

Microkinetic modeling for exhaust gas after-treatment technologies

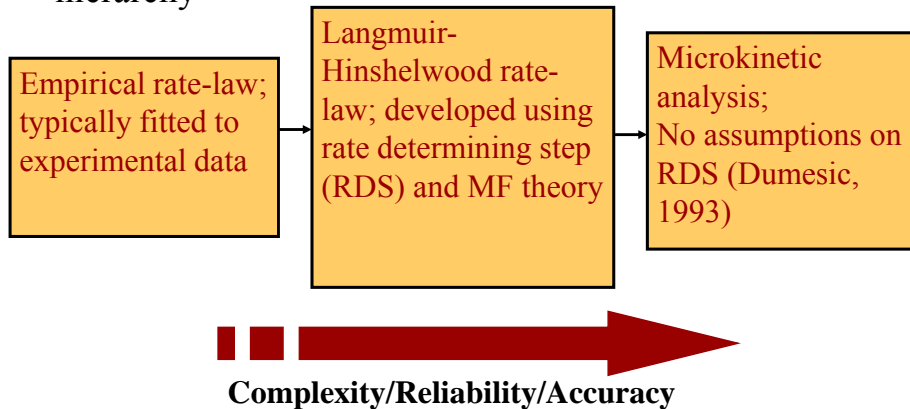
Dion Vlachos
Department of Chemical Engineering and Center for
Catalytic Science and Technology
University of Delaware
Newark, DE 19716
www.che.udel.edu/vlachos, vlachos@udel.edu

Outline

- **Evolution of catalytic kinetics modeling**
 - Modeling approaches
- **Development of microkinetic models**
- **Use**
- **Applications**
 - $2\text{NH}_3 \rightarrow 3\text{H}_2 + \text{N}_2$
 - Combustion (H_2 , CO , $\text{CO} + \text{O}_2 + \text{H}_2\text{O}$, PROX: $\text{CO} + \text{H}_2 + \text{O}_2$; HCs)
 - WGS reaction ($\text{CO} + \text{H}_2\text{O}$)
 - Reforming (steam, dry, autothermal), partial oxidation of small alkanes (syngas, alkenes, biomass)
 - Hydrogenation/dehydrogenation
 - Chemicals: ethylene, propylene, acrolein production
 - Exhaust related systems (CO oxid., CO oxid. with little H_2 , NO oxid., NH_3 decomposition)

Surface reaction rate calculation paradigm

- Calculation of surface reaction rates has followed the hierarchy

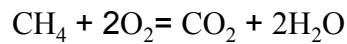


Summary of LH rate expressions

- LH expressions are based on *a priori assumptions* and intuition
- They are usually fitted using a limited number of data
- Multiple rate expressions can describe the same data
- Multiple parameters even for the same rate expression may exist
- Even if data is well-fitted, parameters may be physically unreasonable
- LH expressions, even if correct, are limited to one regime and cannot describe changes in RDS, MARI, etc. with operating conditions

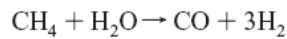
LH rates on Rh

- **CH₄ total oxidation (combustion)**



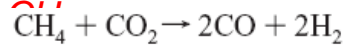
$$r_{TO} = \frac{k_{TO} \cdot P_{\text{CH}_4}}{(1 + K_{\text{H}_2\text{O}}^{ads} \cdot P_{\text{H}_2\text{O}})^2}$$

- **Steam reforming of CH₄**



$$r_{SR} = \frac{k_{SR} \cdot P_{\text{CH}_4} \cdot (1 - \eta_{SR})}{(1 + K_{\text{O}_2}^{ads} \cdot P_{\text{O}_2} + K_{\text{CO}}^{ads} \cdot P_{\text{CO}})^2}$$

- **CO₂-reforming of CH₄**



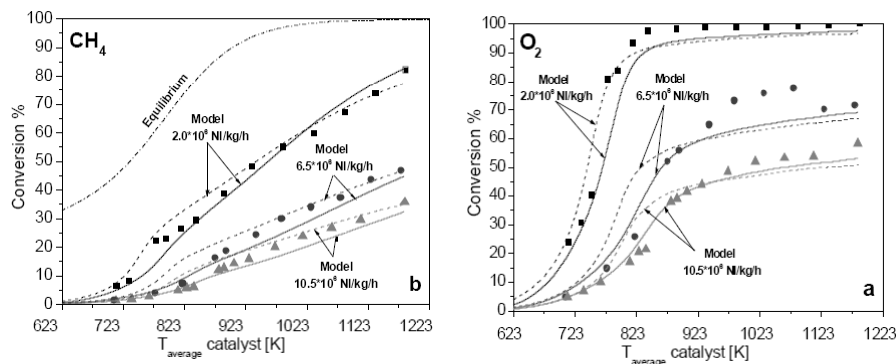
$$r_{\text{CO}_2\text{-R}} = \frac{k_{\text{CO}_2\text{-R}} \cdot P_{\text{CH}_4} \cdot (1 - \eta_{\text{CO}_2\text{-R}})}{(1 + K_{\text{O}_2}^{ads} \cdot P_{\text{O}_2} + K_{\text{CO}}^{ads} \cdot P_{\text{CO}})^2}$$

- **RWGS**
CO + H₂O → CO₂ + H₂

$$r_{RWGS} = \frac{k_{RWGS} \cdot P_{\text{CO}_2} \cdot P_{\text{H}_2} \cdot (1 - \eta_{RWGS})}{(1 + K_{\text{O}_2}^{ads} \cdot P_{\text{O}_2} + K_{\text{CO}}^{ads} \cdot P_{\text{CO}})^2}$$

η = effectiveness factor

Comparison of model to data: Conversion



- Process is away from equilibrium
 - Model fits data fairly well
 - Reactions in series is proposed
 - Combustion of syngas is important
- dashed lines = model w/o consecutive combustion of CO and H₂;
solid lines = model with consecutive CO and H₂ combustion

Are the parameters/model reasonable?

