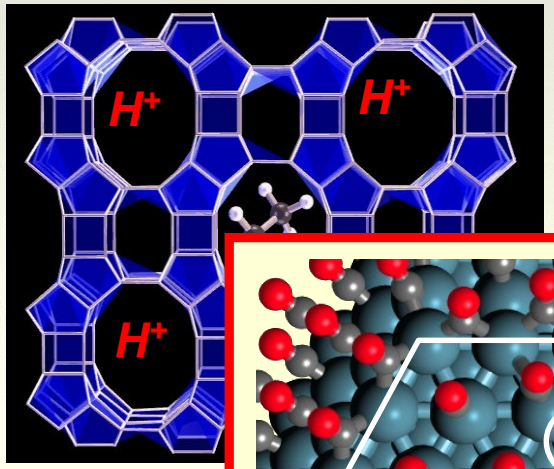
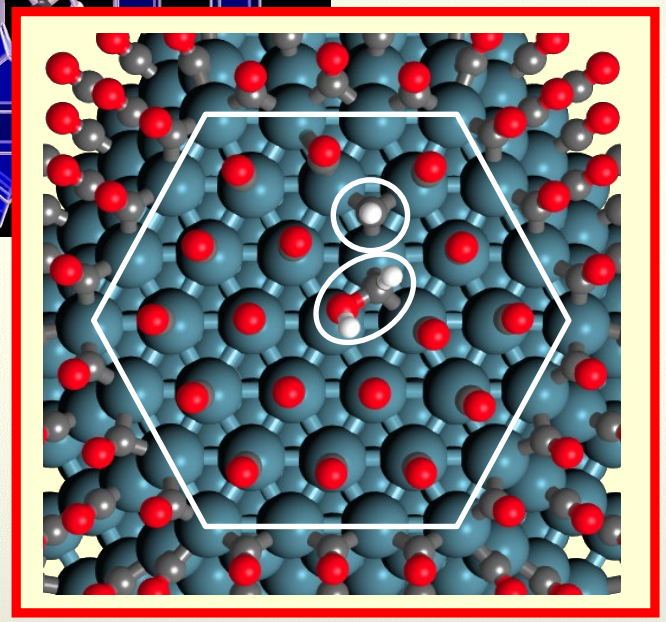
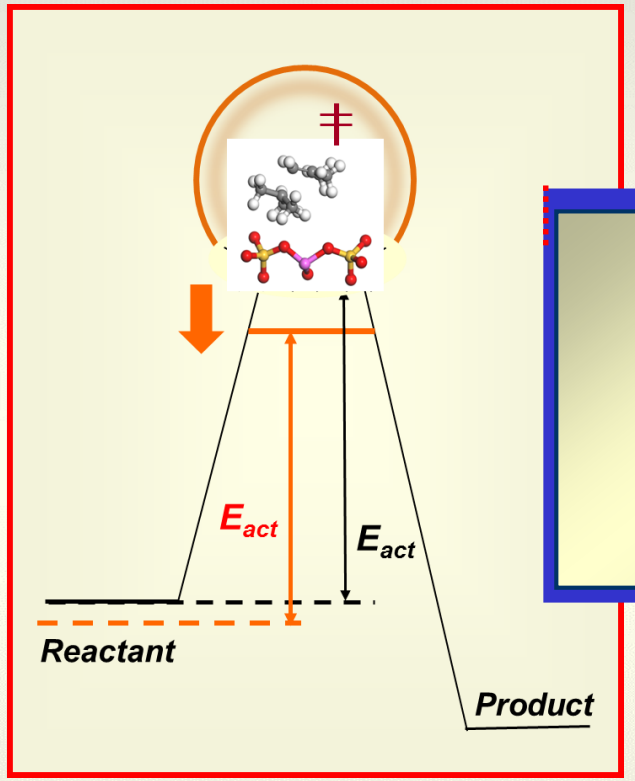
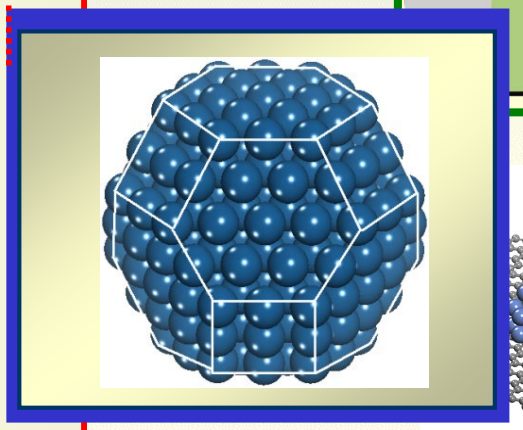
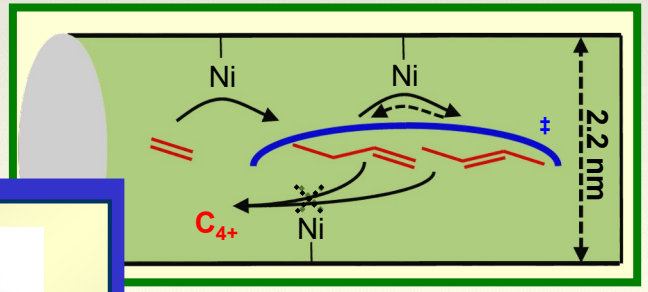
Surface Catalysis Beyond the Binding Site
(…. theory and practice in catalyst design)

