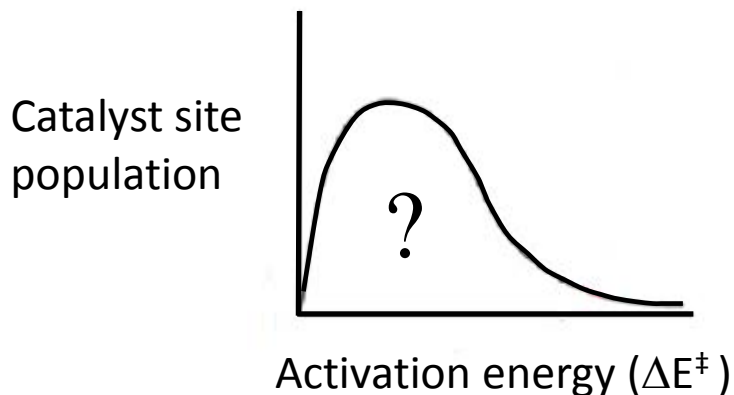# *Ab initio* framework for uncovering structure-property relationships of amorphous catalysts
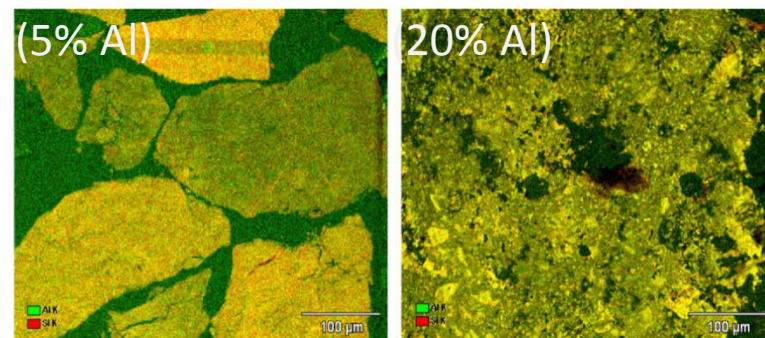
Bryan R. Goldsmith, Evan Sanderson, Daniel Bean, Baron Peters

Modeling amorphous catalysts is a difficult problem

Diversity of site environments

Catalyst site population

Activation energy ($\Delta E^{\ddagger}$)

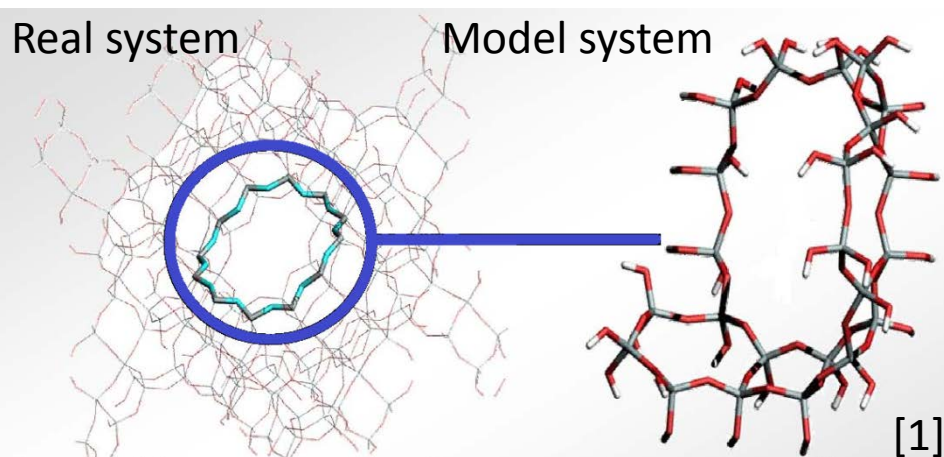Preparation-dependent properties

(5% Al)   20% Al)

Amorphous silica-alumina [1]

Many reasons to try

- Some catalysts only work on amorphous supports
- Unknown initiation mechanism
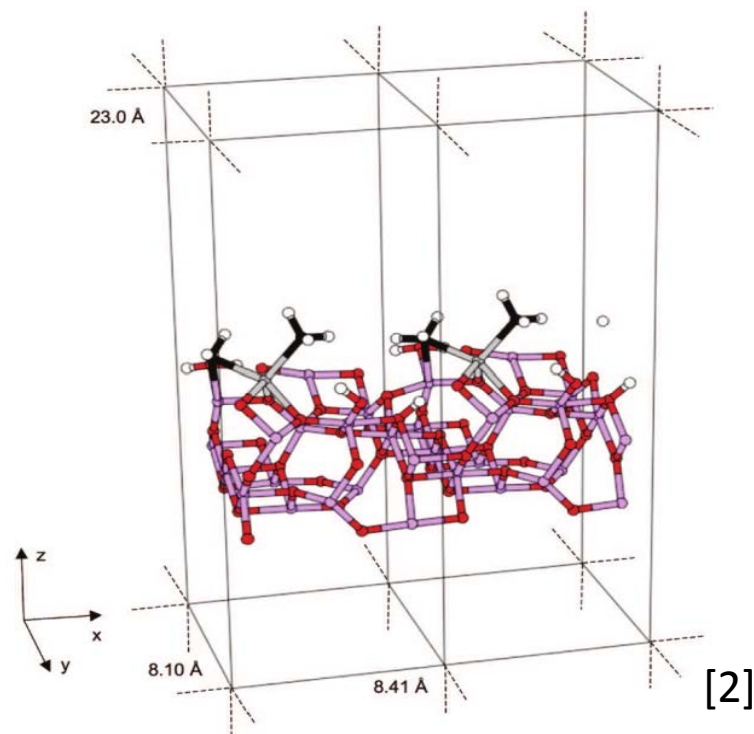- Differences between active and inactive sites?

[1]. E. J. M. Hensen et al. J. Catalysis. 269, 201 (2010)

Typical modeling approach:
from structure to properties

Cluster models

Slab models

Real system   Model system

[1]

Cut, cap and *constrain*
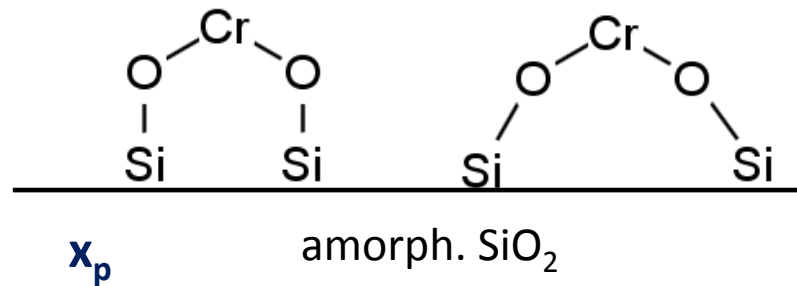

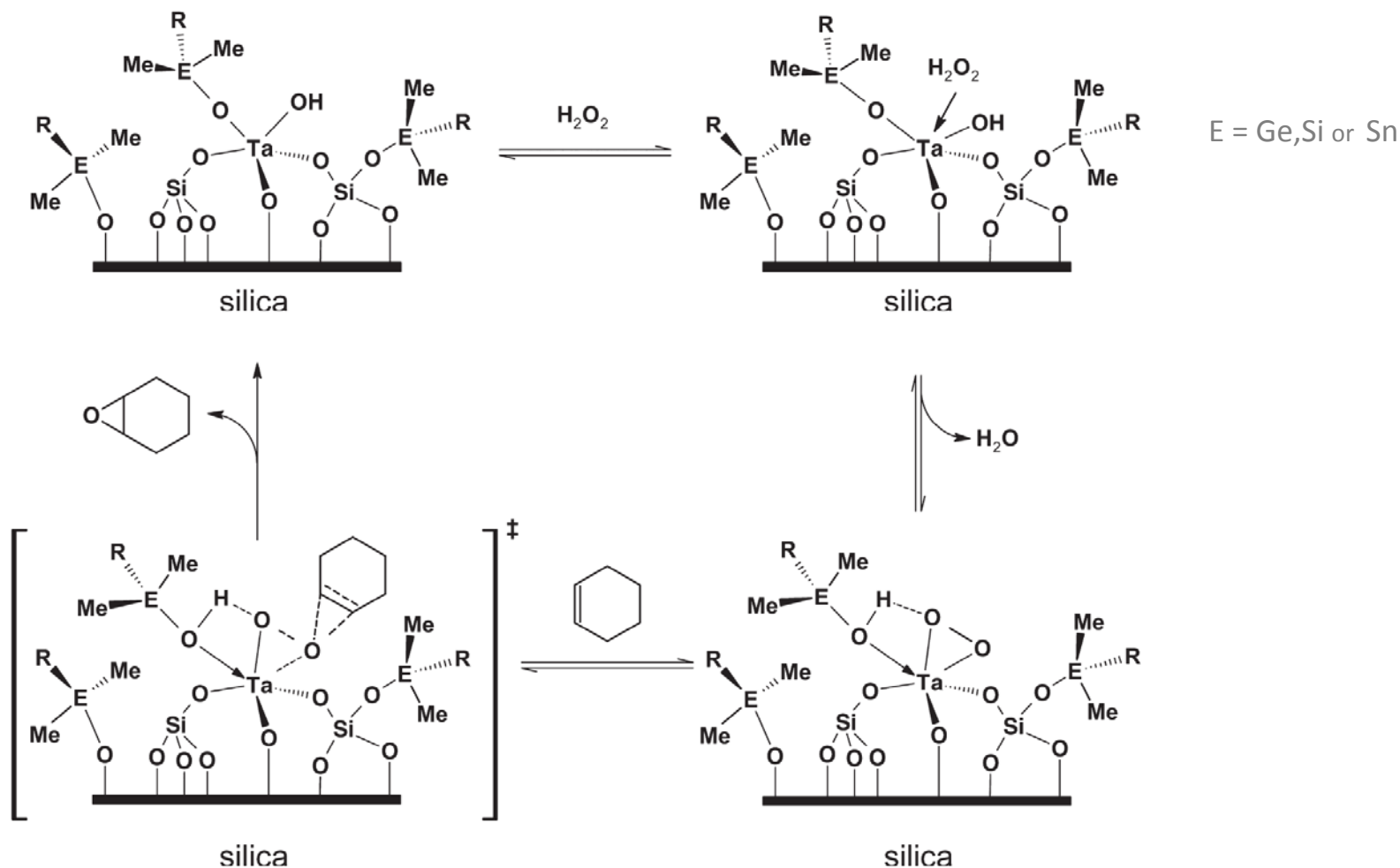23.0 Å

8.10 Å

8.41 Å

[2]