Estimated parameters

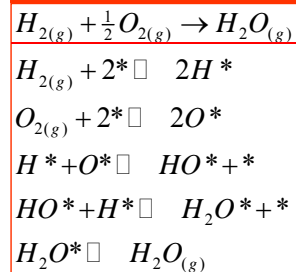
Surface adsorption	$K_{ads,j}^{873[K]}$ [atm ⁻¹]	ΔH_{ads} [kcal/mol]	species	heat of chemisorption Q (kcal/mol)	selected refs
O_2	42.53	13.9	O^*	$100 - 21\theta_O$	expts, ⁵⁰⁻⁵² DFT ⁵³⁻⁵⁵
H_2O	$2.216 \cdot 10^{-1}$	39.5	CO^*	$38.5 - 17\theta_{CO} - 3.7\theta_H$	expts, ^{46,56-58} DFT ^{11,59,60}
CO	15	6.2	CO_2^*	5.2	expts, ^{61,62} UBI-QEP ⁶³
			H^*	$62.3 - 2.5\theta_H - 3.7\theta_{CO}$	expts, ⁶⁴ DFT ^{11,53,65-67}
			OH^*	$70 - 33\theta_O + 25\theta_{H_2O}$	UBI-QEP, ⁶³ DFT ^{53,66}
			H_2O^*	$10.8 - 4.5\theta_{H_2O} + 25\theta_{OH}$	expts, ⁶⁸ DFT ^{53,69}
			$COOH^*$	62.2	DFT ¹⁷
			$HCOO^{**}$ (bidentate)	69.2	DFT ¹⁷
			C^*	159.0	DFT ¹⁷
			CH^*	151.2	DFT (this work)
			CH_2^*	109.3	DFT (this work)
			CH_3^*	42.4	DFT ¹⁸
			CH_4	6.0	expts, ¹⁶
			CH_3OH^*	11.0	expts, ²¹
			CH_3O^*	35.2	DFT ²²
			CH_2O^*	22.0	DFT ²²
			HCO^*	64.7	DFT ²²
			CH_2OH^*	56.4	DFT ²²

- Models may fit but they most often than not include unrealistic parameters

Microkinetic modeling

- All relevant elementary reactions
 - Written by hand or computer generated
- No simplifying assumptions
 - e.g., on a rate determining step (RDS), partial equilibrium (PE), quasi-steady state (QSS), and a most abundant reaction intermediate (MARI)
- Mass action kinetics
- Reactor + Catalyst model needed
 - Solution via a suitable numerical method
 - Computer software, such as surface CHEMKIN or Matlab makes use trivial
- Microkinetic models may hold over the entire parameter space
 - More robust numerics than global rate expressions!

An example



Microkinetic modeling

- Output
 - Coverages (concentrations), Rates, Conversion, Selectivity
 - RDS, QSS, PE, important steps
- Input
 - Reaction rate const. parameters
- **Rate constants of all elementary reactions are not necessarily available for most reactions**

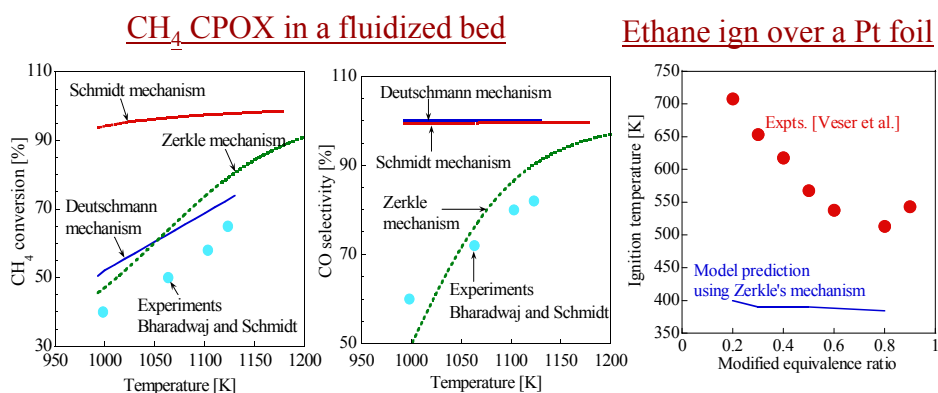
Parameter estimation techniques

- Fitted to data
 - Empirical; multiple parameter sets; limited predictive power
- Semi-empirical theoretical methods
 - Fast; fairly accurate; not first principles
- Density functional theory (DFT)
 - First principles; expensive; limited to small mechanisms and 'bimolecular' type of reactions (combinatorial explosion)
- Independent of theoretical method, parameters are uncertain and models are semi-quantitative in most cases
 - Parameter refinement is necessary

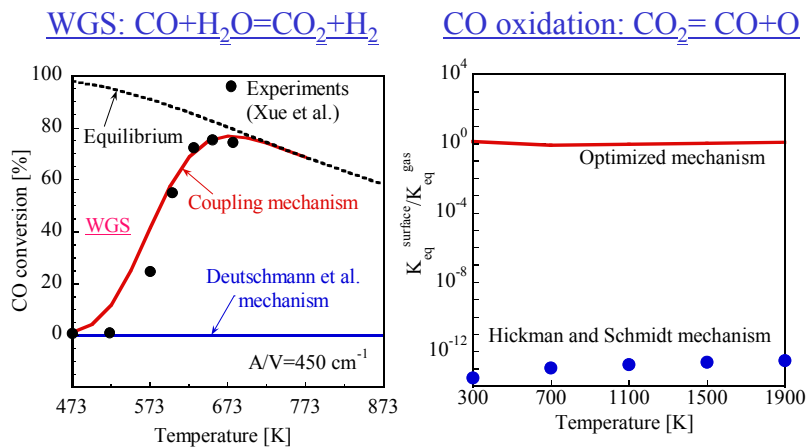
Limitations of most microkinetic models

- Inability to predict multiple experimental sets
- Thermodynamic inconsistency
- Coverage dependence on activation energies of surface rxns
- Lack of a comprehensive set of reaction paths
- Coupling effects appear in multicomponent systems
- Mean field assumption for both catalyst and adsorbates
- Materials and pressure gaps
 - From UHV/single crystals parameters to actual conditions

