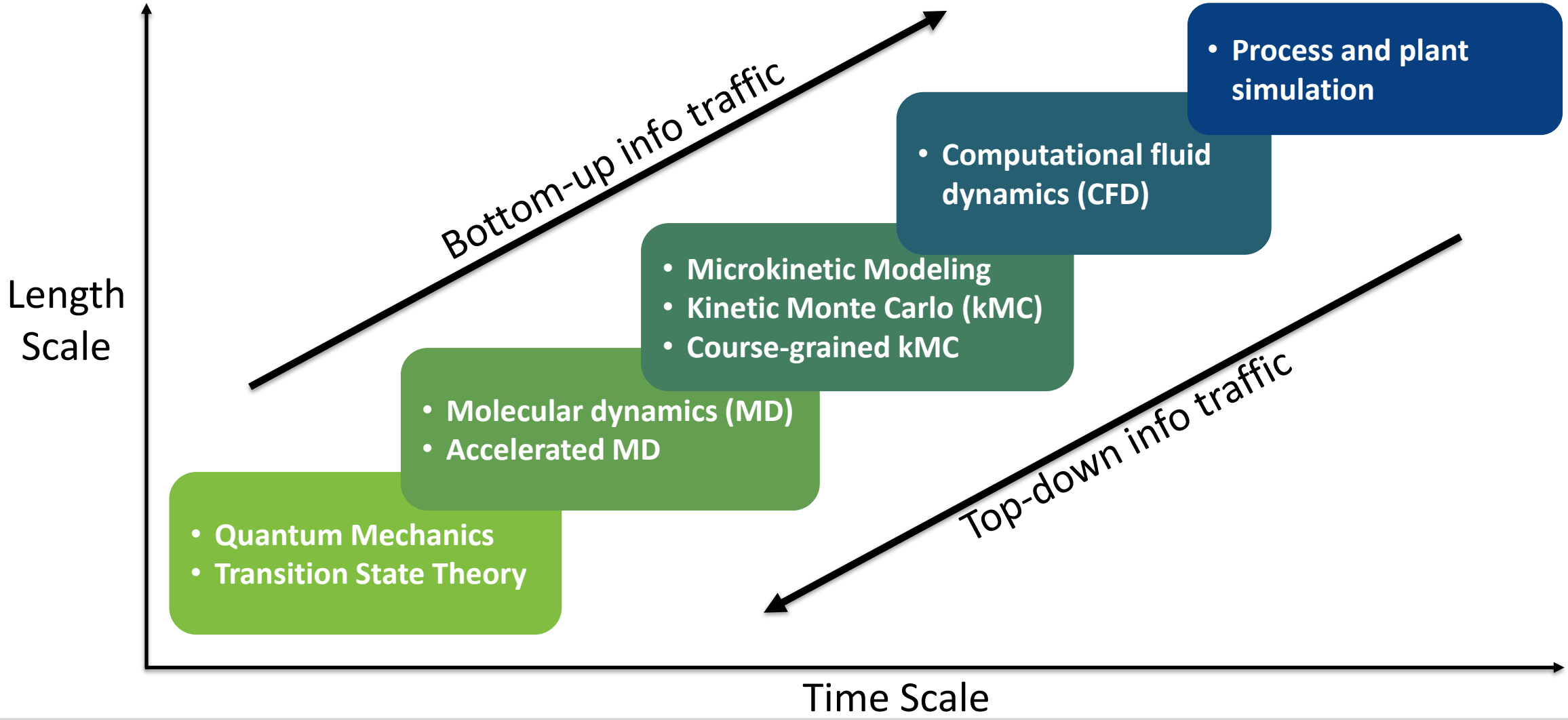
Theory, Applications, and Tools for Multiscale Kinetic Modeling: Thermochemistry