Constrain bulk atoms

[1]. British Zeolite Association webpage http://www.bza.org/
[2]. Sautet et al. Chem. Rev. 110, 1788 (2010

Drawings specify topology, but also $\Delta E^{\neq} = \Delta E^{\neq}(x_p)$

x_p   amorph. SiO_2

Drawings specify topology, but also $\Delta E^{\neq} = \Delta E^{\neq}(x_p)$
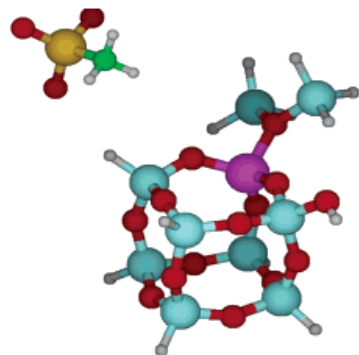

E = Ge, Si or Sn

[1]. Ruddy and Tilley, JACS, 130, 11088 (2008)
[2]. Cordeiro and Tilley, Langmuir, 27, 8295 (2011)
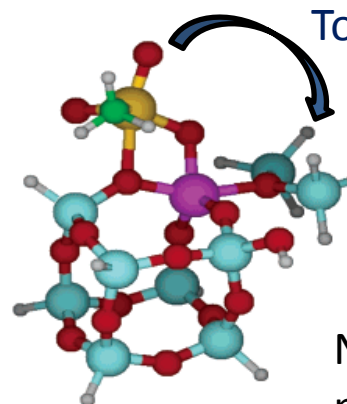
Many ways to model amorphous materials, but they are *not* systematic

CH_3ReO_3 on Aluminosilsesquioxane[1]

Re
Al
Si
O
C
H

- 36 kJ/mol

Too flexible

No constraints to mimic solid support!

[1]. Moses et al. Organometallics, 25, 9 (2006)

Many ways to model amorphous materials, but they are *not* systematic

Mo/Silica catalyst cut from β-cristobalite [1]
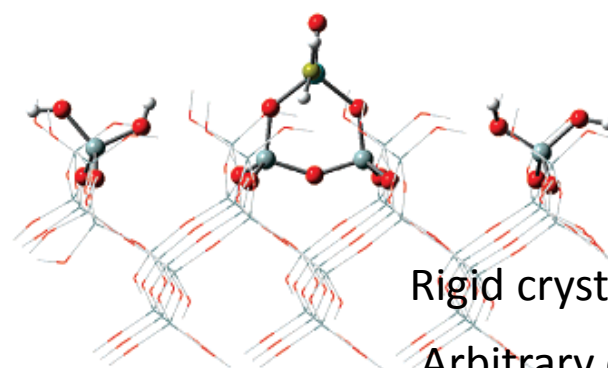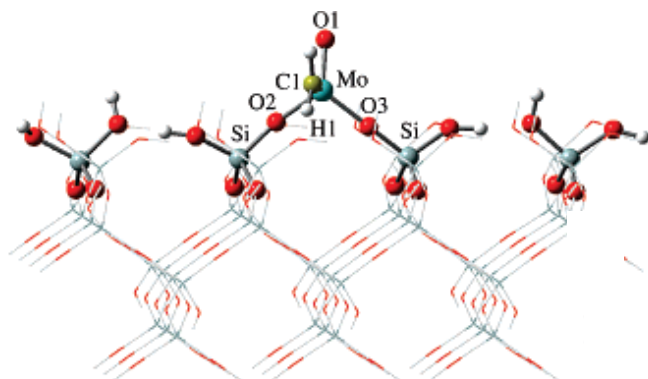
Rigid crystalline support

Arbitrary constraints

[1]. Handzlik, J. J. Phys. Chem. 111, 26 (2007)

Our approach to modeling amorphous materials

Literature model

Our type of model
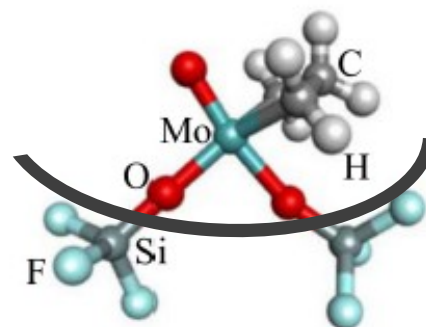
Specific structural assumptions

Constrained periphery atoms (x_p)
(amorphous environment)

amorph. SiO_2

[1]. Handzlik, J. J. Phys. Chem. 111, 26 (2007)

Our approach to modeling amorphous materials

Our type of model
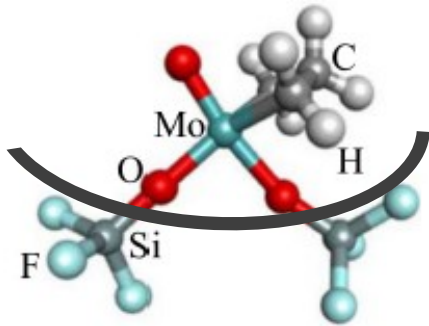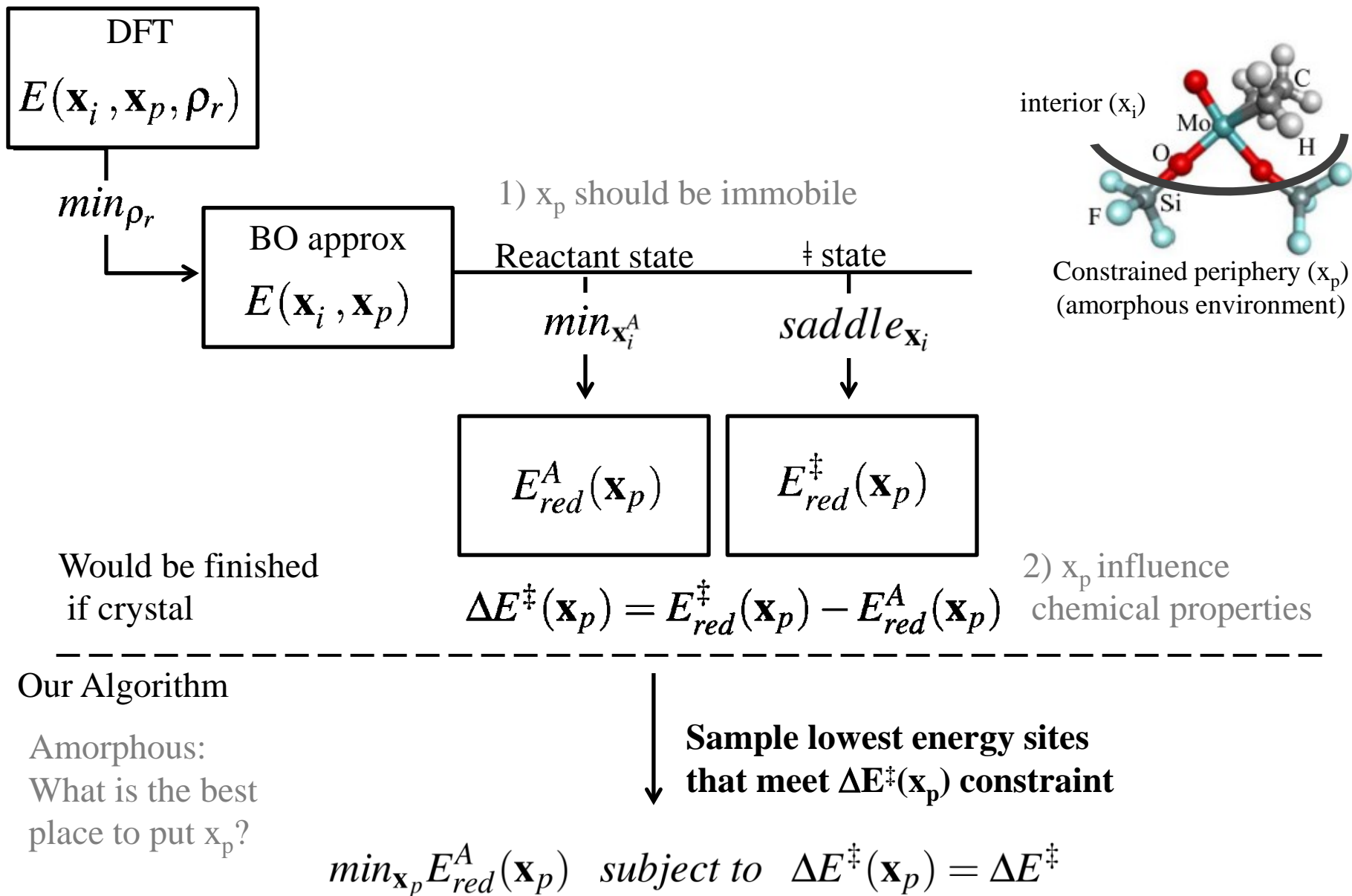

Constrained periphery atoms (x_p)
(amorphous environment)

Modeling premises

1) Periphery atoms (x_p) should be immobile

2) x_p influence chemical properties of the site

3) x_p arranged in an *unknown and continuous distribution*

4) For any $\Delta E^{\ddagger}(x_p)$, assume low energy sites prevalent

Connecting our algorithm to usual modeling approach

DFT

$$E(\mathbf{x}_i, \mathbf{x}_p, \rho_r)$$

interior (x_i)

min_{ρ_r}

1) x_p should be immobile

BO approx

$$E(\mathbf{x}_i, \mathbf{x}_p)$$

Constrained periphery (x_p)
(amorphous environment)

Reactant state   ‡ state

$$min_{\mathbf{x}_i^A} \qquad saddle_{\mathbf{x}_i}$$

$$E_{red}^A(\mathbf{x}_p) \qquad E_{red}^{\ddagger}(\mathbf{x}_p)$$

Would be finished
if crystal

$$\Delta E^{\ddagger}(\mathbf{x}_p) = E_{red}^{\ddagger}(\mathbf{x}_p) - E_{red}^A(\mathbf{x}_p)$$

2) x_p influence
chemical properties

- -

Our Algorithm

Amorphous:
What is the best
place to put x_p?