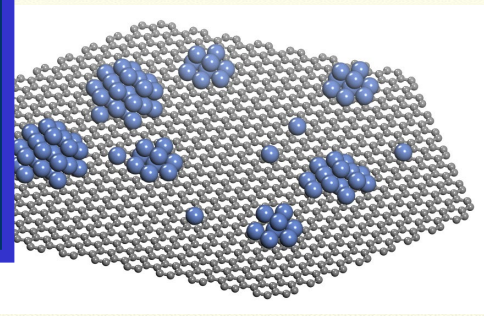












Enrique Iglesia, et al.
University of California at Berkeley

Pregl Colloquium Lecture
National Institute of Chemistry
Ljubljana, Slovenia
18 May 2023

KEMIJSKI INŠTITUT
Kemijski inštitut
Hajdrihova 19, 1000 Ljubljana
www.ki.si

Predavanja

Preglovi kolokviji

Fritz Pregl
The Nobel Prize in Chemistry 1923

Born: 3 September 1869, Laibach, Austria-Hungary (now Ljubljana, Slovenia)

Died: 13 December 1930, Graz, Austria

Affiliation at the time of the award: Graz University, Graz, Austria

Prize motivation: “for his invention of the method of micro-analysis of organic substances”

Catalysts everywhere …… with binding centers and some surroundings

A cigar lighter (1823)

Hydrogenation of fats/oils (1900)

Nitrogen fixation (ammonia synthesis) (1910)

Clean/efficient fuels (fossil/biogenic)

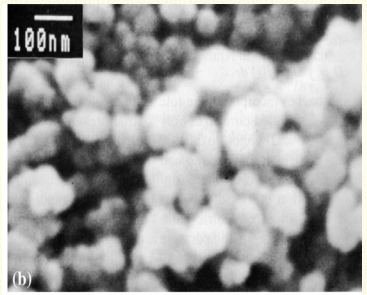
Hydrogen production

Emissions control *Environmental remediation*

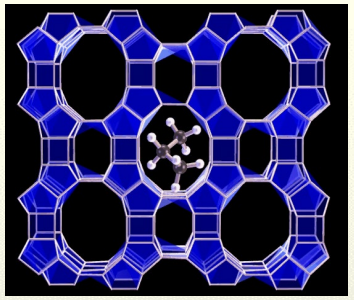
Fuel cells *Polymer synthesis*

Biological catalysts (enzymes)