Jonathan Lym, Gerhard Wittreich, Bharat Medasani, Dionisios Vlachos

7/13/2020

Rapid Advancement in Process Intensification Deployment

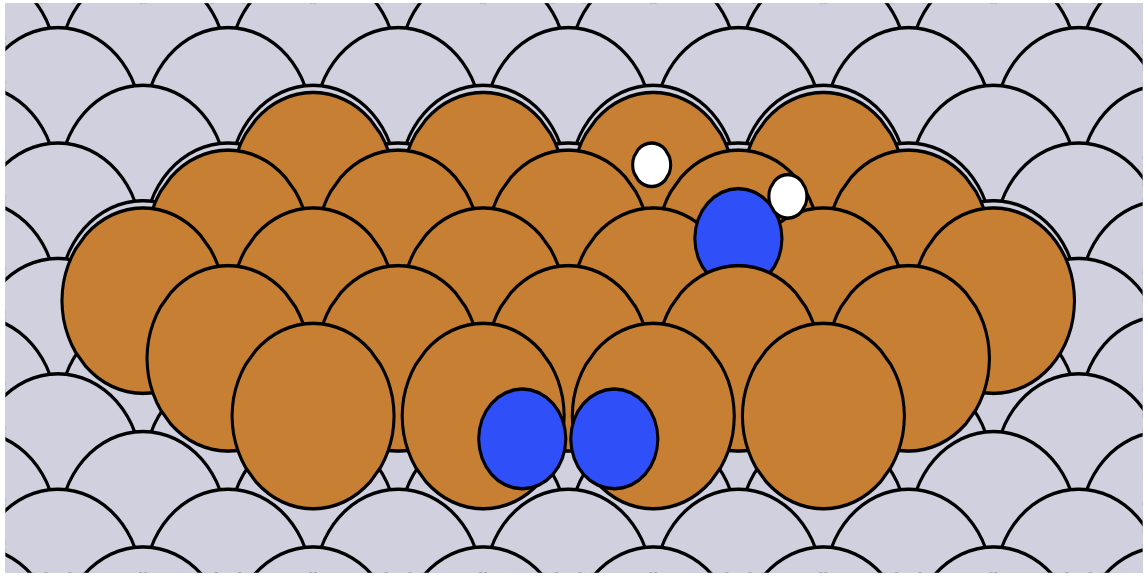
Multiscale Modeling



[1] Salciccioli, M. et al. *Chem. Eng. Sci.* **2011**, *66* (19), 4319–4355.

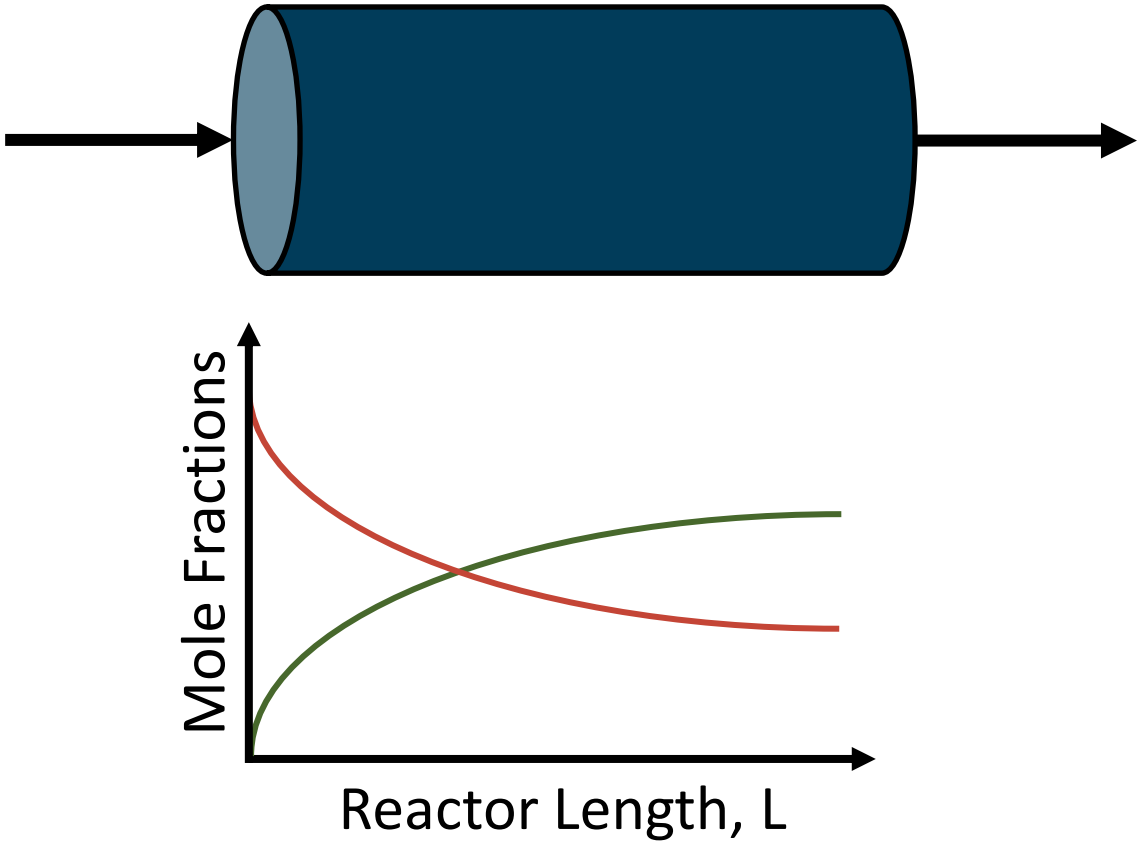
Bridging the Gap Between Catalyst Scale and Reactor Scale