**Sample lowest energy sites
that meet $\Delta E^{\ddagger}(x_p)$ constraint**

$$min_{\mathbf{x}_p} E_{red}^A(\mathbf{x}_p) \quad subject\ to \quad \Delta E^{\ddagger}(\mathbf{x}_p) = \Delta E^{\ddagger}$$

From properties to structures, instead of from structures to properties

Generates low energy catalyst structures
with varying degrees of reactivity
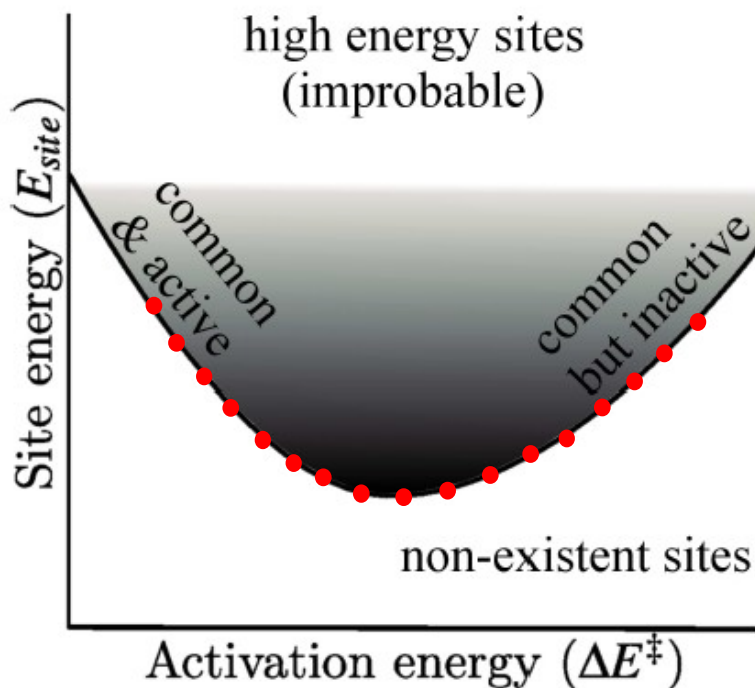
Each point on curve thought
of as a different catalyst site

Algorithm Formulation

Key
Reactant state - superscript A
gradient vector - g
Hessian matrix – H
Interior coordinate – x_i
Periphery coordinate – x_p

Local quadratic expansion

$$E(\mathbf{x}_i^A + \Delta\mathbf{x}_i^A, \mathbf{x}_p + \Delta\mathbf{x}_p) - E(\mathbf{x}_i^A, \mathbf{x}_p) =$$

$$\begin{bmatrix} \Delta\mathbf{x}_i^A & \Delta\mathbf{x}_p \end{bmatrix} \begin{bmatrix} \mathbf{g}_i^A \\ \mathbf{g}_p^A \end{bmatrix} + \frac{1}{2} \begin{bmatrix} \Delta\mathbf{x}_i^A & \Delta\mathbf{x}_p \end{bmatrix} \begin{bmatrix} H_{ii}^A & H_{ip}^A \\ H_{pi}^A & H_{pp}^A \end{bmatrix} \begin{bmatrix} \Delta\mathbf{x}_i^A \\ \Delta\mathbf{x}_p \end{bmatrix}$$
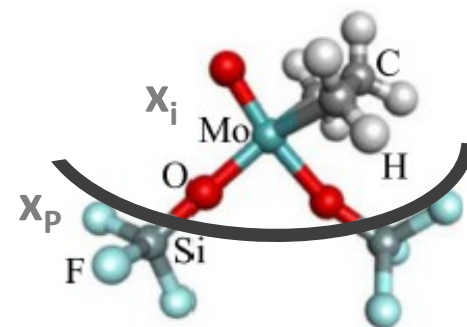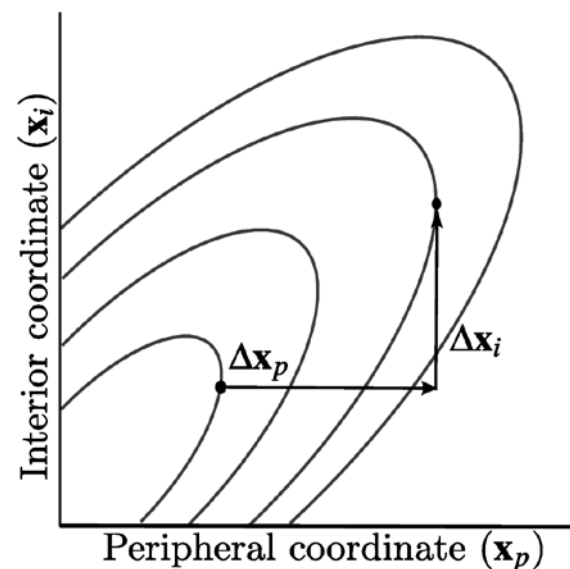

Minimize $E(\mathbf{x}_i^A, \mathbf{x}_p)$ given any $\Delta\mathbf{x}_p$ by interior optimization

$$\Delta\mathbf{x}_i^A = -(H_{ii}^A)^{-1}(\mathbf{g}_i^A + H_{ip}^A \Delta\mathbf{x}_p)$$
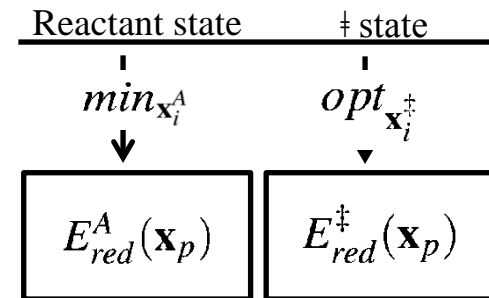
Optimize interior
atoms for given Δx_p