Most literature mechanisms fail to describe multiple data



Most literature mechanisms are thermodynamically inconsistent



Complex feeds cannot be captured



CO and H₂ oxidation on a platinum monolith diesel oxidation catalyst

S. Salomons^{a,b}, M. Votsmeier^{c,*}, R.E. Hayes^a, A. Drochner^b, H. Vogel^b, J. Gieshof^c

- H₂ even at ppm level promotes CO light off
 - Heat effect (unimportant for ppm H₂)
 - Chemical effect
- Predicted trend is opposite from the experimental one
- Complex feed composition also in PROX conditions (H₂ rich-CO lean)

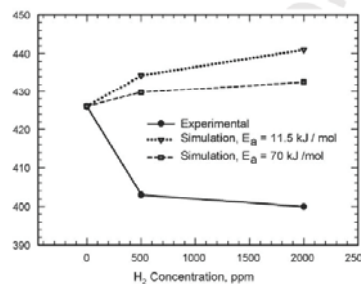
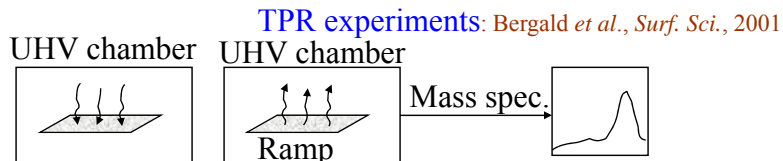


Fig. 4. CO light-off temperature vs. hydrogen concentration for the experimental and simulated ($E_a = 11.5$ and 70 kJ/mol) light-offs.

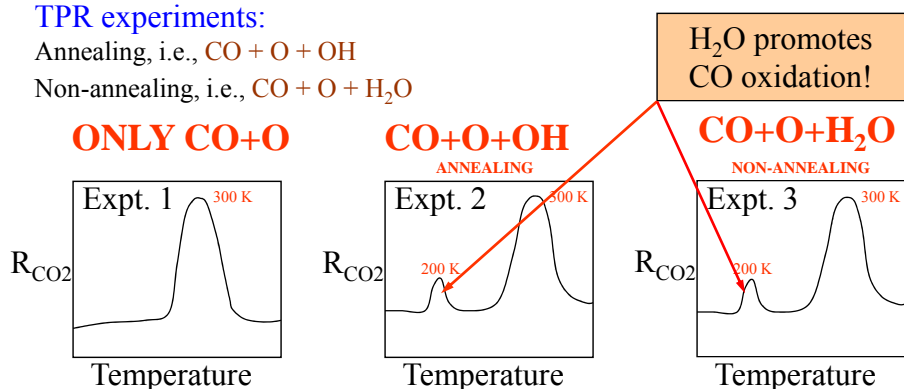
Role of H₂O in CO oxidation on Pt



TPR experiments:

Annealing, i.e., CO + O + OH

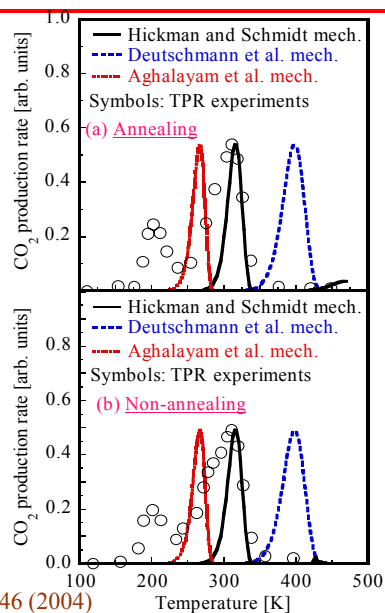
Non-annealing, i.e., CO + O + H₂O



Performance of literature mechanisms

- Several mechanisms are available for H₂, CO, and CH₄ oxidation on Pt
- Oxidation pathways include
 - CO+O → CO₂
 - H+O → OH and H+OH → H₂O
 - No other oxidation paths exist
- Literature mechanisms do not capture the H₂O promotion and are **thermodynamically inconsistent**

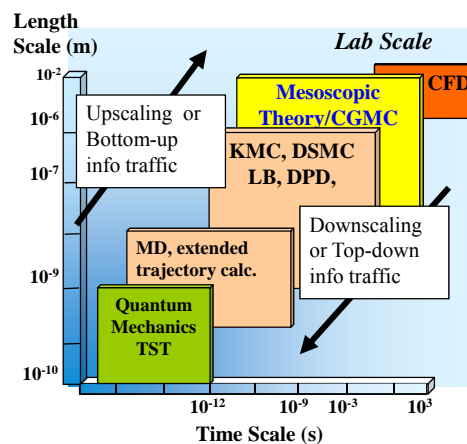
Mhadeshwar and Vlachos, *J. Phys. Chem. B.* **108**, 15246 (2004)



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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)