Density Functional Theory (DFT)



$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}(\boldsymbol{r})\right)\phi_i(\boldsymbol{r}) = \varepsilon_i\phi_i(\boldsymbol{r})$$

Microkinetic Modeling (MKM)



Microkinetic Model Inputs: Reactor Conditions

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Microkinetic Model Inputs: Reactor Conditions

Q_0 = 1 mL s^{-1}

Inlet composition, x_0:

- N_2
- H_2
- Inert

T = 673 K

P = 100 bar

V = 1 cm^3

m_{cat} = 0.1 g Ru/Al_2O_3 catalyst

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Microkinetic Model Inputs: Elementary Steps

Q_0 = 1 mL s^{-1}

Inlet composition, x_0:

- N_2
- H_2
- Inert

T = 673 K

P = 100 bar

V = 1 cm^3

m_{cat} = 0.1 g Ru/Al_2O_3 catalyst

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Elementary reversible reactions:

- Adsorption/Desorption
  1. $N_2 + * \leftrightarrow N_2*$
  2. $H_2 + * \leftrightarrow 2H*$
  3. $NH_3 + * \leftrightarrow NH_3*$
- Surface Reactions
  4. $N_2* + * \leftrightarrow 2N*$
  5. $N* + H* \leftrightarrow NH*$
  6. $NH* + H* \leftrightarrow NH_2*$
  7. $NH_2* + H* \leftrightarrow NH_3*$

Microkinetic Model Inputs: Mass Balance for N_2*

$$\frac{d}{dt}[N_2^*] = k_1^{fwd} P_{N_2}[*] - k_1^{rev}[N_2^*] - k_4^{fwd}[N_2^*][*] + k_4^{rev}[N^*]^2$$

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Elementary reversible reactions:

- Adsorption/Desorption
  1. $N_2 + * \leftrightarrow N_2*$
  2. $H_2 + * \leftrightarrow 2H*$
  3. $NH_3 + * \leftrightarrow NH_3*$
- Surface Reactions
  4. $N_2* + * \leftrightarrow 2N*$
  5. $N* + H* \leftrightarrow NH*$
  6. $NH* + H* \leftrightarrow NH_2*$
  7. $NH_2* + H* \leftrightarrow NH_3*$

Microkinetic Model Inputs: Mass Balance for N_2*

$$\frac{d}{dt}[N_2^*] = \underbrace{k_1^{fwd} P_{N_2}[*] - k_1^{rev}[N_2^*]}_{\text{Adsorption}} - \underbrace{k_4^{fwd}[N_2^*][*] + k_4^{rev}[N^*]^2}_{\text{Surface Reactions}}$$

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Elementary reversible reactions:

- Adsorption/Desorption
  1. $N_2 + * \leftrightarrow N_2*$
  2. $H_2 + * \leftrightarrow 2H*$
  3. $NH_3 + * \leftrightarrow NH_3*$
- Surface Reactions
  4. $N_2* + * \leftrightarrow 2N*$
  5. $N* + H* \leftrightarrow NH*$
  6. $NH* + H* \leftrightarrow NH_2*$
  7. $NH_2* + H* \leftrightarrow NH_3*$

