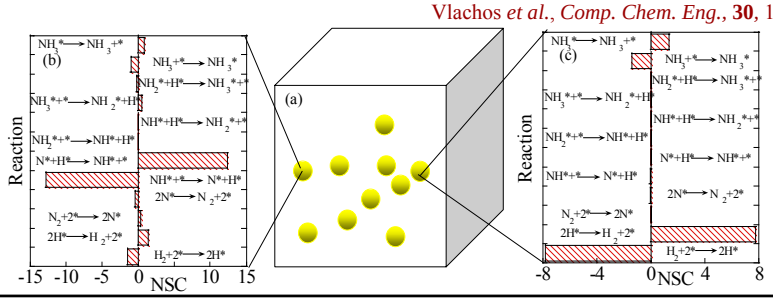
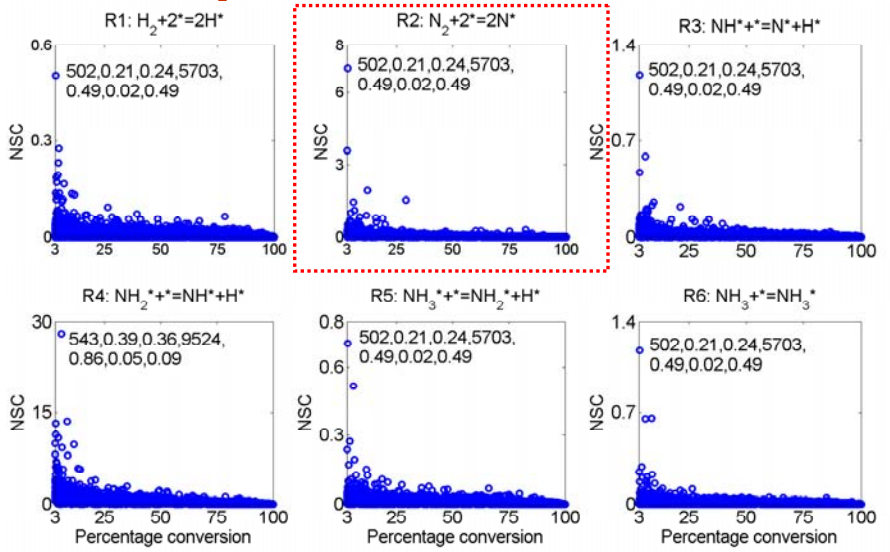
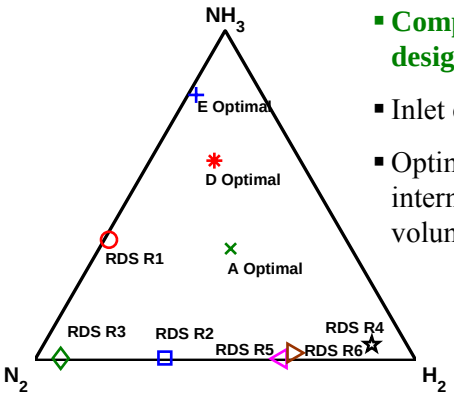


Normalized parameter sensitivity vs. conversion (CSTR)

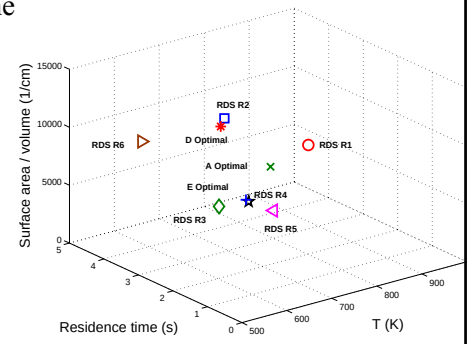
NH_2*+*=NH*+H* is the most sensitive reaction



Optimal statistical and physics-aided designs

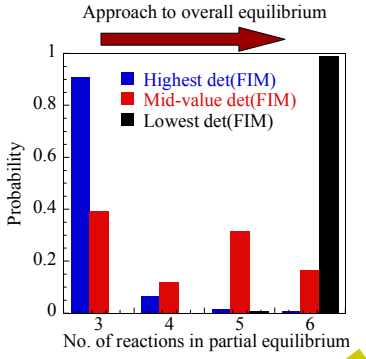


- **Compared D, A, E and physics-aided designs**
- Inlet composition space – no clear pattern
- Optimum at relatively low temperature, intermediate cat. surface area/reactor volume