Move periphery
atoms

Reduced potential energy surface

$$E_{red}^A(\mathbf{x}_p + \Delta\mathbf{x}_p) = E_{red}^A(\mathbf{x}_p) + (\Delta\mathbf{x}_p)^T \mathbf{g}_{red}^A + \frac{1}{2}(\Delta\mathbf{x}_p)^T H_{red}^A \Delta\mathbf{x}_p$$
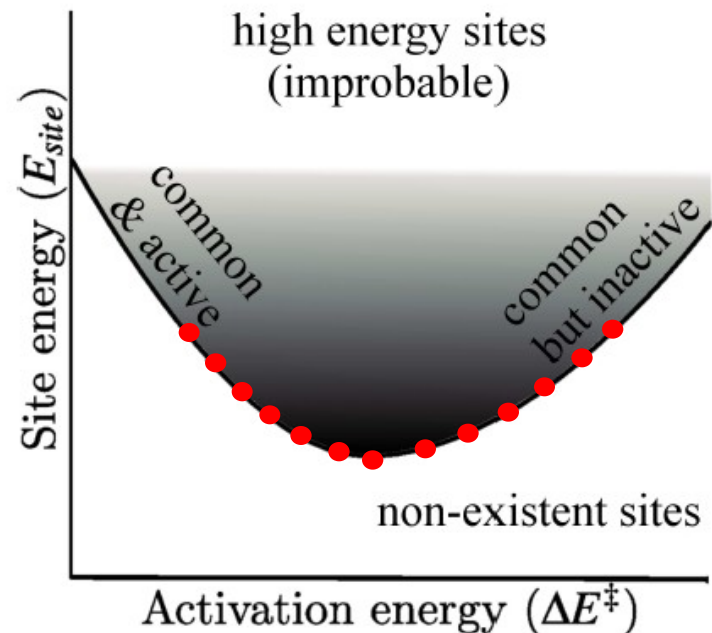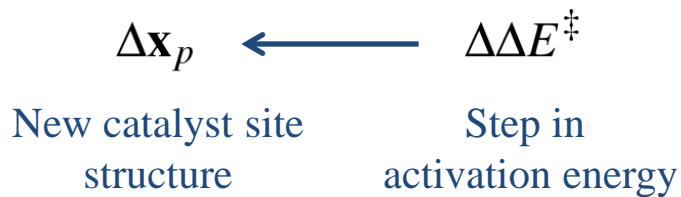
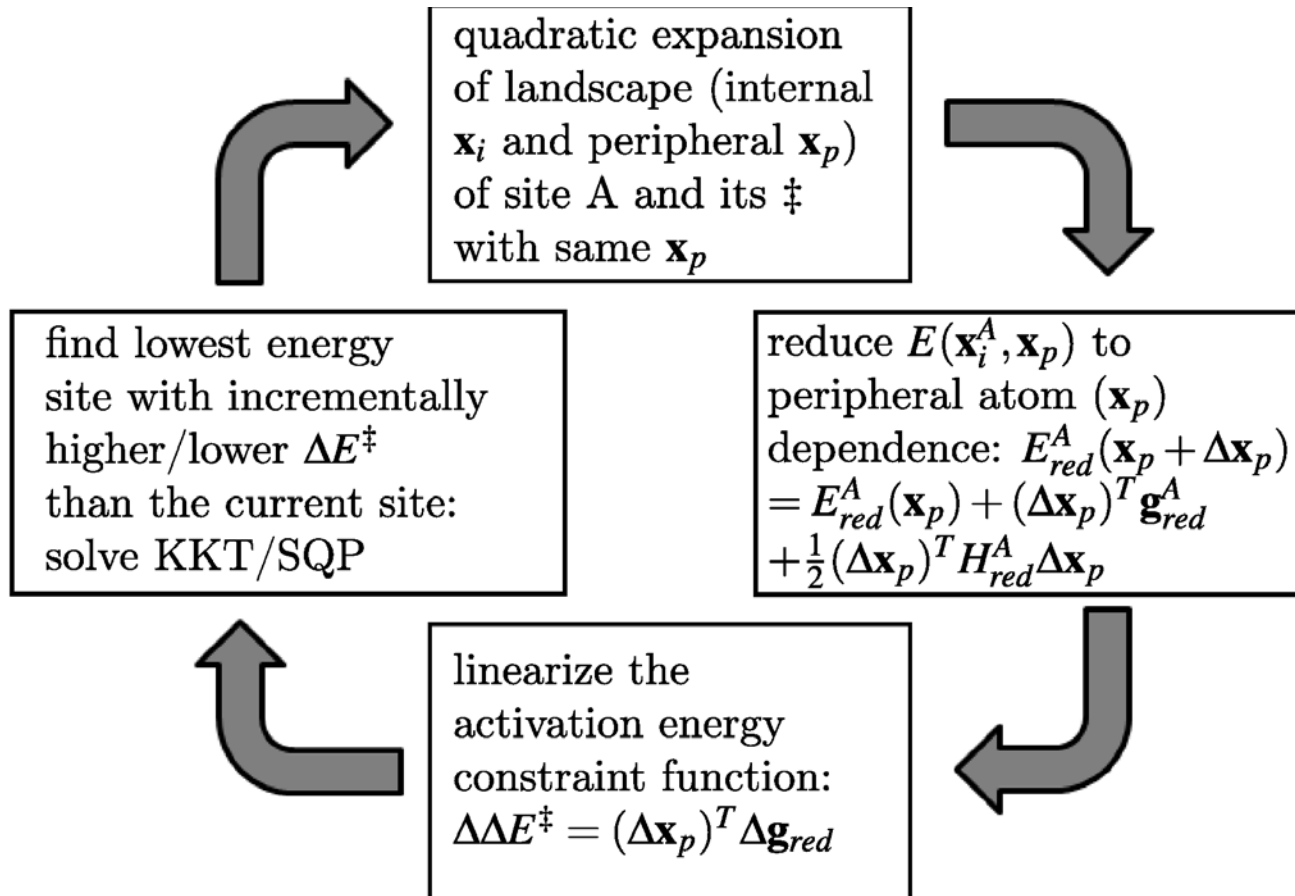| Reactant state	‡ state
$min_{\mathbf{x}_i^A}$	$opt_{\mathbf{x}_i^‡}$
$E_{red}^A(\mathbf{x}_p)$	$E_{red}^‡(\mathbf{x}_p)$

Find the lowest energy sites with a given activation energy

$$min_{\mathbf{x}_p} E_{red}^A(\mathbf{x}_p) \quad subject\ to \quad \Delta E^‡(\mathbf{x}_p) = \Delta E^‡$$

Sequential Quadratic Programming

'*Dial*' the activation energy
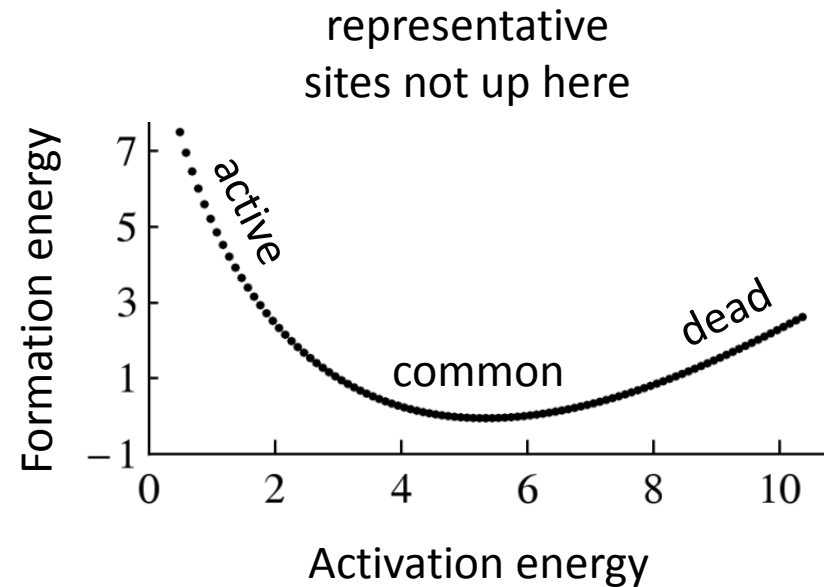
$$\Delta\mathbf{x}_p \longleftarrow \Delta\Delta E^‡$$

New catalyst site structure

Step in activation energy

high energy sites (improbable)

common & active

common but inactive

Site energy (E_{site})

non-existent sites

Activation energy $(\Delta E^‡)$

Sequential quadratic programming

quadratic expansion of landscape (internal $\mathbf{x}_i$ and peripheral $\mathbf{x}_p$) of site A and its $\ddagger$ with same $\mathbf{x}_p$

reduce $E(\mathbf{x}_i^A, \mathbf{x}_p)$ to peripheral atom $(\mathbf{x}_p)$ dependence: $E_{red}^A(\mathbf{x}_p + \Delta\mathbf{x}_p)$
$= E_{red}^A(\mathbf{x}_p) + (\Delta\mathbf{x}_p)^T \mathbf{g}_{red}^A$
$+ \frac{1}{2}(\Delta\mathbf{x}_p)^T H_{red}^A \Delta\mathbf{x}_p$

linearize the activation energy constraint function:
$\Delta\Delta E^{\ddagger} = (\Delta\mathbf{x}_p)^T \Delta\mathbf{g}_{red}$

find lowest energy site with incrementally higher/lower $\Delta E^{\ddagger}$ than the current site: solve KKT/SQP