Microkinetic Model Inputs: Modified Arrhenius Rate Constant

$$\frac{d}{dt}[N_2^*] = k_1^{fwd} P_{N_2}[*] - k_1^{rev}[N_2^*] - k_4^{fwd}[N_2^*][*] + k_4^{rev}[N^*]^2$$

$$k_j^{fwd} = A_j' \left(\frac{T}{T_{ref,j}}\right)^{\beta_j} \exp\left(-\frac{E_{A,j}}{RT}\right)$$

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Microkinetic Model Inputs: Modified Arrhenius Rate Constant

$$\frac{d}{dt}[N_2^*] = k_1^{fwd} P_{N_2}[*] - k_1^{rev}[N_2^*] - k_4^{fwd}[N_2^*][*] + k_4^{rev}[N^*]^2$$

$$k_j^{fwd} = \underbrace{A_j' \left(\frac{T}{T_{ref,j}}\right)^{\beta_j}}_{A_{Arrhenius}} \exp\left(-\frac{E_{A,j}}{RT}\right)$$

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

- Arrhenius equation when $\beta_i = 1$ and $T_{ref,i} = 1\ K$

Microkinetic Model Inputs: Reverse Rate Constant

$$\frac{d}{dt}[N_2^*] = k_1^{fwd} P_{N_2}[*] - k_1^{rev}[N_2^*] - k_4^{fwd}[N_2^*][*] + k_4^{rev}[N^*]^2$$

$$k_j^{fwd} = A_j' \left(\frac{T}{T_{ref,j}}\right)^{\beta_j} \exp\left(-\frac{E_{A,j}}{RT}\right) \xrightarrow{\text{By microscopic reversibility}} k_j^{rev} = \frac{k_j^{fwd}}{K_j^{eq}}$$

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Microkinetic Model Inputs: Reverse Rate Constant

$$\frac{d}{dt}[N_2^*] = k_1^{fwd} P_{N_2}[*] - k_1^{rev}[N_2^*] - k_4^{fwd}[N_2^*][*] + k_4^{rev}[N^*]^2$$

$$k_j^{fwd} = A_j' \left(\frac{T}{T_{ref,j}}\right)^{\beta_j} \exp\left(-\frac{E_{A,j}}{RT}\right)$$

By microscopic reversibility

$$k_j^{rev} = \frac{k_j^{fwd}}{K_j^{eq}}$$

$$K_j^{eq} = \exp\left(-\frac{\Delta G_j}{RT}\right)$$

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Microkinetic Model Inputs: Adsorption Preexponential

$$\frac{d}{dt}[N_2^*] = k_1^{fwd} P_{N_2}[*] - k_1^{rev}[N_2^*] - k_4^{fwd}[N_2^*][*] + k_4^{rev}[N^*]^2$$

$$k_{ads,j}^{fwd} = A'_{ads,j}\left(\frac{T}{T_{ref,j}}\right)^{\beta_j} \exp\left(-\frac{E_{A,j}}{RT}\right)$$

By collision theory

$$A'_{ads,j} = \frac{s_j}{(\sigma)^{n_{surf}}}\sqrt{\frac{RT}{2\pi M_i}}$$

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Microkinetic Model Inputs: Surface Reaction Preexponential

$$\frac{d}{dt}[N_2^*] = k_1^{fwd} P_{N_2}[*] - k_1^{rev}[N_2^*] - k_4^{fwd}[N_2^*][*] + k_4^{rev}[N^*]^2$$

$$k_{surf,j}^{fwd} = A'_{surf,j} \left(\frac{T}{T_{ref,j}}\right)^{\beta_j} \exp\left(-\frac{E_{A,j}}{RT}\right)$$

By transition-state theory

$$E_{A,j} = \Delta H_j^{\neq}$$

$$A'_{surf,j} = \frac{k_B}{h} \frac{1}{(\sigma)^{n_{surf}-1}} \exp\left(\frac{\Delta S_j^{\neq}}{R}\right)$$

Legend

Set by user

Calculated by MKM

Derived from DFT

i – Species i

j – Reaction j

Microkinetic Modeling Input Summary

Set by user

- Reactor conditions
  - T, P, Q, V, x_{i0}, m_{cat}
- Elementary steps
  - Adsorption
  - Surface reactions
- Reaction parameters
  - s_j, σ, $T_{ref,j}$, β_j