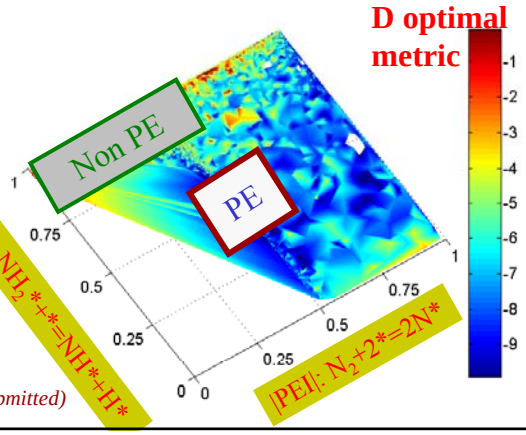


Prasad and Vlachos, *Ind. Eng. Chem. Res. (submitted)*

Kinetic relevance – D Optimality and partial equilibrium (PE)



High values of the det. of the Fisher info matrix correlate with fewer reactions in PE and farther from equil.



Partial equil. index:
$PEI=r_f/(r_f+r_b)$

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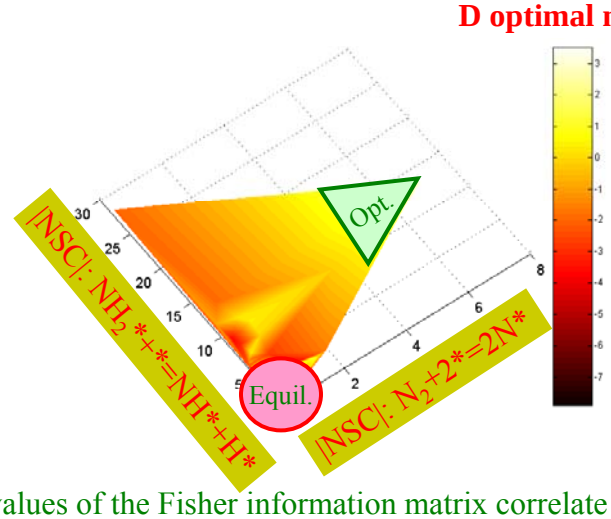
Kinetic relevance – D Optimality and sensitivity coefficients



High values of the Fisher information matrix correlate with larger normalized sensitivity coefficients of the sensitive reactions

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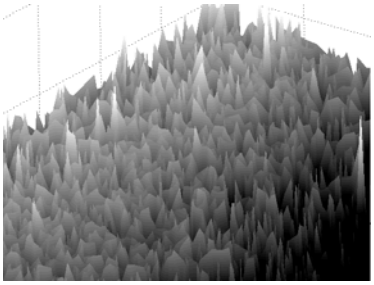
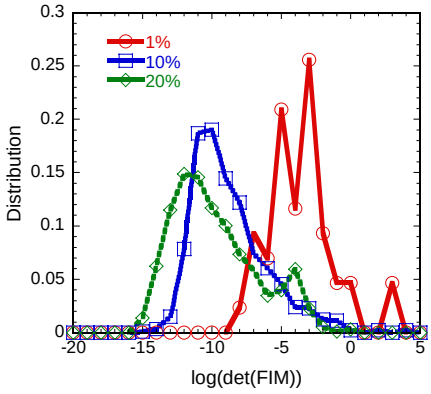
Is a Single Optimal Point Good Enough?