Porous solids

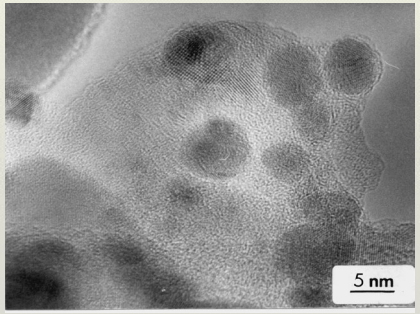


Zeolites



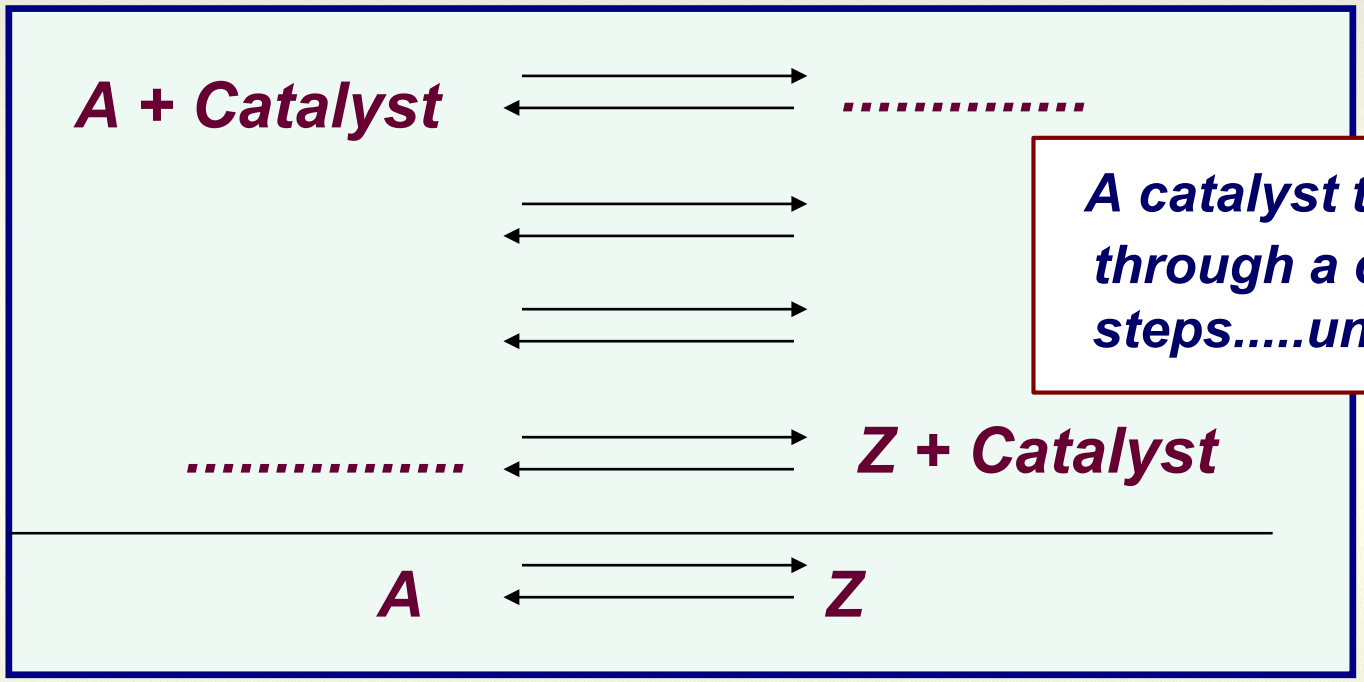
Metal-organic frameworks

Metal/oxide clusters/nanoparticles



Tailoring the binding center and its environment…..