Calculated by MKM

- Surface coverages
- Gas-phase compositions
- Rates

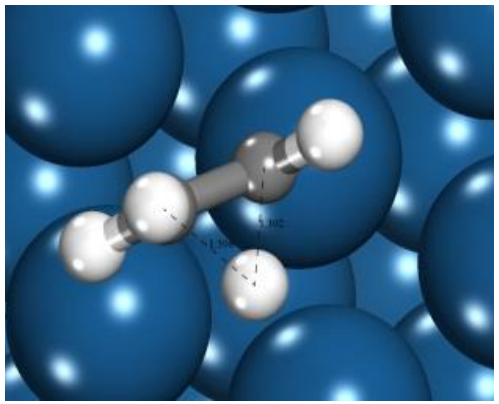
Derived from DFT

- Enthalpies (H) and entropies (S) of:
  - Reactants
  - Products
  - Intermediates
  - Transition states

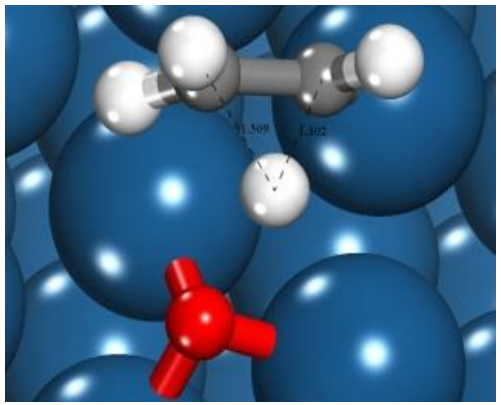
Coverage Effects Impact Reaction Kinetics And Thermodynamics

Presence of co-adsorbates can affect:

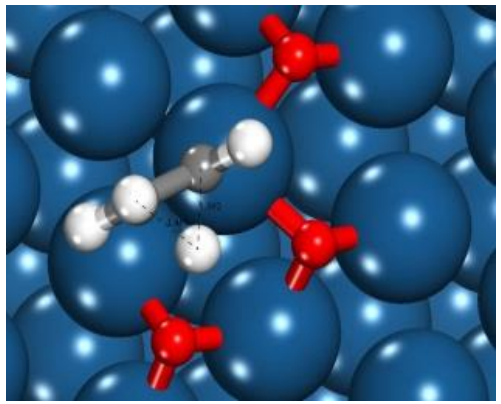
- Activation energies
- Enthalpies of intermediates
- Usually necessary for over binding species



(a) E_a = 54 kcal/mol

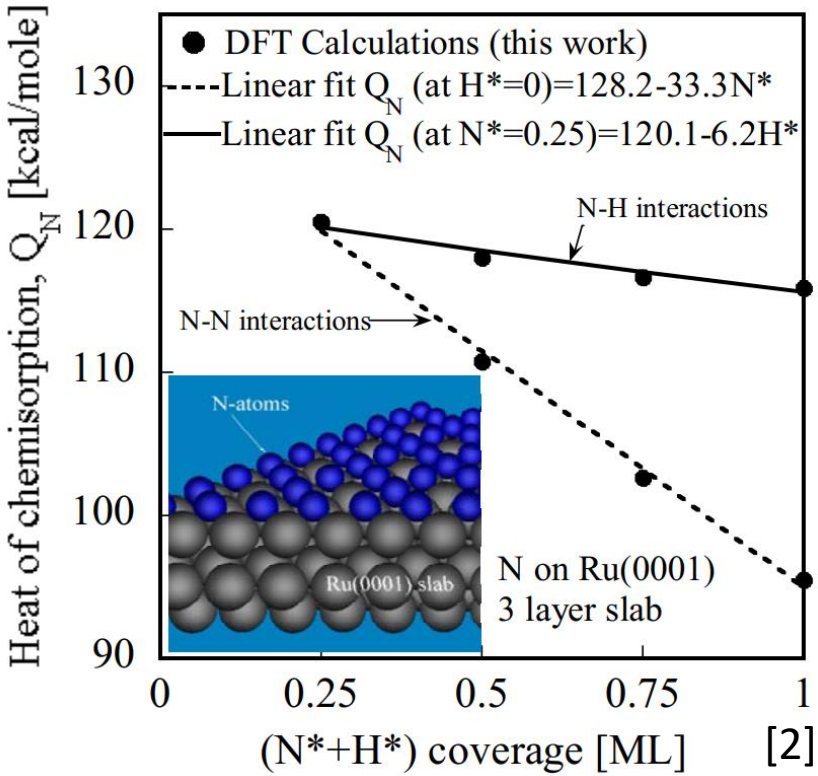


(b) E_a = 41 kcal/mol



(c) E_a = 23 kcal/mol

[1]