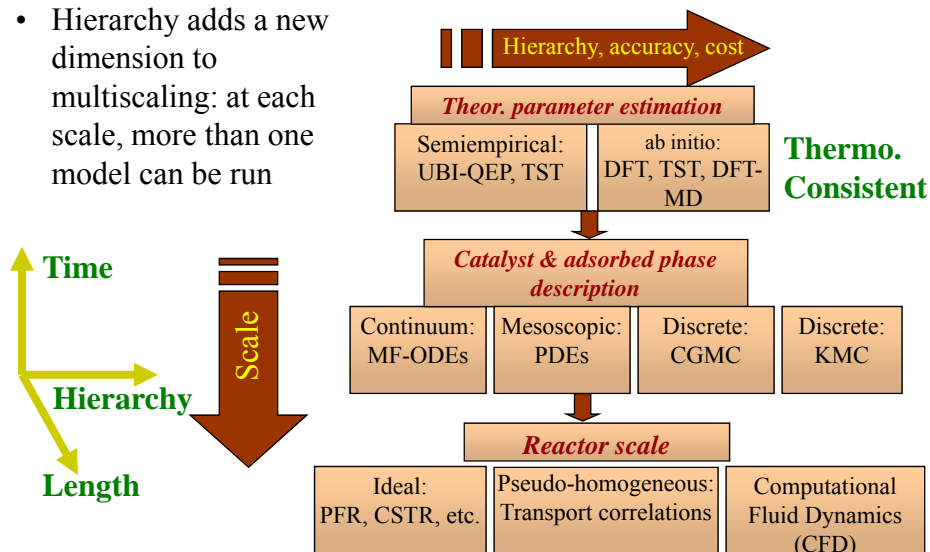
- Direct multiscale simulation (hybrid, coarse graining) is possible for systems of moderate complexity
- It is plagued by computational cost for complex systems, such as chemical reactors
- Are all scales and phenomena important?

Overarching concept of hierarchical multiscale modeling

- Start with a sufficiently simple but physically relevant model at each scale
 - Link all models
 - Perform a sensitivity analysis
 - Identify important scale and parameter(s)
 - Use higher level theory for this scale and parameter(s)
 - Iterate
- Irrespective of how good job we do, there is always **uncertainty** in models: **Need for data**

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



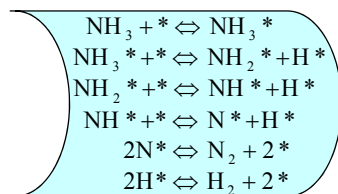
Bond-order conservation (BOC) and TST: Features

- **Activation energies**
 - Semi-empirical technique
 - Coverage dependent binding energies
 - Coverage dependent activation energies
 - Accuracy within 2-4 kcal/mole
 - High computational efficiency
 - Thermodynamic consistency at enthalpic level

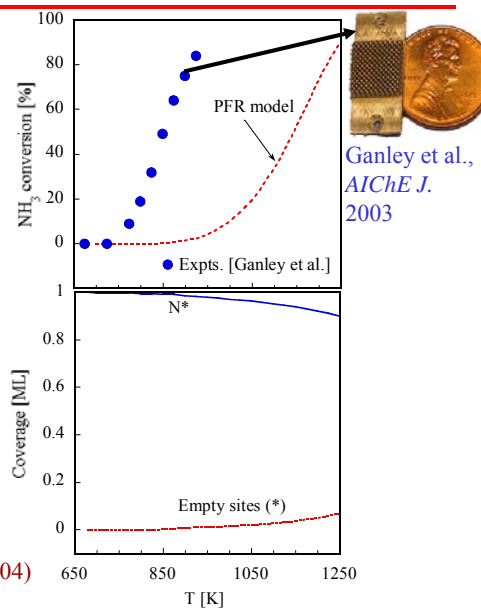
- **Pre-exponentials**
 - Severely constrained from TST and thermodynamic consistency
 - Refined with experimental data

NH₃ decomposition on Ru: 2NH₃ = N₂ + 3H₂

- NH₃ as a storage medium
- ‘Pure’ H₂ – No CO_x
- A microkinetic model is build using BOC and TST
- Our microkinetic model captures the trend
- High N* coverages

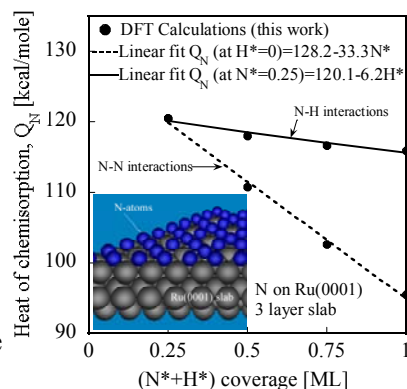


Mhadeshwar et al., *Cat. Letters* **96**, 13-22 (2004)



DFT is used to estimate lateral interactions

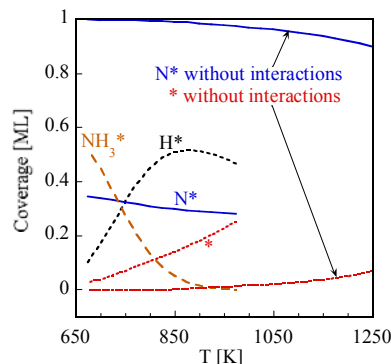
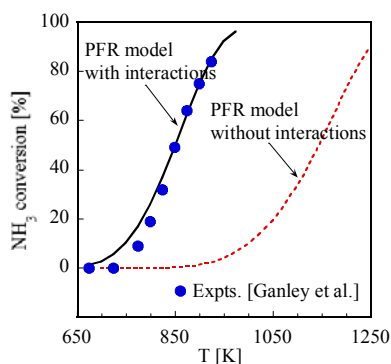
- DACAPO (solid-state electronic structure package by Hammer and coworkers*)
- 3-Layer slab of Ru(0001)
- 2×2 unit cell
- All layers are relaxed
- Plane wave cutoff = 350eV
- 18 k-points for surface Brillouin zone
- Generalized gradient approximation (PW-91)



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)