Catalysts everywhere …… with a binding center and some surroundings

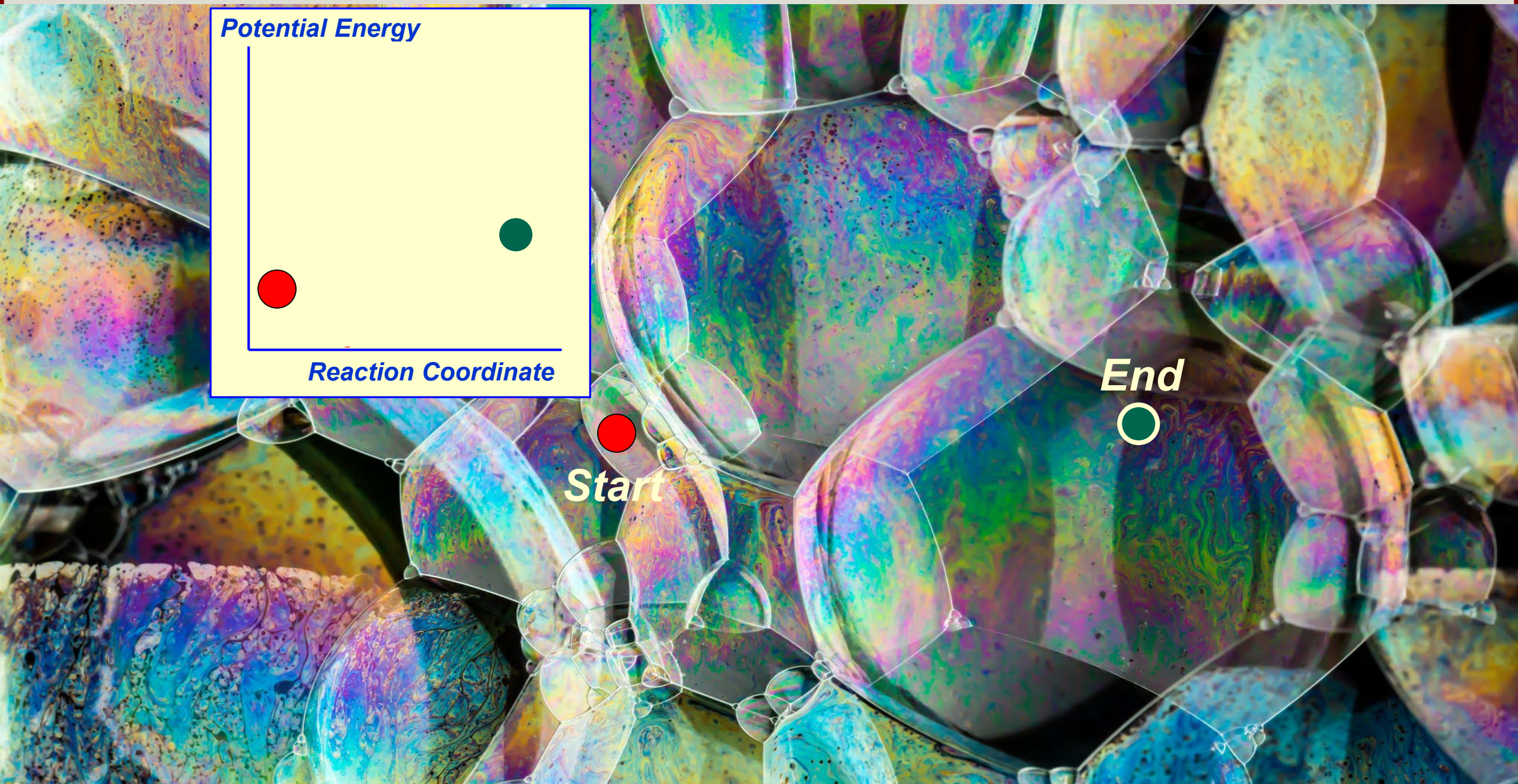


A catalyst transforms reactants into products through a cycle of ("smaller") elementary steps.....until the last step regenerates the catalyst

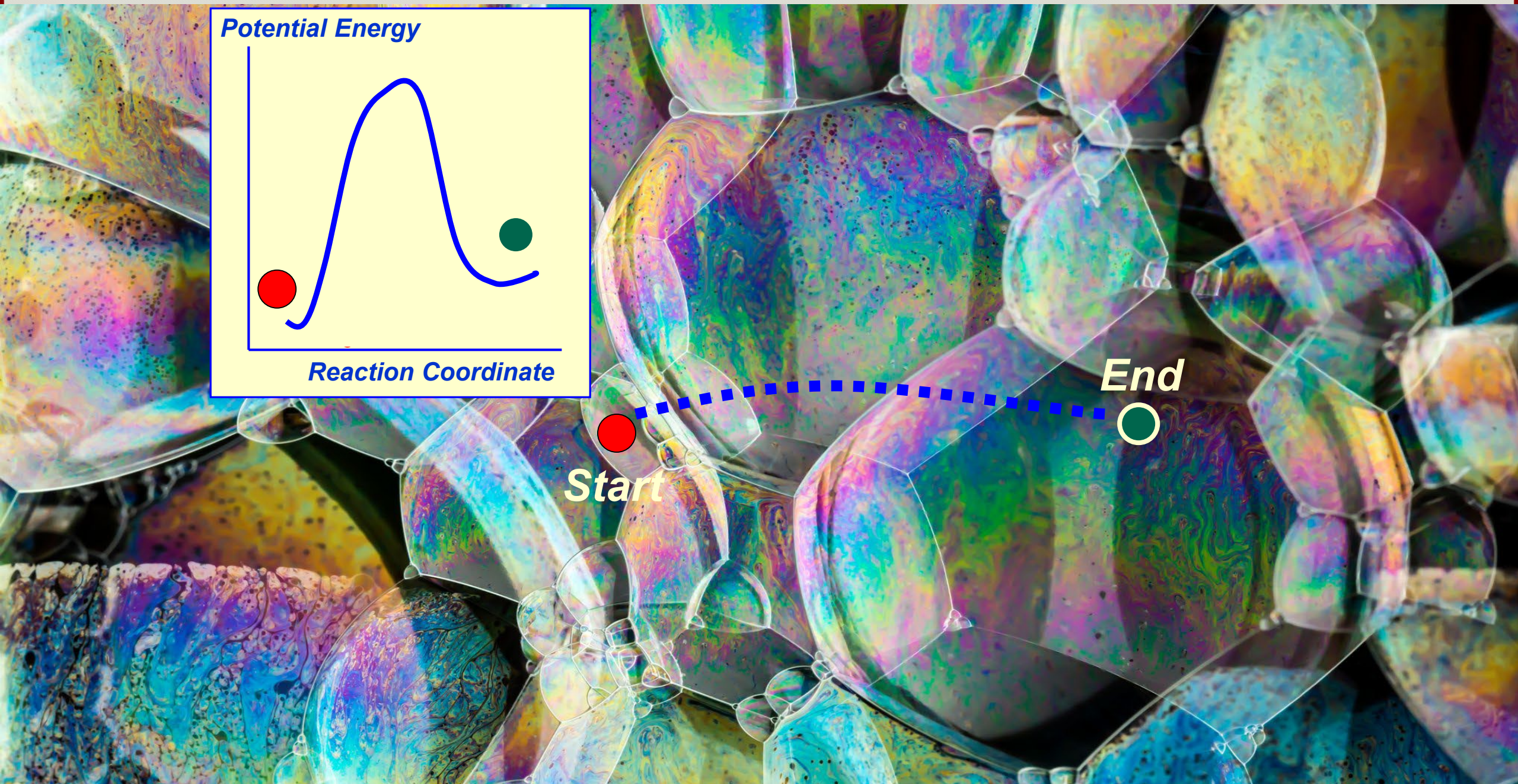
Tailoring the binding center and its environment…..