[2]

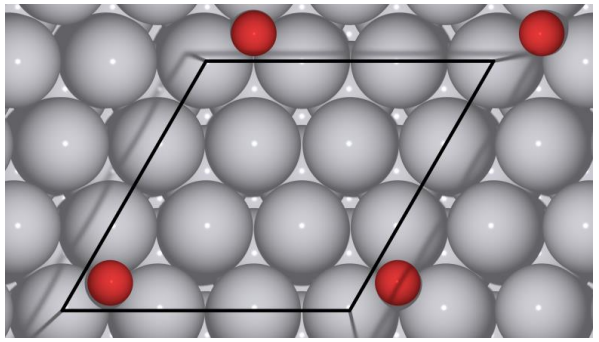
[1] Salciccioli, M. et al. *Chem. Eng. Sci.* **2011**, *66* (19), 4319–4355.
[2] Mhadeshwar, A. B. et al. *Catal. Letters* **2004**, *96* (1–2), 13–22.

Modelling Coverage Effects using DFT

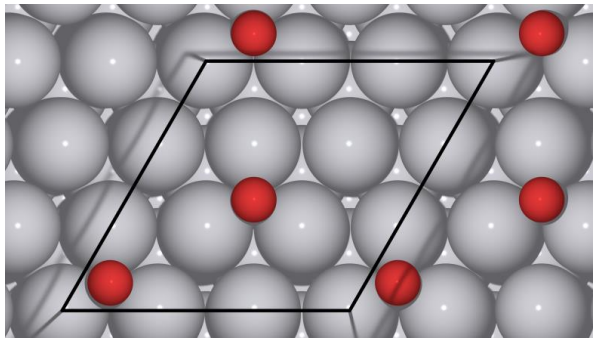
$$H_i(T, \boldsymbol{\theta}) = \underbrace{H_i(T, \theta_* \to 0)}_{\text{Low coverage}} + \underbrace{\sum_{j}^{\text{Adsorbates}} \omega_{ijk}\theta_j + b_{ijk}}_{\text{Finite coverage}}$$

- Gradually increase coverage in DFT cell
- Calculate binding energy as coverage increases
- Linear piece-wise is often sufficient