Energetics and interactions for H₂/O₂ on Pt: Comparison with experiments

Reaction	$\theta_{*}=1.$	$\theta_{H^{*}}=1.$	$\theta_{O^{*}}=1.$	Anton & Cadogan (1991)	Eisert & Rosen (1997)	Williams et al. (1992)
1) $H^{*} + O^{*} \rightarrow OH^{*} + *$	12.1	8.8	13.4	$\leq 13.$	13.8	2.5
2) $OH^{*} + * \rightarrow H^{*} + O^{*}$	24.4	25.9	18.4	$\leq 29.$		5.0
3) $H^{*} + OH^{*} \rightarrow H_2O^{*} + *$	12.4	9.3	0.0	$16 \pm 2.$	16.0	15.0
4) $H_2O^{*} + * \rightarrow H^{*} + OH^{*}$	18.4	20.2	39.1	25.0		37.0
5) $2OH^{*} \rightarrow H_2O^{*} + O^{*}$	18.9	18.9	0.0	$18 \pm 3.$	18.0	
6) $H_2O^{*} + O^{*} \rightarrow 2OH^{*}$	12.6	12.6	34.1	10.0		31.0

Coverage-dependent reaction energetics necessary to capture experimental trends

Park et al., J. Phys. Chem. **103**, 8101 (1999)

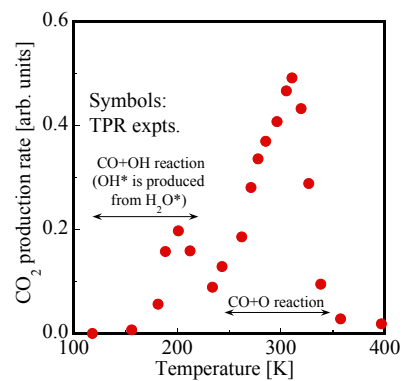
What can we use detailed models for?

- | | | |
|-------------|---|---|
| Traditional | { | <ul style="list-style-type: none"> • Reconcile apparently contradictory experimental data • Mechanistic understanding • Perform reactor optimization |
| Modern | { | <ul style="list-style-type: none"> • Model-based design of experiments to assess model • Rational catalyst design <ul style="list-style-type: none"> – Composition – Size – Shape |

What can we use detailed models for?

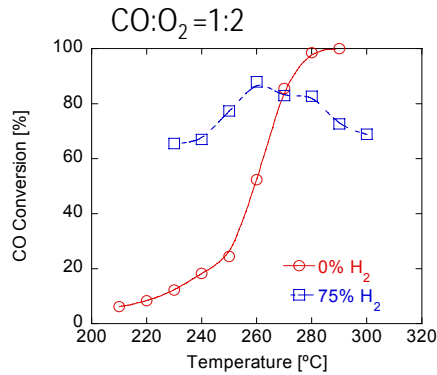
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H₂O promotes CO oxidation at UHV conditions



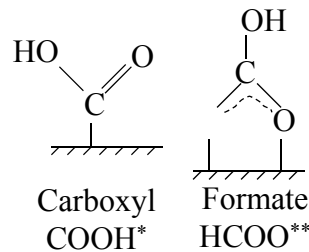
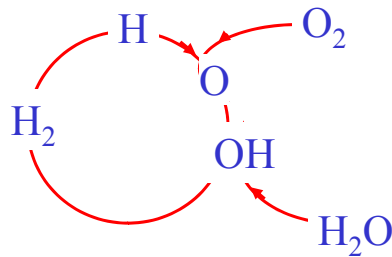
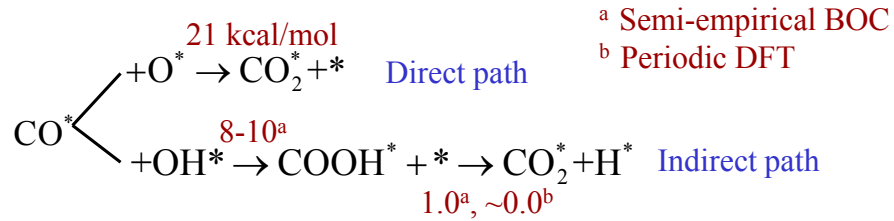
TPR data: Bergald *et al.*, *Surf. Sci.* (2001)
Mhadeshwar and Vlachos, *J. Phys. Chem. B.*
108, 15246 (2004)

Effect of Excess Hydrogen on CO Conversion: PROX conditions



- The carbon monoxide conversion increases in the presence of H₂ at low temperatures but is inhibited at high temperatures

CO oxidation mechanisms on Pt



Incorporating hydrogen bonding effects into a microkinetic model for CO-H₂O coupling

Heats of chemisorption are parameterized using DFT calc. of Michaelides and Hu, *JACS* (2001)

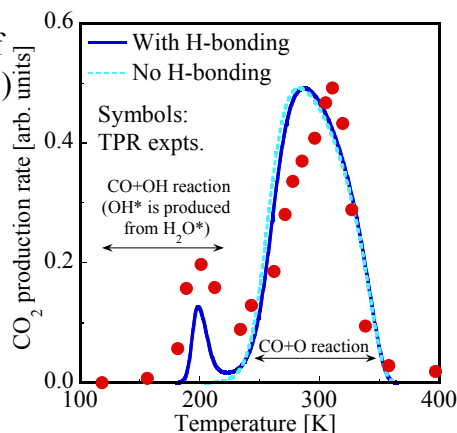
$$Q_{\text{H}_2\text{O}} = Q_{\text{H}_2\text{O}}^0 + 25\theta_{\text{OH}}$$

$$Q_{\text{OH}} = Q_{\text{OH}}^0 + 25\theta_{\text{H}_2\text{O}}$$

↓
Coverage dependent
activation energies

Our microkinetic model:

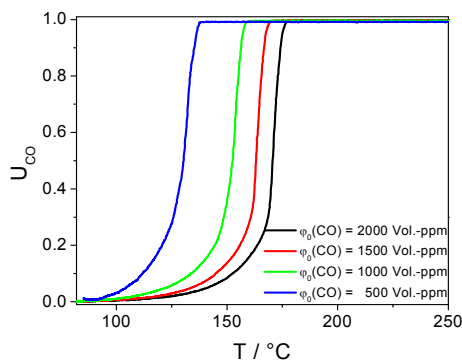
- H-bonding is important
- Coupling steps are required
(no peak without coupling)



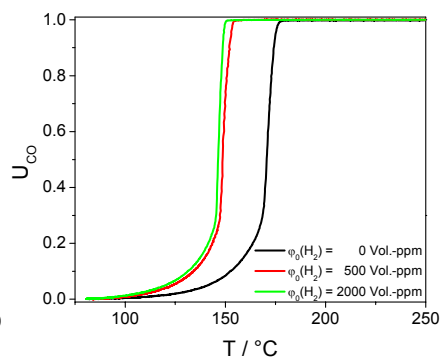
TPR data: Bergald *et al.*, *Surf. Sci.* (2001)
Mhadeshwar and Vlachos, *J. Phys. Chem. B.* **108**, 15246 (2004)

Effect of exhaust composition on light-off temperature of CO

Effect of CO fraction

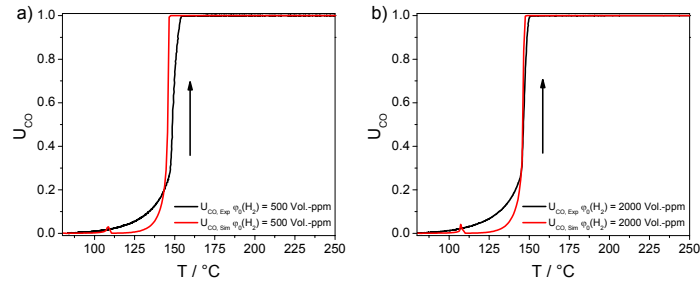


Effect of H₂ fraction



Experiments by Salomons *et al.*
Simulations by Wulf Hauptmann

Simulated CO light-off temperature

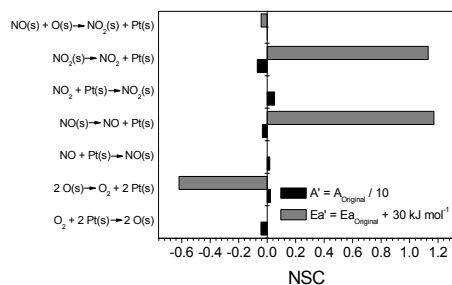


Effect of H₂ on CO light-off temperature

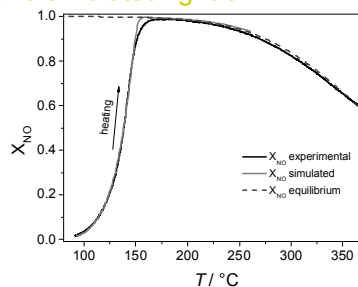
		$\varphi_0(\text{CO}) / \text{Vol.-ppm}$	$\varphi_0(\text{H}_2) / \text{Vol.-ppm}$	CO Light-Off Temperature / °C	
				Experiment	Simulation
CO oxidation	}	500	0	131	148
		1000	0	153	159
		1500	0	166	165
		2000	0	171	171
H ₂ effect	}	2000	225	153	145
		2000	300	154	145
		2000	1000	150	145
		1000	500	130	134
		1000	2000	127	134

NO oxidation to NO₂ on Pt

Sensitivity analysis



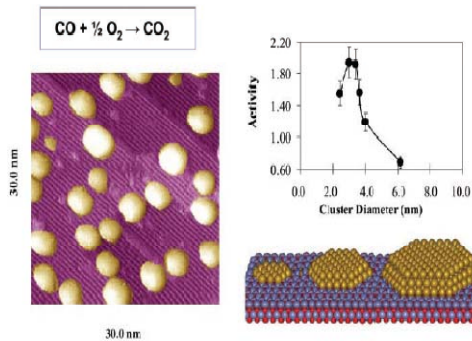
Comparison between experimental and simulated light-off



430 vol.-ppm NO and 6 vol.-% O₂
 Heating rate was 5 °C min⁻¹
 GHSV was 25 000 h⁻¹.

CO oxidation on supported Au catalyst

- Bulk Au is a chemically inert metal



Haruta et al., *Chem. Lett.* 405, (1987)
 Valden et al., *Science* 281, 1647 (1998)
 Bell, *Science* 299, 1688 (2003)

¹ Mavrikakis et al., *Cat. Lett.* 64, 101 (2000)
² Molina, *J. Phys. Chem. C* 111, 6668 (2007)
³ Haruta, *Cattech* 6, 102-115, (2002)

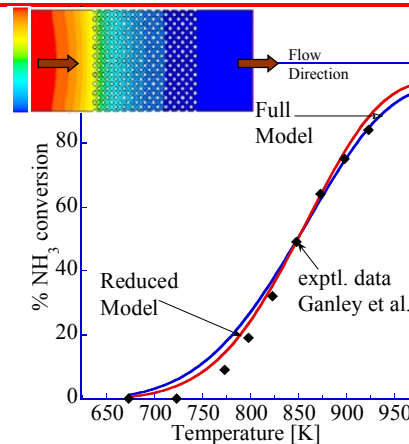
- Only edges, corners, steps of NPs are active¹
- Au clusters and NPs (3-5 nm) are chemically active²
- Reducible supports are most active for CO oxidation on Au, whereas irreducible supports are less active³

What can we use detailed models for?