(1 October 2022) Rocky Mountain National Park

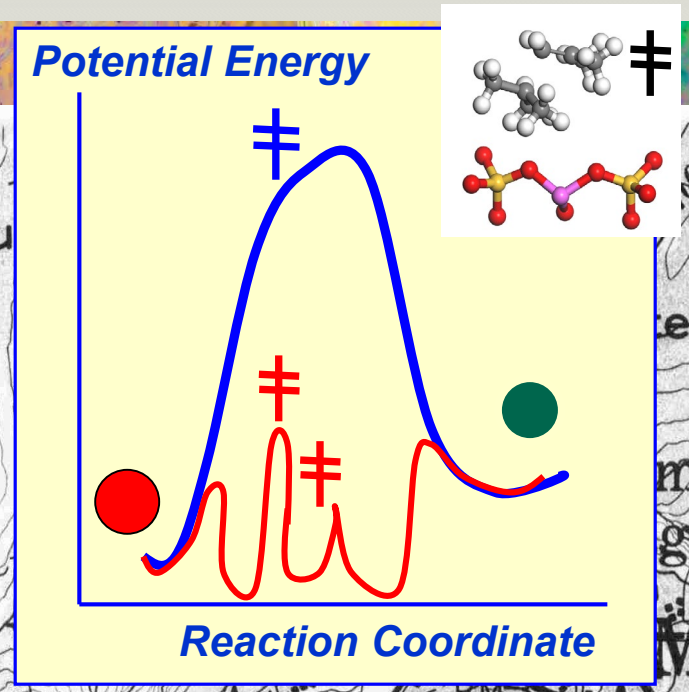
Surface catalysis …. channeling molecules through energy landscapes