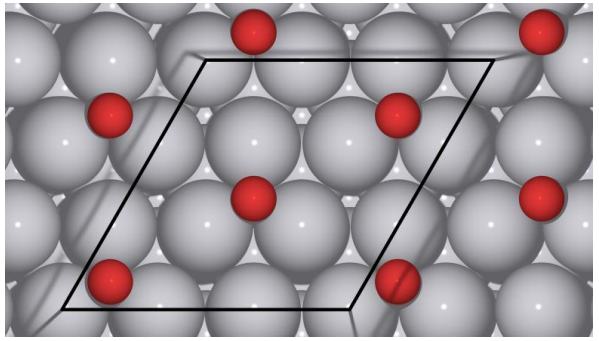
$\theta_O = \frac{1}{9}$ ML



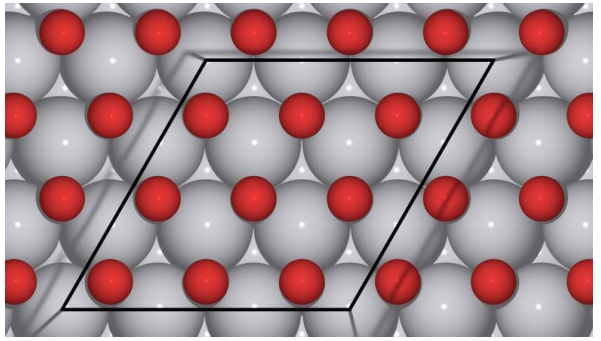
$\theta_O = \frac{2}{9}$ ML



$\theta_O = \frac{3}{9}$ ML

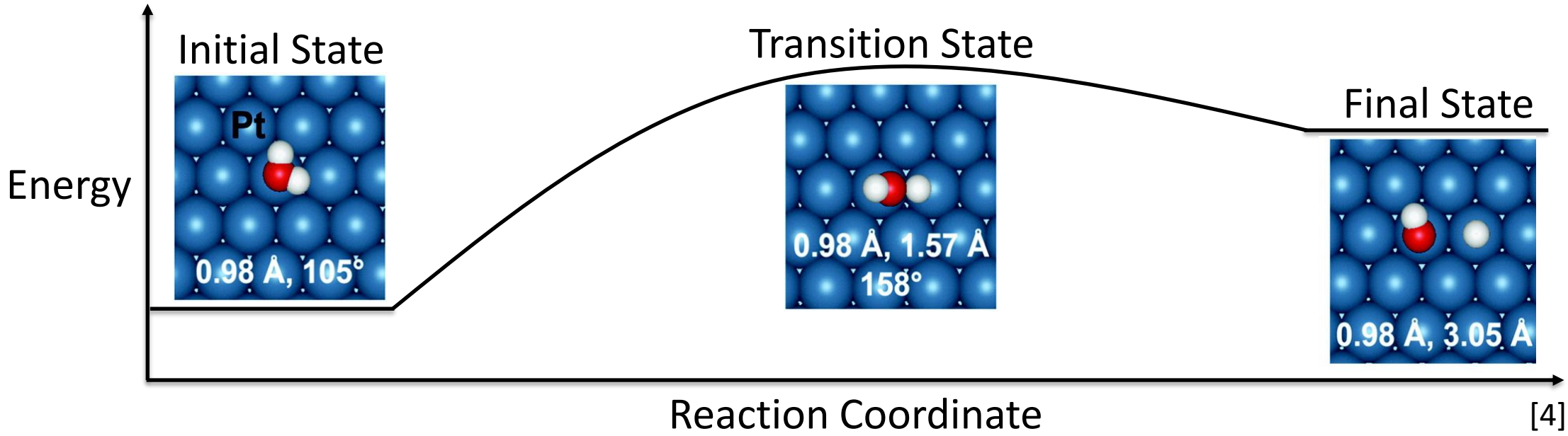


$\theta_O = 1$ ML



Locating Transition States Using DFT

- Common techniques:
  - Nudged elastic band (NEB)[1]
  - Climbing image nudged elastic band (CINEB)[2]
  - Dimer[3]
- Vibrational analysis of transition state species yield one imaginary frequency



[4]

[1] Mills, G.; Jónsson, H.; Schenter, G. K. Surf. Sci. **1995**, *324* (2–3), 305–337.
[2] Henkelman, G., et al. *J. Chem. Phys.* **2000**, *113* (22), 9901–9904.
[3] Henkelman, G.; Jónsson, H. *J. Chem. Phys.* **1999**, 111 (15), 7010–7022.
[4] Phatak, A. A. et al. *J. Phys. Chem. C* **2009**, 113 (17), 7269–7276.

Using Statistical Mechanics for Property Conversion

Useful DFT Properties

- Bond lengths
- Electronic energies
- Vibrational frequencies
- Coverage effects

MKM Inputs

- Enthalpy (H)
- Entropy (S)
- Activation Energies (E_A)
- Preexponential factors (A)
- Equilibrium constants (K_{eq})

Statistical Mechanical Equations are Tedious and Error Prone

Statistical Mechanics

$$\frac{U^{IG}}{Nk_BT} = 3 + \sum_i^{3n-6}\left(\frac{\Theta_{V,i}}{2T} + \frac{\Theta_{V,i}}{T}\frac{\exp\left(-\frac{\Theta_{V,i}}{T}\right)}{1-\exp\left(-\frac{\Theta_{V,i}}{T}\right)}\right) + \frac{\varepsilon_{elect,1}}{k_BT}$$

$$\frac{S^{IG}}{Nk_B} = \begin{cases} 4 + \ln\left[\left(\frac{2\pi\sum_i m_i k_B T}{h^2}\right)^{\frac{3}{2}}\frac{V}{N}\right] + \ln\frac{\sqrt{\pi}}{\sigma}\left(\frac{T^3}{\Theta_{R,A}\Theta_{R,B}\Theta_{R,C}}\right)^{\frac{1}{2}} \\ + \sum_i^{3n-6}\left[\frac{\Theta_{V,i}}{T}\frac{\exp\left(-\frac{\Theta_{V,i}}{T}\right)}{1-\exp\left(-\frac{\Theta_{V,i}}{T}\right)}\right. \\ \left. - \ln\left(1-\exp\left(-\frac{\Theta_{V,i}}{T}\right)\right)\right] + \ln\omega_{elect,1} \end{cases}$$