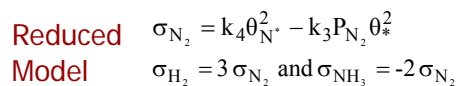
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Computer-aided chemistry reduction

- 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)

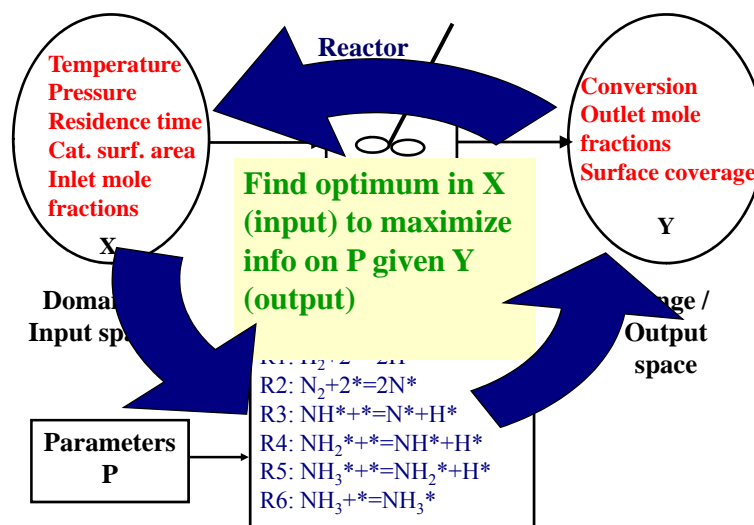


$$\theta_{N^*} = \frac{1}{1 + \frac{k_{11} P_{NH_3}}{k_{12}} + \sqrt{\frac{k_1}{k_2}} P_{H_2} + \sqrt{\frac{k_3}{k_4}} P_{N_2} + \sqrt{\frac{k_5}{k_1}} \frac{k_7 k_9 k_{11}}{2 k_4 k_{10} k_{12}} P_{NH_3} P_{H_2}^{-0.5}}$$

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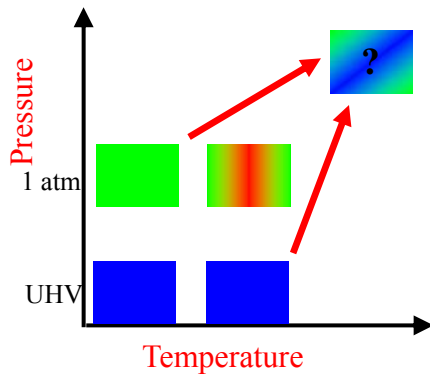
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Model, System and Parameters

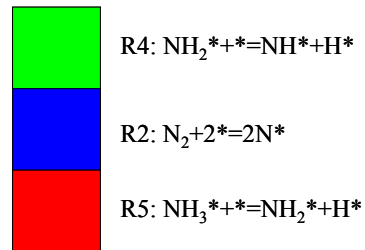


Optimal Designs

- Experiments: vary 1-2 variables (pressure, temperature), conducted at disparate conditions (UHV, atmospheric pressure)
- Model response over all variables (including industrial conditions) for **synthesis and decomposition**

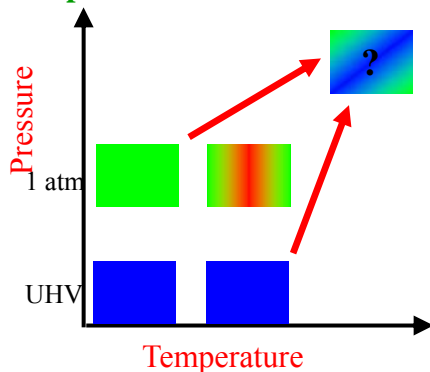


Other variables explored:
residence time, inlet
compositions, catalyst
dispersion and loading

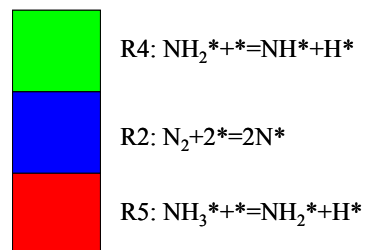


Optimal Designs

- Experiments: vary 1-2 variables (pressure, temperature), conducted at disparate conditions (UHV, atmospheric pressure)
- Model response over all variables (including industrial conditions) for **synthesis and decomposition**
- Varying all parameters in increments leads to **combinatorial explosion**

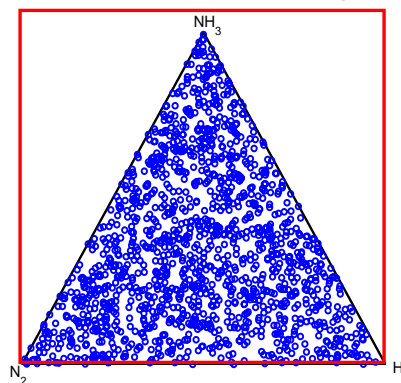
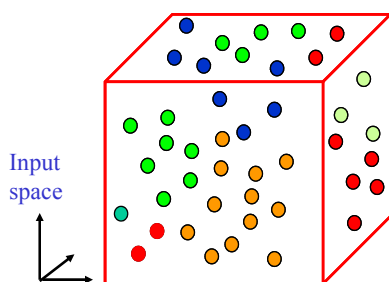


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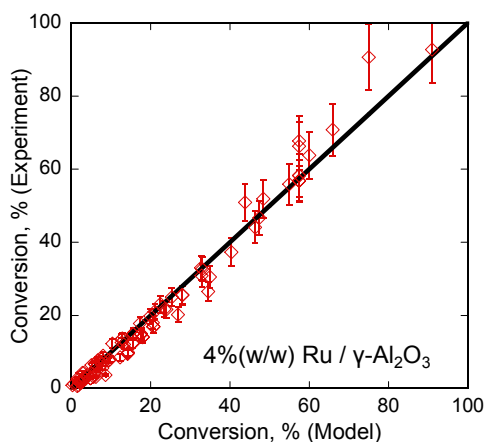


Generating a Large Ensemble of Operating Conditions (HTM)