Surface catalysis …. channeling molecules through energy landscapes



Surface catalysis …. channeling molecules through energy landscapes



……. staring at transition states

Start

End

Basket Dome

Quarter Domes

North Dome

Mirror Lake

Half Dome

Snow Cr

Tenaya

Sunrise

Little Yosemite Valley

Liberty Cap

Merced

Nevada Fall

Vernal Fall

Gaging Sta

Glacier Pt

Sentinel Rock

Sentinel Dome

Panorama Cliff

Starr King Lake

Profile Cliff

Taft

Camp Curry

Valley

BM 3980

BM 4094

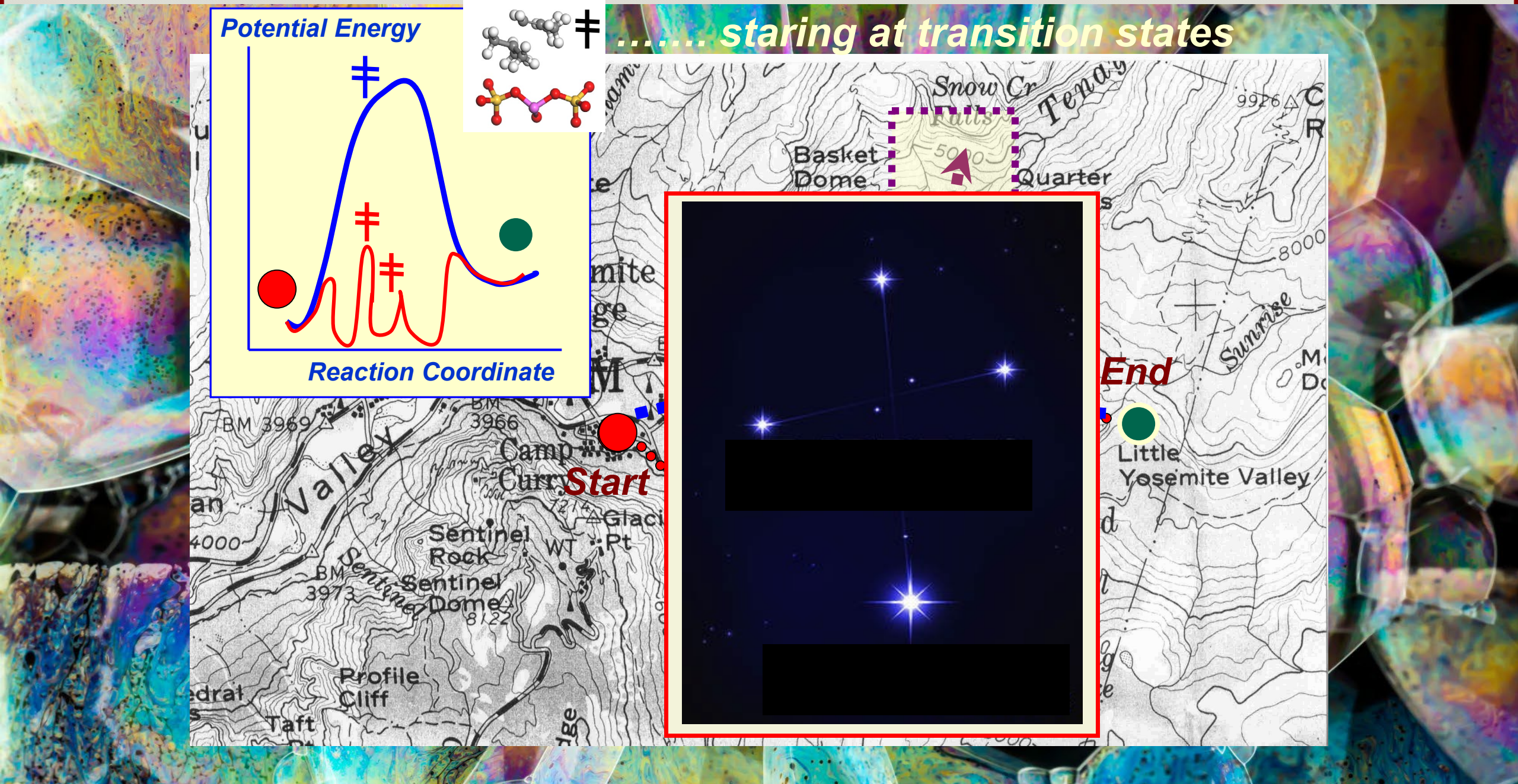
BM 3969

BM 3966

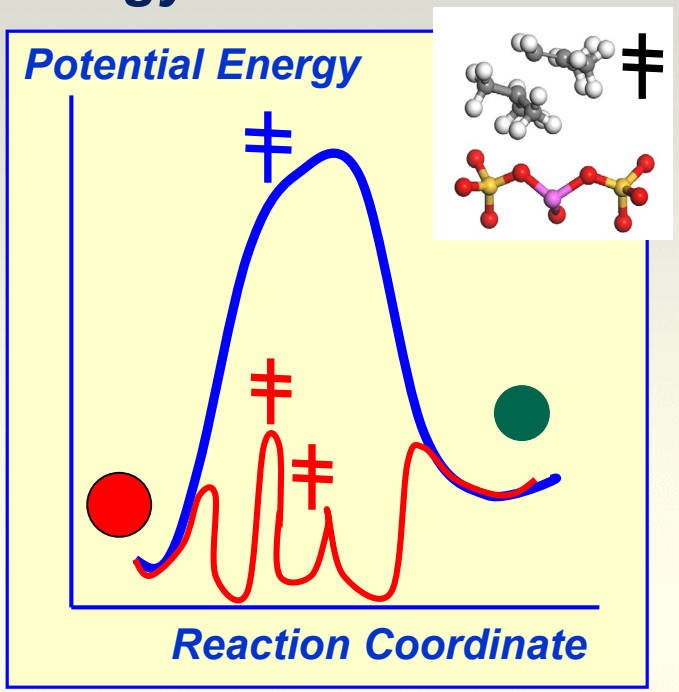
BM 3973

WT

Surface catalysis …. channeling molecules through energy landscapes



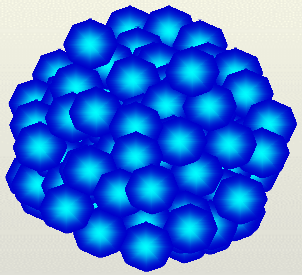
…. the energy dialects of molecules … as they make and break chemical bonds