Example: Empirical Valence Bond Model Energy Landscape

representative sites not up here
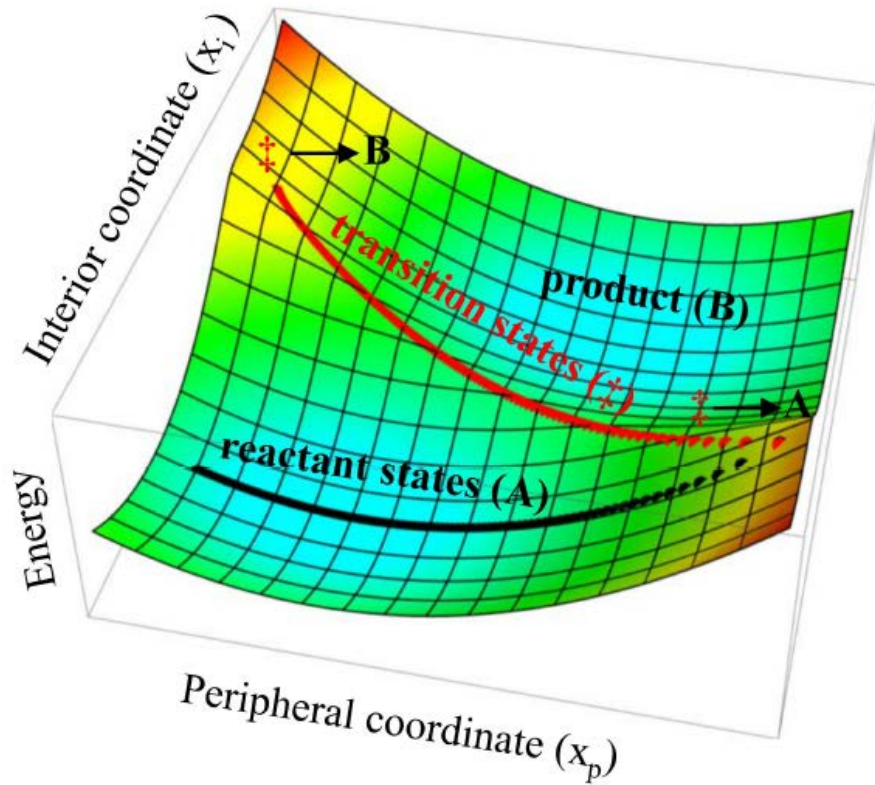
Olefin metathesis by isolated Mo(VI) on amorphous SiO$_2$
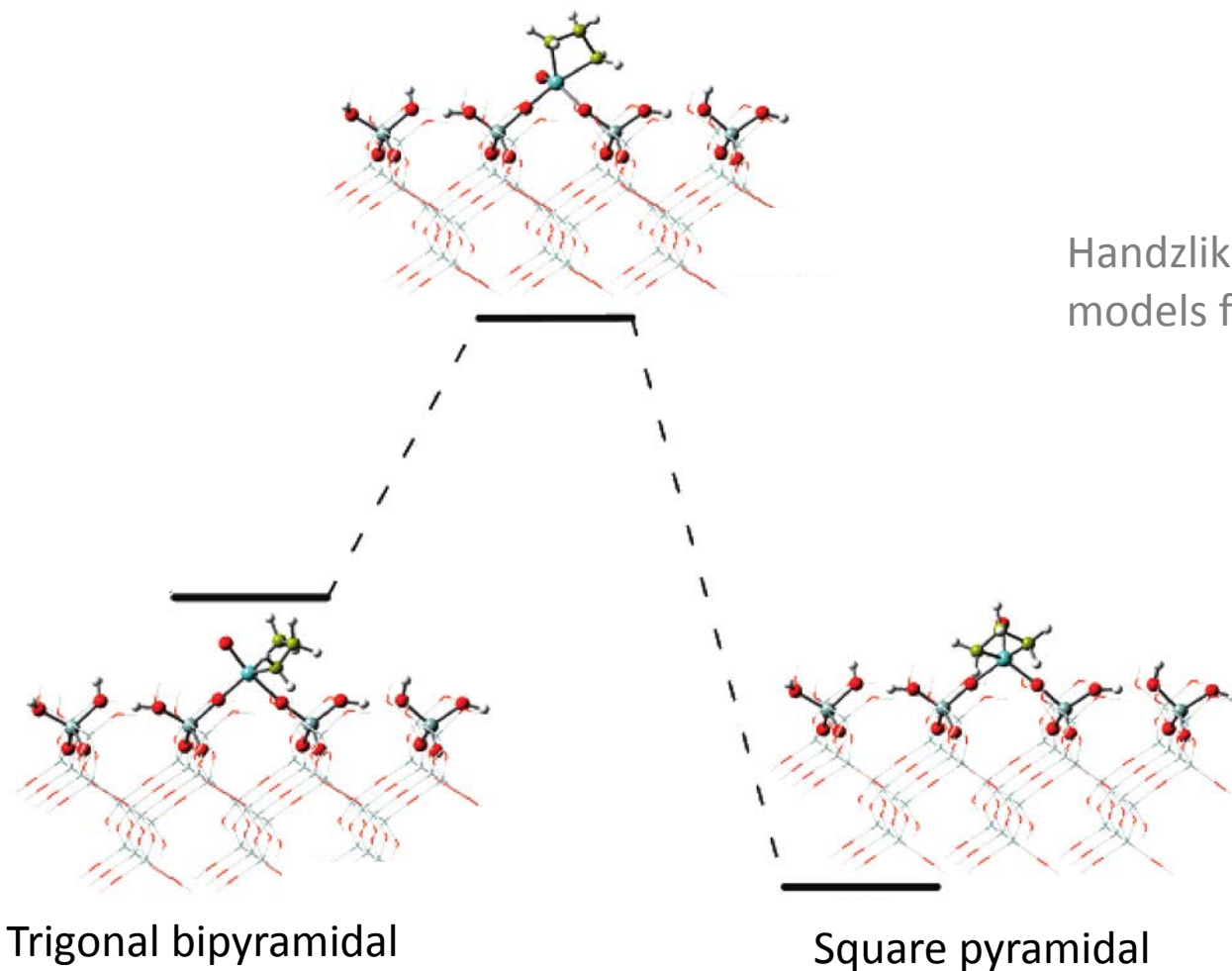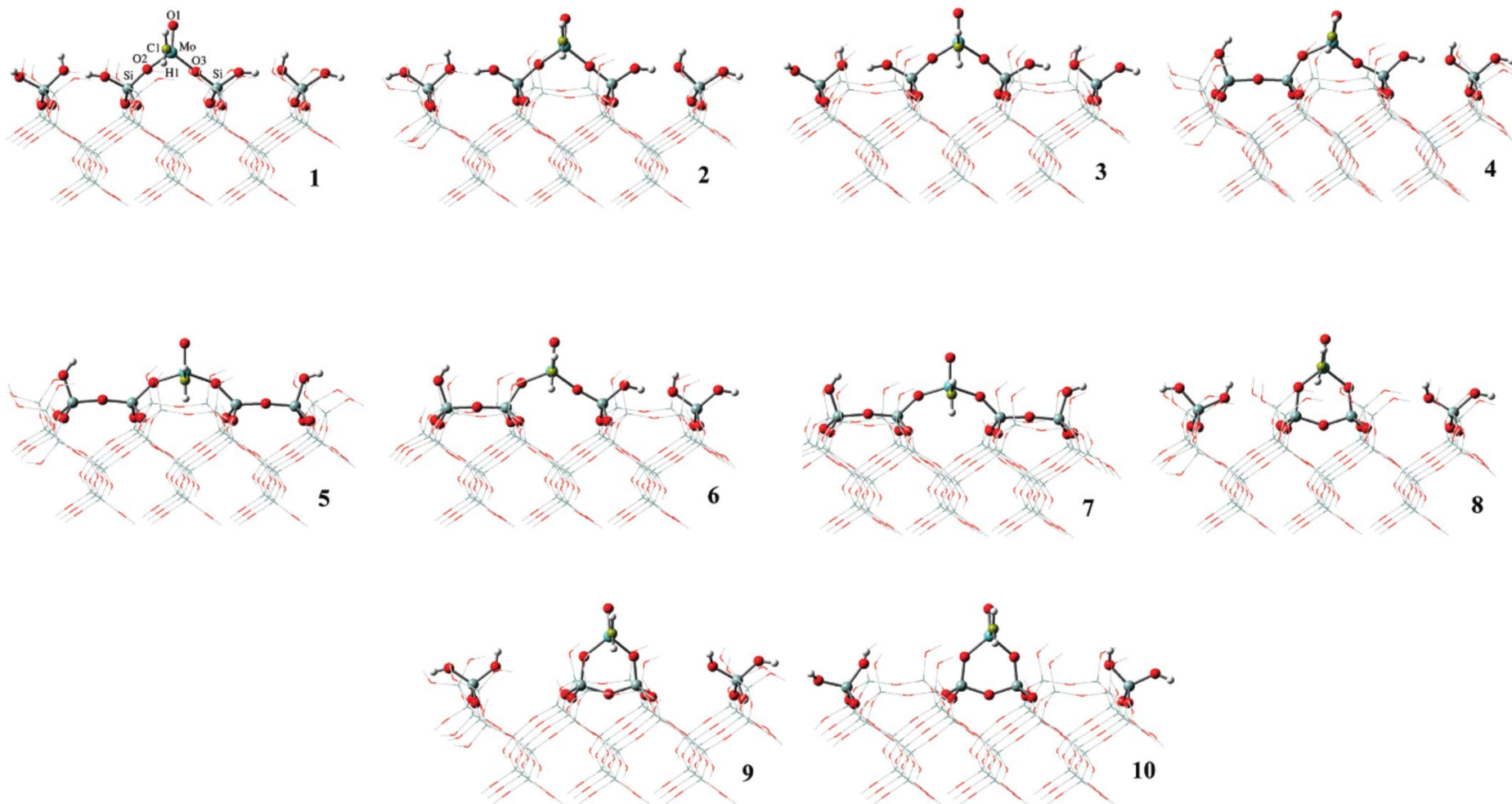
Olefin metathesis
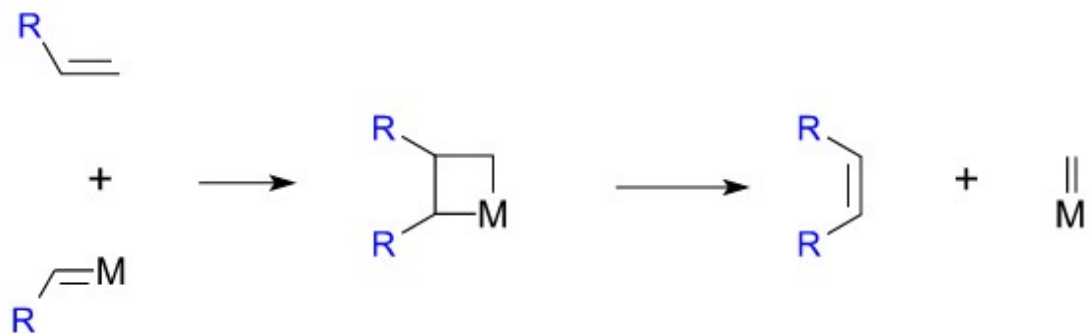
Olefin metathesis by isolated Mo(VI) on amorphous SiO$_2$