- Global **Monte Carlo** search in **input space** (τ , P, T, composition, catalyst A/V).
- Uniformly randomly distributed operating conditions.
- Composition space spanned in unbiased manner using constraint $\sum_i x_i = 1$



Microkinetic model assessed via throughput-model based design of experiments



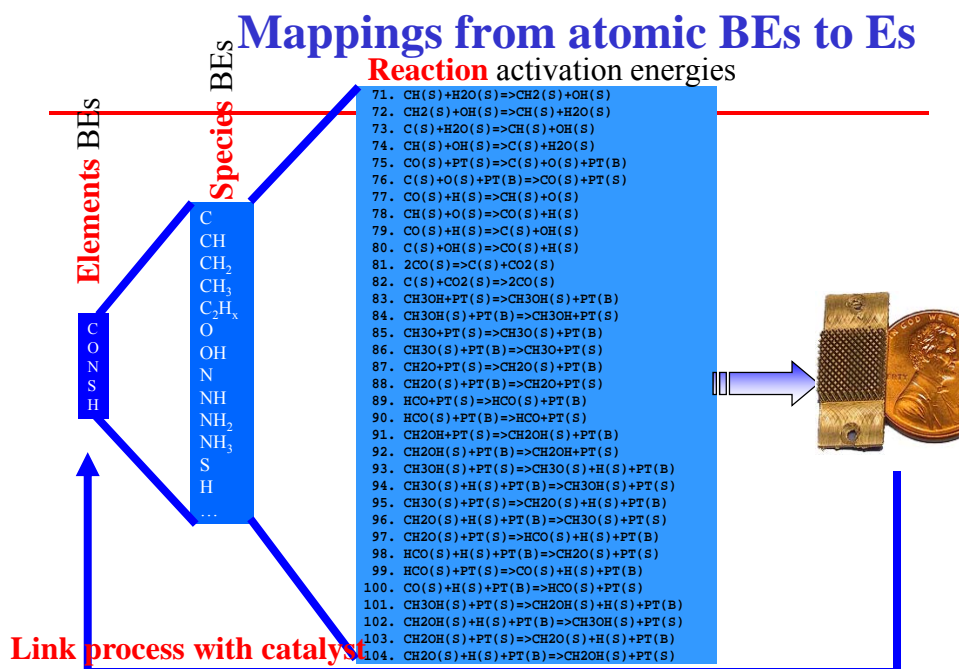
- Experiments with varying inlet composition, temperature, amount of catalyst, dilution, flow rate
- Bioinformatics tools are used for 'clustering', i.e., identification of regions where one should do experiments

Prasad and Vlachos, *Ind. Eng. Chem. Res.* **47**, 6555 (2008).

Prasad, Karim, Arya, and Vlachos, *Ind. Eng. Chem. Res.* **48**, 5255 (2009).

What can we use detailed models for?

- | | | |
|-------------|---|---|
| Traditional | } | <ul style="list-style-type: none"> • Reconcile apparently contradictory experimental data • Mechanistic understanding • Perform reactor optimization |
| Modern | | <ul style="list-style-type: none"> • Model-based design of experiments to assess model • Rational catalyst design <ul style="list-style-type: none"> – Composition – Size – Shape |



Prasad, Ulissi, Zagrobelny, and Vlachos, *Chem. Eng. Sci.* (in press)

Coverage Dependence Through DFT-based Scaling Relationships

Adsorption Energies for AH_x Species on Transition Metals

F. Abild-Pedersen et al. Phys. Rev. Letters **99**, 016105 (2007)

$$Q_{AH_x} = \gamma Q_A + \xi$$

$$\gamma = (x_{\max} - x) / x_{\max}$$

A = C,S,N,O

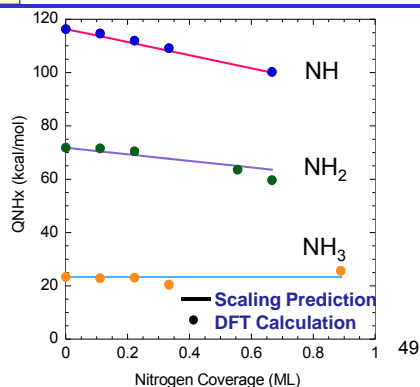
x_{max}=maximum # H on molecule

ξ= Constant

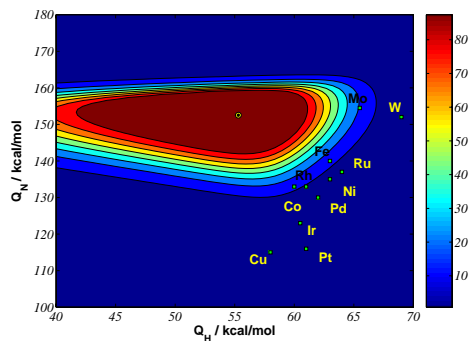
Our Coverage Dependence Extension & Application to NH₃ System

$$Q_{AH_x} = \gamma Q_A(\theta_{AH_x}, \theta_A) + \xi$$

$$\gamma = (3 - x) / 3$$



Multiscale model-based catalyst design



- Search is done on **atomic descriptors** while running the full chemistry model
 - **Link macro and micro scales**
- Potential catalyst candidates are identified

Prasad, Ulissi, Zagrobelny, and Vlachos, *Chem. Eng. Sci.* (in press)

Summary of microkinetic models

- Hierarchical multiscale modeling framework delivers reliable reaction mechanisms in an efficient manner
- **Key concepts**
 - Models describe multiple data for a single fuel
 - Models describe coupling effects in multicomponent systems
 - Thermodynamic consistency
 - Coverage dependence on activation energies of surface rxns
 - Different reaction paths can easily be explored

Summary

- Complex models can be reduced to simple ones for system optimization/scale up studies
 - Enables CFD simulation
- A framework for model-based design of experiments has been proposed
 - Model validation and mechanism understanding
- Complex models could be used for rational, model-based catalyst design