Statistical Mechanical Equations are Tedious and Error Prone

Statistical Mechanics

$$\frac{U^{IG}}{Nk_BT} = 3 + \sum_i^{3n-6}\left(\frac{\Theta_{V,i}}{2T} + \frac{\Theta_{V,i}}{T}\frac{\exp\left(-\frac{\Theta_{V,i}}{T}\right)}{1-\exp\left(-\frac{\Theta_{V,i}}{T}\right)}\right) + \frac{\varepsilon_{elect,1}}{k_BT}$$

$$\frac{S^{IG}}{Nk_B} = \begin{cases} 4 + \ln\left[\left(\frac{2\pi\sum_i m_i k_B T}{h^2}\right)^{\frac{3}{2}}\frac{V}{N}\right] + \ln\frac{\sqrt{\pi}}{\sigma}\left(\frac{T^3}{\Theta_{R,A}\Theta_{R,B}\Theta_{R,C}}\right)^{\frac{1}{2}} \\ + \sum_i^{3n-6}\left[\frac{\Theta_{V,i}}{T}\frac{\exp\left(-\frac{\Theta_{V,i}}{T}\right)}{1-\exp\left(-\frac{\Theta_{V,i}}{T}\right)}\right. \\ \left. - \ln\left(1-\exp\left(-\frac{\Theta_{V,i}}{T}\right)\right)\right] + \ln\omega_{elect,1} \end{cases}$$

pMuTT

```
U_IG = get_U(T)
S_IG = get_S(T)
```

Symbol Reference Sheet

Symbol	Description	Slide #
m_{cat}	Mass of catalyst in reactor	6-7
P	Pressure	6-7
Q_0	Volumetric flow rate of inlet stream	6-7
T	Temperature	6-7, 10-15, 19, 22-23
V	Volume	6-7
$\mathbf{x_0}$	Vector of initial mole fractions	6-7
$*$	Empty site	7-8
$[A^*]$	Surface concentration of species A	8-15
k_j^{fwd}	Forward rate constant of reaction j	8-15
k_j^{rev}	Reverse rate constant of reaction j	8-15
t	Time	8-15

Symbol Reference Sheet

Symbol	Description	Slide #
$E_{A,j}$	Activation energy of reaction j	10-15
R	Molar gas constant	10-15
$T_{ref,j}$	Reference temperature of modified Arrhenius of reaction j	10-15
β_j	Modified Arrhenius parameter of reaction j	10-15
K_j^{eq}	Equilibrium constant of reaction j	12-13, 21
ΔG_j	Change in Gibbs energy between products and reactants of reaction j	13
M_i	Molecular weight of i	14
n_{surf}	Number of surface reactants	14-15

Symbol Reference Sheet

Symbol	Description	Slide #
s_j	Sticking coefficient for adsorption reaction j	14
σ	Site density	14-15
h	Planck's constant	15, 22-23
k_B	Boltzmann constant	15, 22-23
$\Delta H_j^{\neq}$	Enthalpy of activation of reaction j	15
$\Delta S_j^{\neq}$	Entropy of activation of reaction j	15
b_{ijk}	Intercept of coverage effect of species j affecting species i in interval k	19
H_i	Enthalpy of species i	19, 22-23
ML	Monolayer	19
$\boldsymbol{\theta}$	Vector of surface coverages	19

Symbol Reference Sheet

Symbol	Description	Slide #
θ_i	Surface coverage of species i	19
ω_{ijk}	Slope of coverage effect of species j affecting species i in interval k	19
m_i	Mass of atom i	22-23
N	Number of molecules	22-23
U^{IG}	Internal energy of ideal gas	22-23
x_{i0}	Initial mole fractions of species i	22-23
$\varepsilon_{elect,1}$	Ground state electronic energy	22-23
$\Theta_{R,A}$	Rotational temperature of Ath mode	22-23
$\Theta_{V,i}$	ith vibrational temperature of molecule	22-23
σ	Symmetry number	22-23