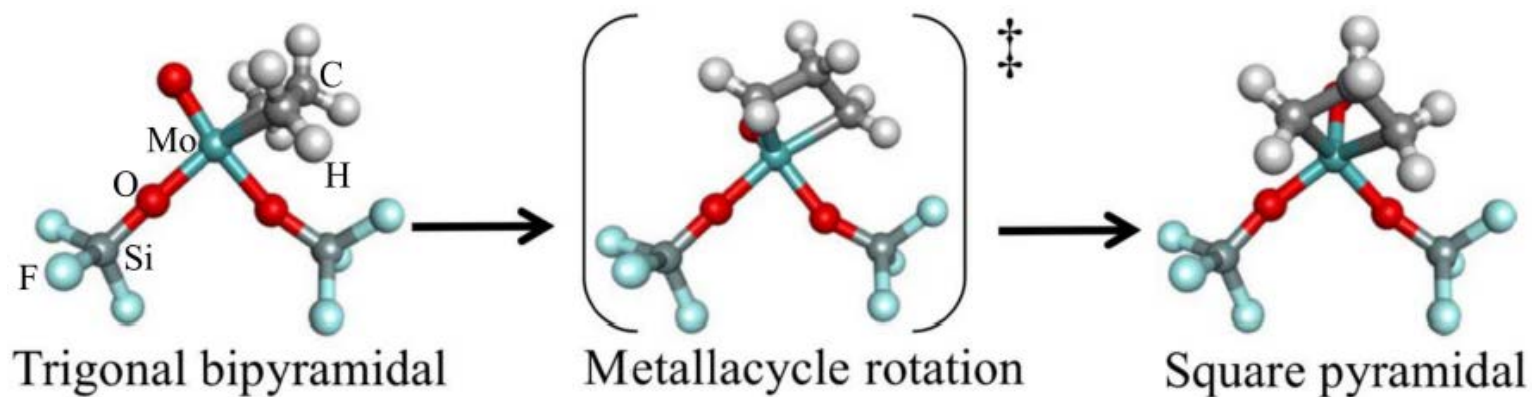Off-pathway intermediate formation

Metallacycle rotation

Handzlik used *ten* QM/MM models from β-cristobalite
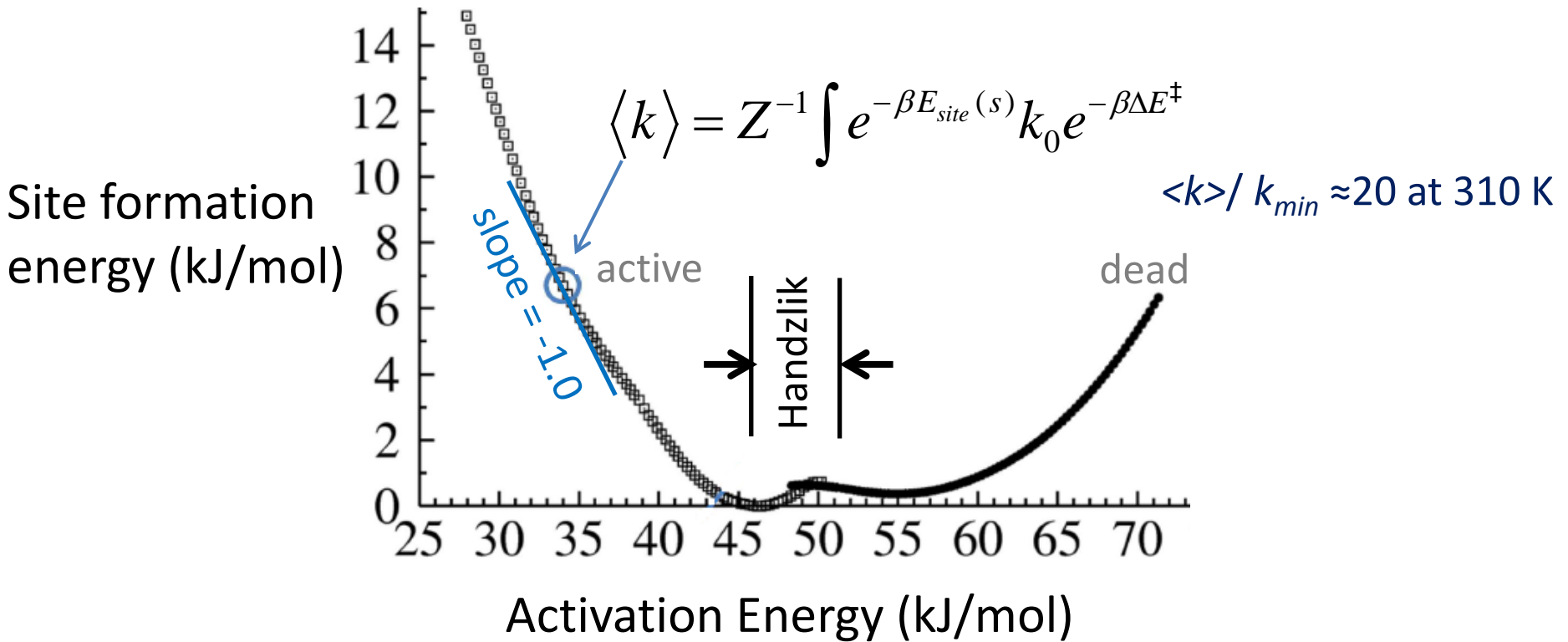
Trigonal bipyramidal

Square pyramidal

[1]. Handzlik, J. J. Phys. Chem. 111, 26 (2007)

Handzlik's *ten* QM/MM models from β-cristobalite

[1]. Handzlik, J. J. Phys. Chem. 111, 26 (2007)

SQP approach to modeling Mo/SiO$_2$

Trigonal bipyramidal → Metallacycle rotation ‡ → Square pyramidal

periphery: terminal F atoms
basis deficient to mimic OH

B. R. Goldsmith, E. D. Sanderson, D. Bean, B. Peters, *J. Chem. Phys.* **138**, 204105 (2013)

Smaller is better!
2 Si & 1 model (us) vs. 35 Si & 10 QM/MM models

Site formation energy (kJ/mol)

$$\langle k \rangle = Z^{-1} \int e^{-\beta E_{site}(s)} k_0 e^{-\beta \Delta E^{\ddagger}}$$

$\langle k \rangle / k_{min} \approx 20$ at 310 K

slope = -1.0

active

Handzlik

dead

Activation Energy (kJ/mol)

B. R. Goldsmith, E. D. Sanderson, D. Bean, B. Peters, *J. Chem. Phys.* **138**, 204105 (2013)

Trigonal bipyramidal → Metallacycle rotation ‡ → Square pyramidal

"stretched" inactive

active

r_{Si-Si} (Å)

Activation Energy (kJ/mol)

B. R. Goldsmith, E. D. Sanderson, D. Bean, B. Peters, *J. Chem. Phys.* **138**, 204105 (2013)
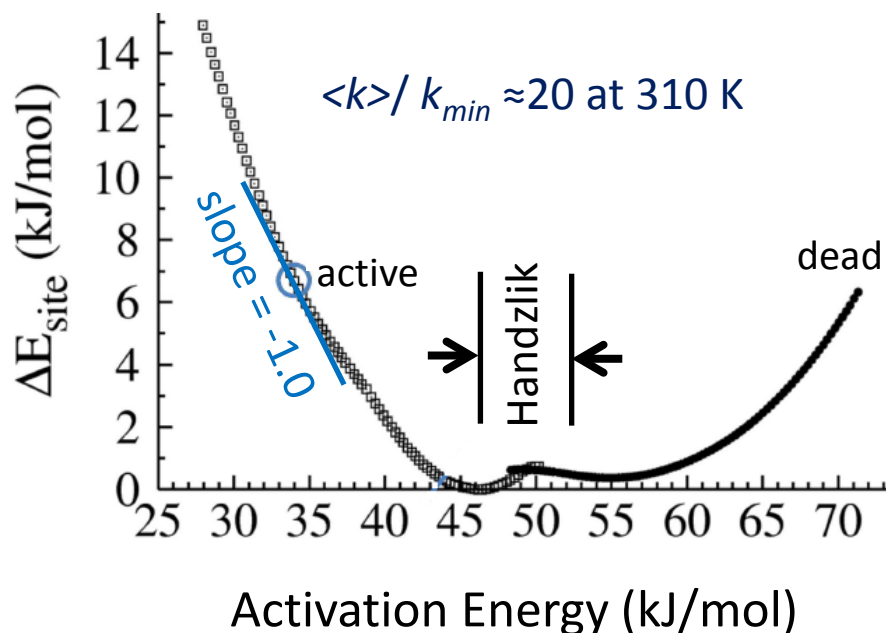
New framework for modeling amorphous catalysts

From properties to structures

- Generate sites with different reactivity
- Contrast dead & active for structural descriptors

$\langle k \rangle / k_{min} \approx 20$ at 310 K

slope = -1.0

active

Handzlik

dead

r_{Si-Si} (A)

"stretched" inactive

active

Activation Energy (kJ/mol)

Activation Energy (kJ/mol)
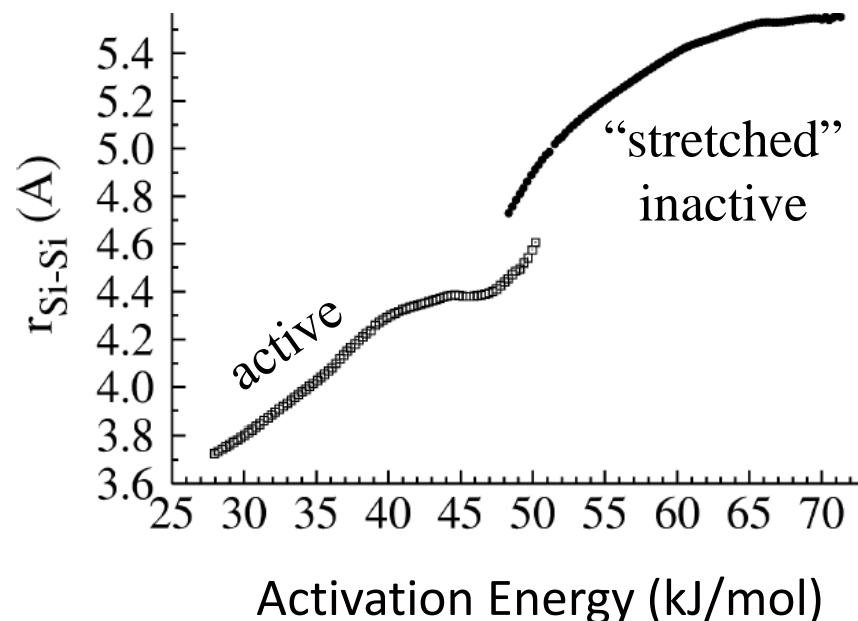
B. R. Goldsmith, E. D. Sanderson, D. Bean, B. Peters, *J. Chem. Phys.* **138**, 204105 (2013)

B. R. Goldsmith *et al.* in Reaction Rate Constant Computations: Theories and Applications, The Royal Society of Chemistry (pp. 213-232). Cambridge, U.K.