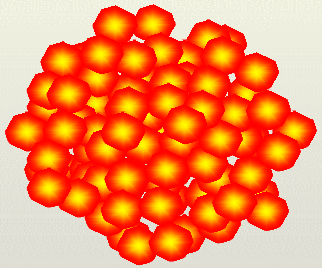


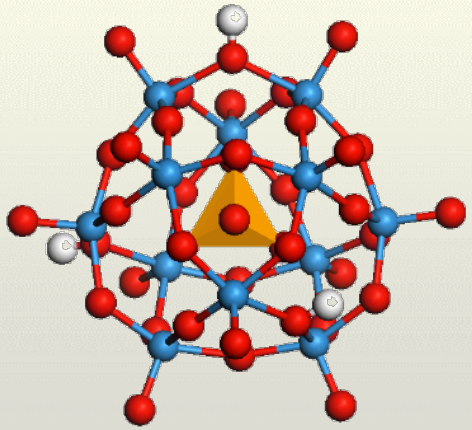
Turnover Rates (per active center)

$$\sim \exp\left(-\Delta G^{\ddagger}/k_B T\right) \cdot f(C_i)$$

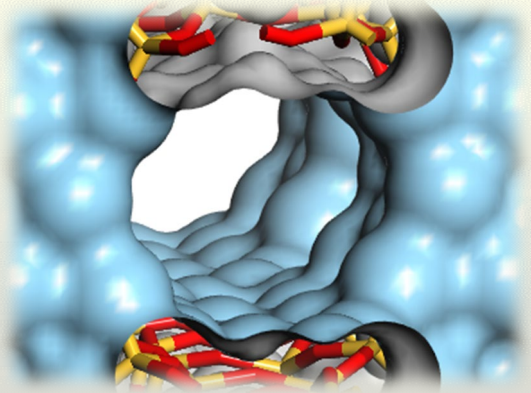
Active centers (metal atoms, active O-atoms, protons)