- The D optimal response surface is highly nonlinear
- You must be very close to the optimal point to ensure optimality
- Experimental constraints may make this unachievable

Representative cross-section of D optimal response surface



D optimal metric vs. distance from optimal poin



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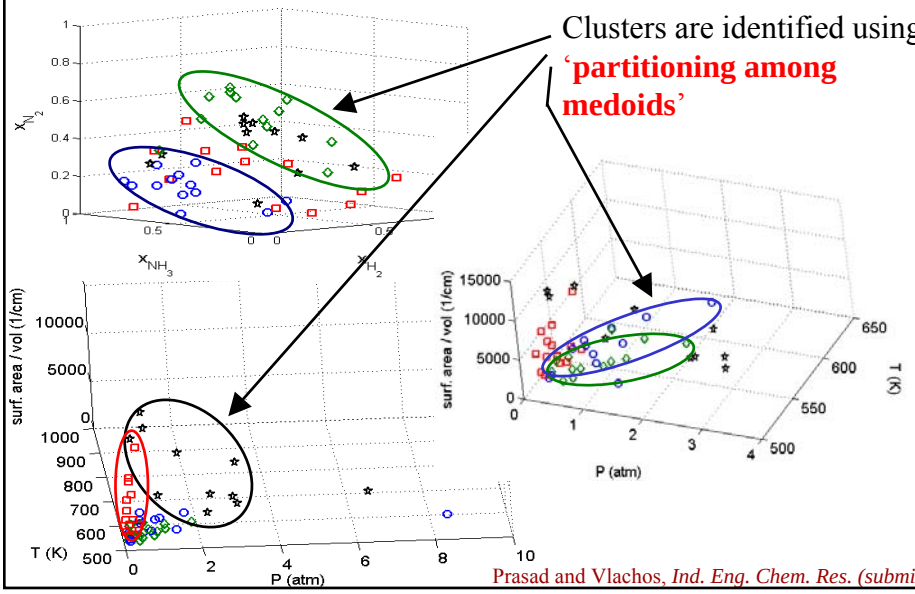
Identifying regions (clusters) of D-optimal data using informatics tools



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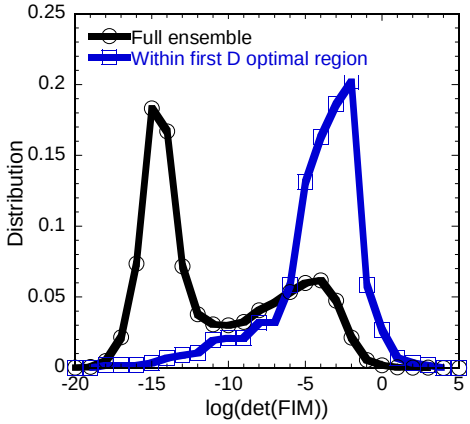
Assessment of Informatics Approach

Distribution of D optimal metric within optimal region and in entire parameter space



Sample anywhere within clusters (experimental flexibility)

Substantial improvement over single optimal points

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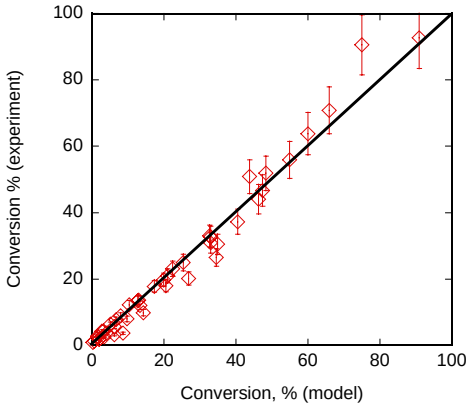
Proof of concept via experiments



- 44 new experiments conducted in optimal region
- Varied
  - Temperature
  - Catalyst amount
  - Inlet composition
- Good agreement of model prediction and data

Karim, Prasad, and Vlachos (in preparation)

Summary and future directions

- Future energy generation will happen at much smaller scales
- Downscaling is different even at the <1 mm scale
  - ✓ Dynamics of microsystems, systems integration, optimization, and control
- **Hierarchical multiscale modeling**
- Application of multiscale modeling to
  - ➢ Microreactor and process design
    - ✓ Model reduction is essential
  - ➢ Experiment design
    - ✓ Informatics tools could be valuable to replace '**the** optimum' point with an ensemble of suitably chosen experiments
  - ➢ Catalyst design
    - ✓ Reverse engineering of processes and products

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  - Justin Federici (UD; Microreactor exps)
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