Acknowledgements

UCSB Department of Chemical Engineering

Prof. Baron Peters
Evan Sanderson
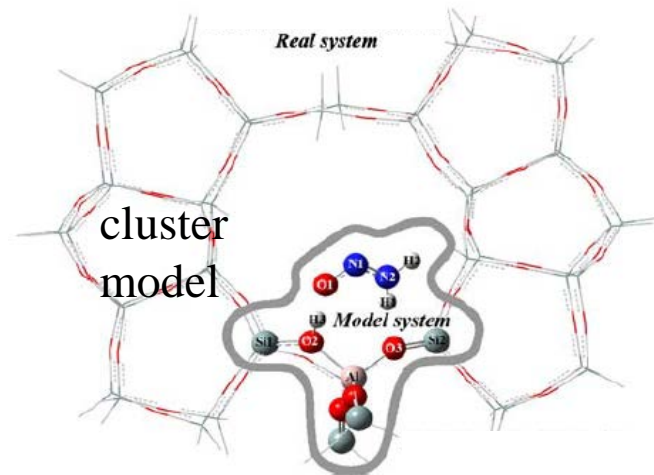Daniel Bean

The Peters group
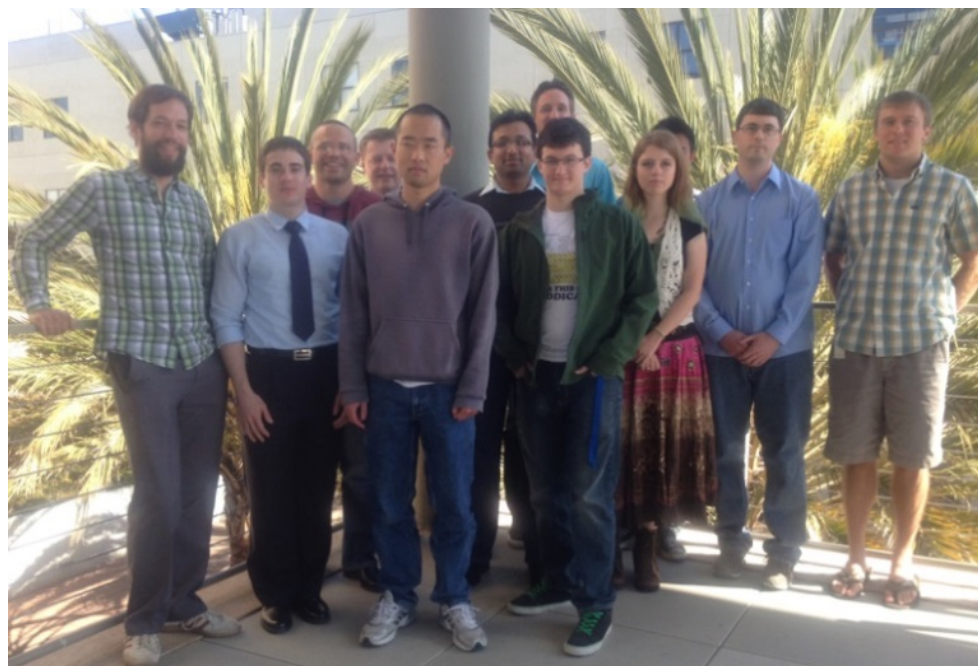
Structural embedding

Real system

cluster
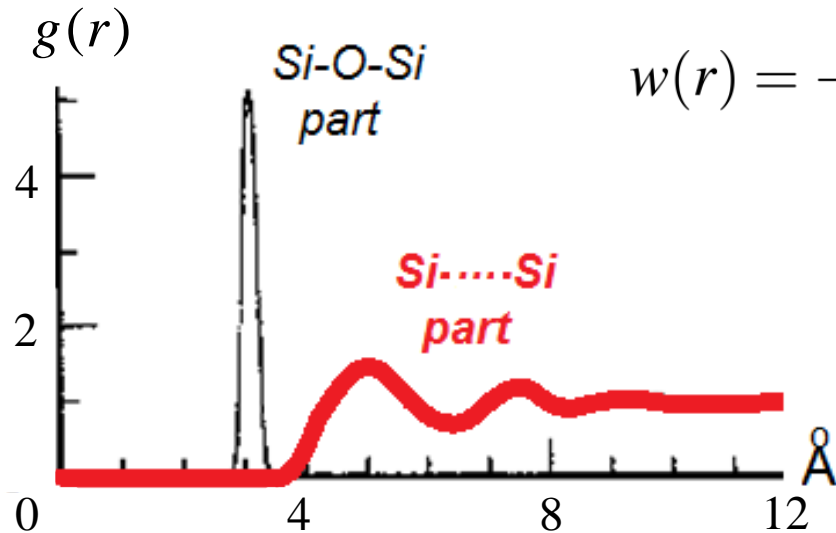model

Real site is embedded, not isolated
- usually have electrostatic effects
- external matrix strain

Bias the distribution of x_p pairs

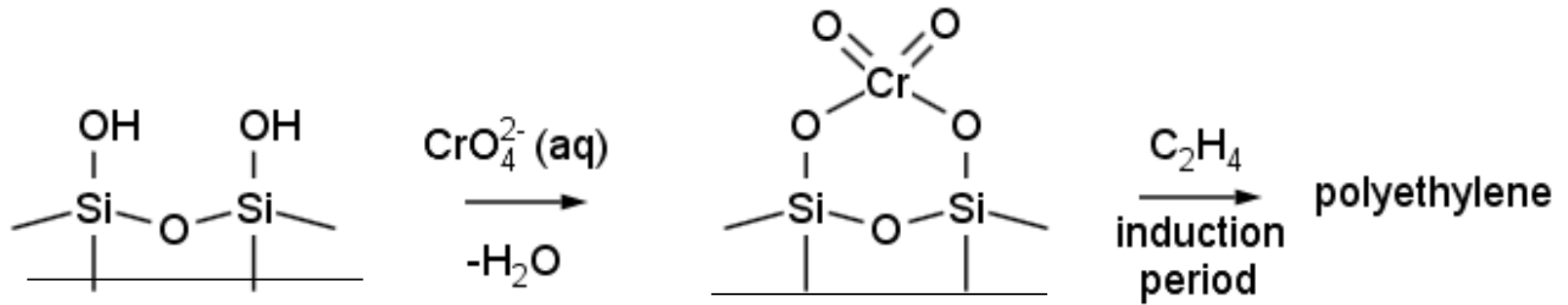$g(r)$

Si-O-Si
part

Si·····Si
part

$$w(r) = -k_B T \ln g_{,2nd}(r)$$

Si-O-Si:
no need to modify
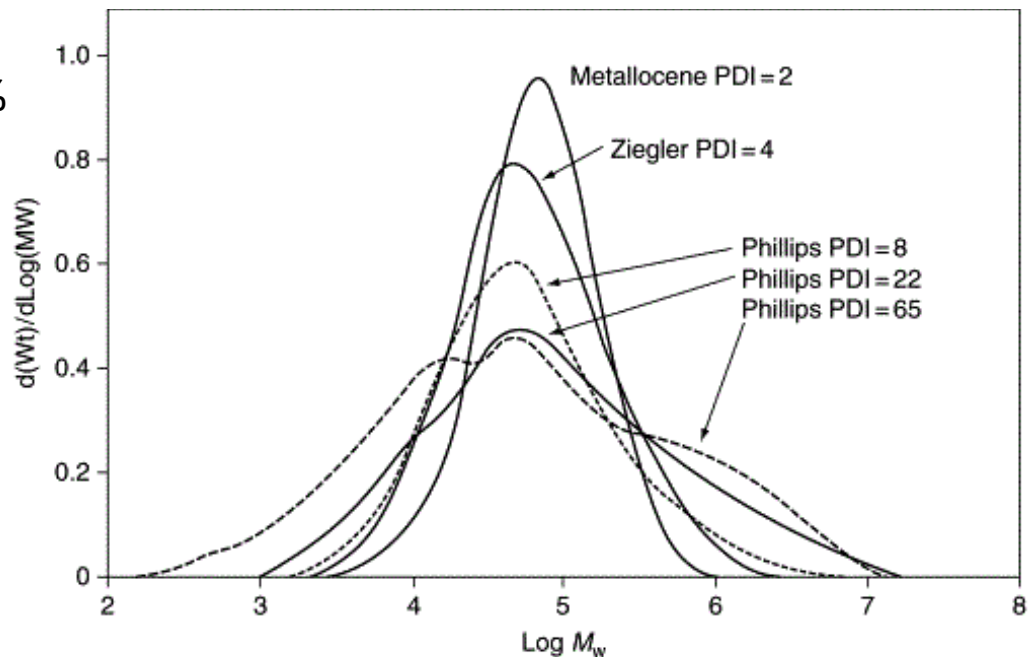
through-
matrix forces

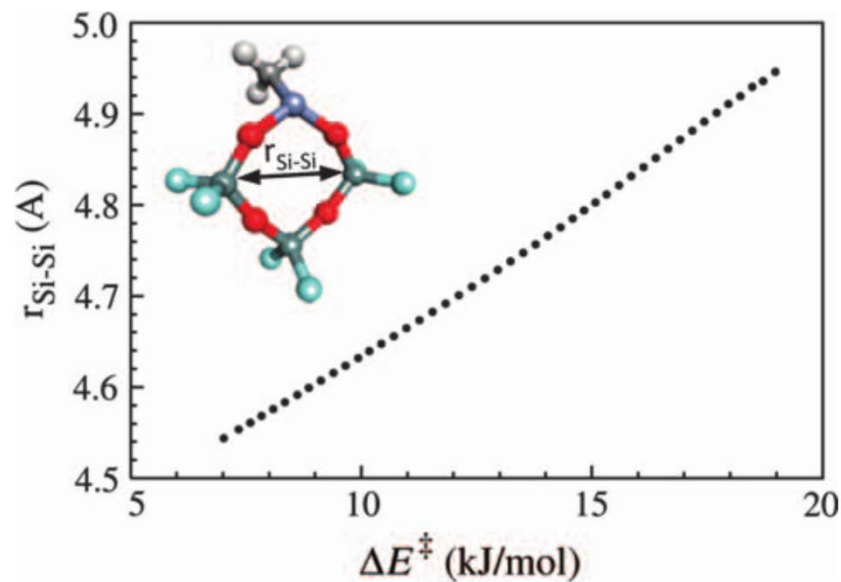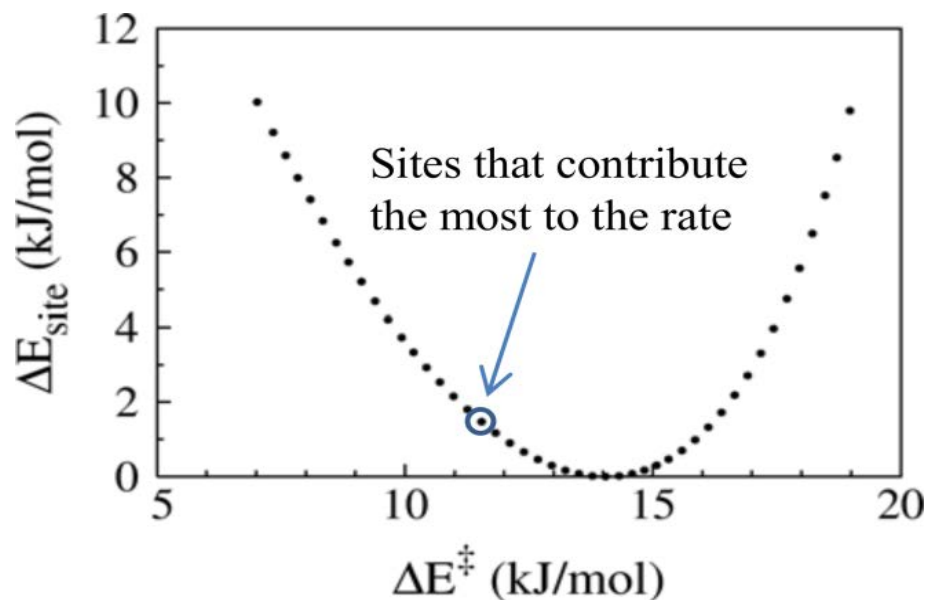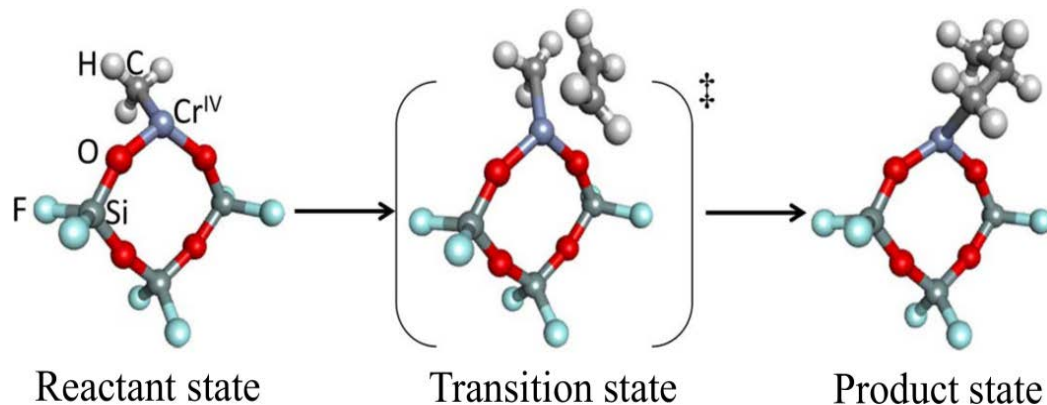Modified from: P. Vashishta, et al. Physical Rev. B. 1989, 41, 197
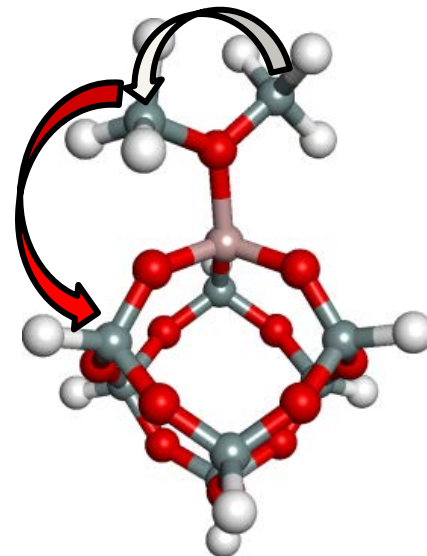
Further applications: Phillips Catalyst

- Low number of active sites ~1%
- unknown mechanism
- 40-50% HDPE produced

Reactant state · Transition state · Product state

Sites that contribute the most to the rate

B. R. Goldsmith *et al.* in Reaction Rate Constant Computations: Theories and Applications, The Royal Society of Chemistry (pp. 213-232). Cambridge, U.K.
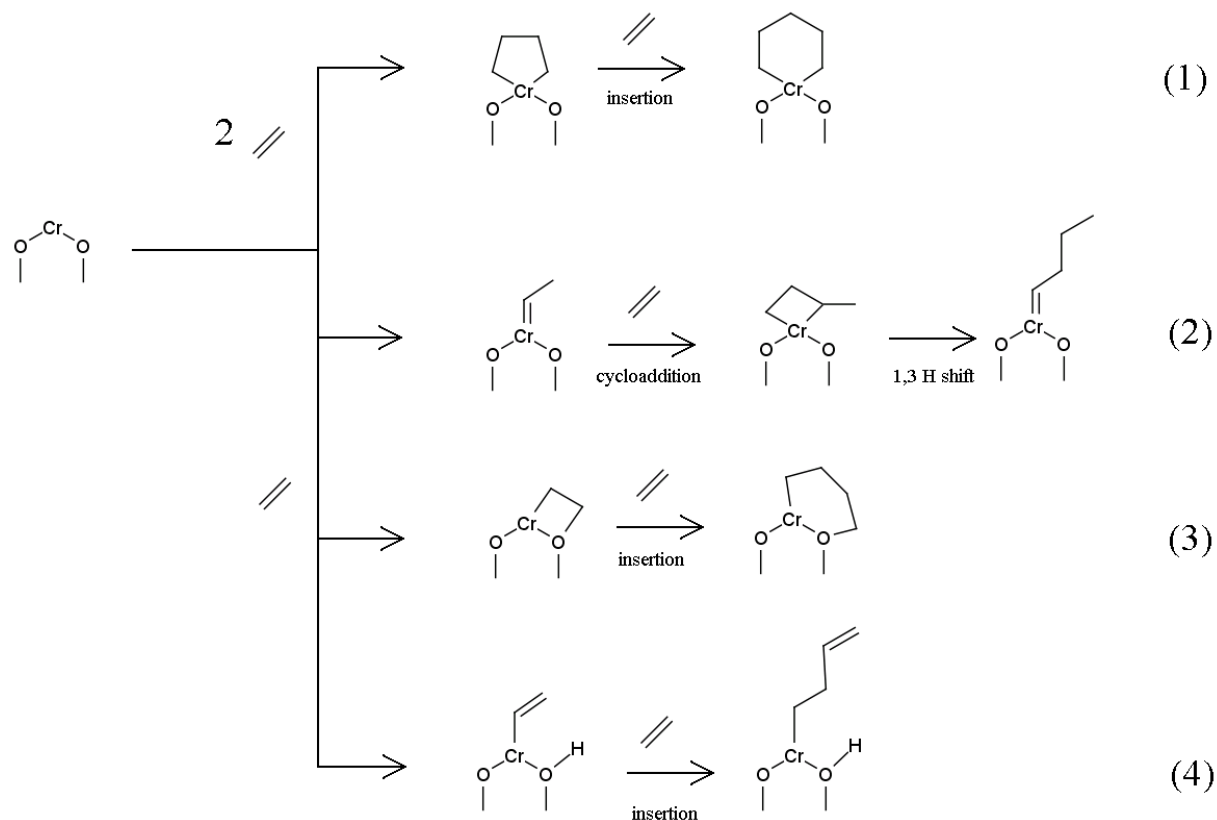
Figure 2.3. Various proposed propagation mechanisms for the Phillips Catalyst. (1) Metallacycle; polymer grow as a ring when ethylene inserts between one of the Cr-C bonds. (2) Alkylidene; ethylene isomerizes into an alkylidene, cycloadds with another ethylene for a substituted metallacycle, which undergoes a 1,3 H shift to reform a alkylidene. (3) Oxachromacycle; polymer ring around Cr-O bond. (4) Allylchromium(μ-OH), chromium is bonded to only one carbon while ethylene inserts in a mechanism similar to the Cossee-mechanism.