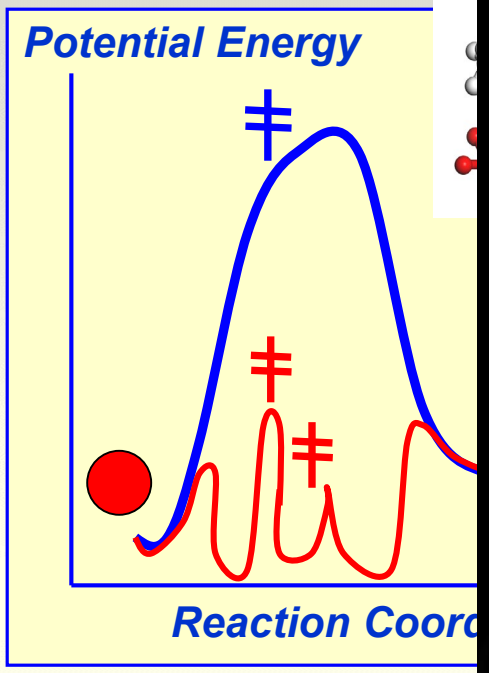


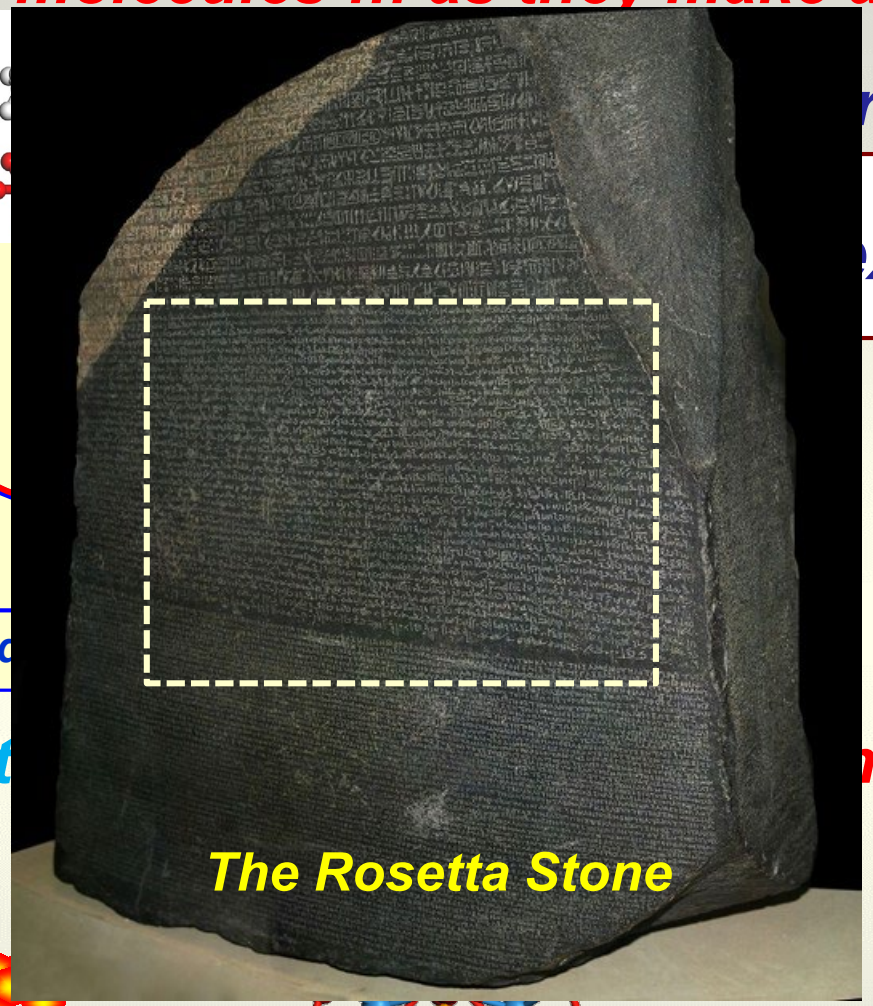


Voids



…. the energy dialects of molecules … as they make and break chemical bonds

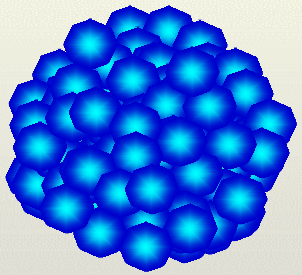


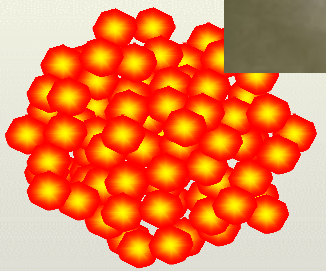


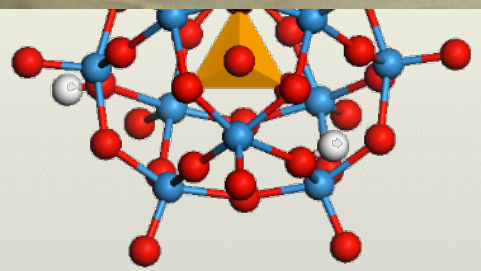
r Rates (per active center)

$$\exp(-\Delta G^{\ddagger}/k_B T) \cdot f(C_i)$$

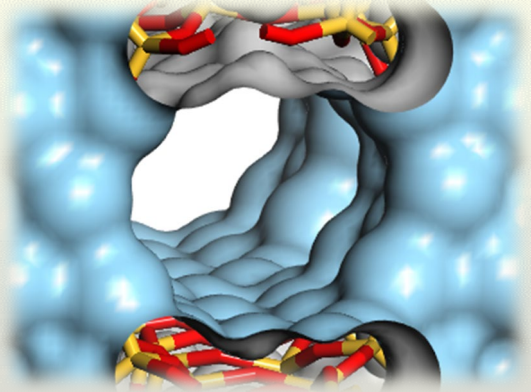
Active centers (metal at … ns)



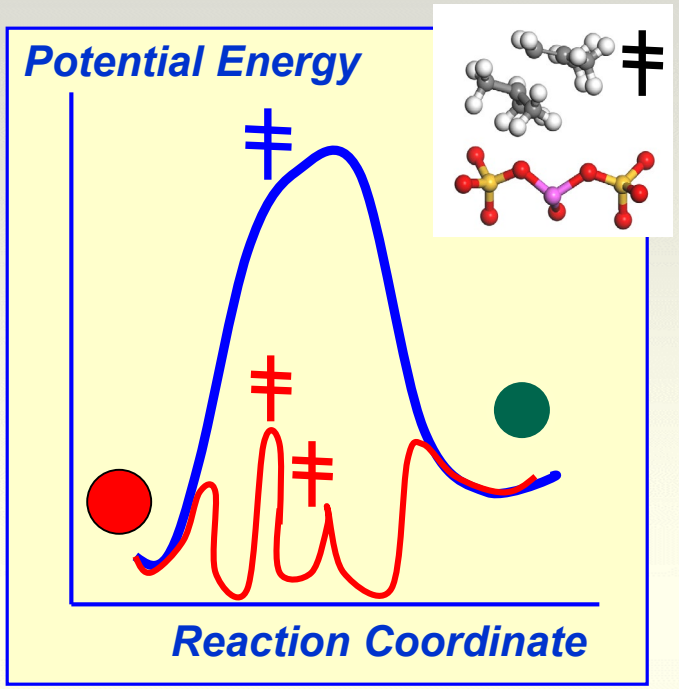




Voids



We are experimentalists abetted by theory ….

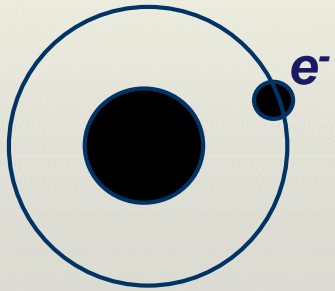


Turnover Rates (per active center)

$$\sim \exp(-\Delta G^{\ddagger}/k_B T) \cdot f(C_i)$$

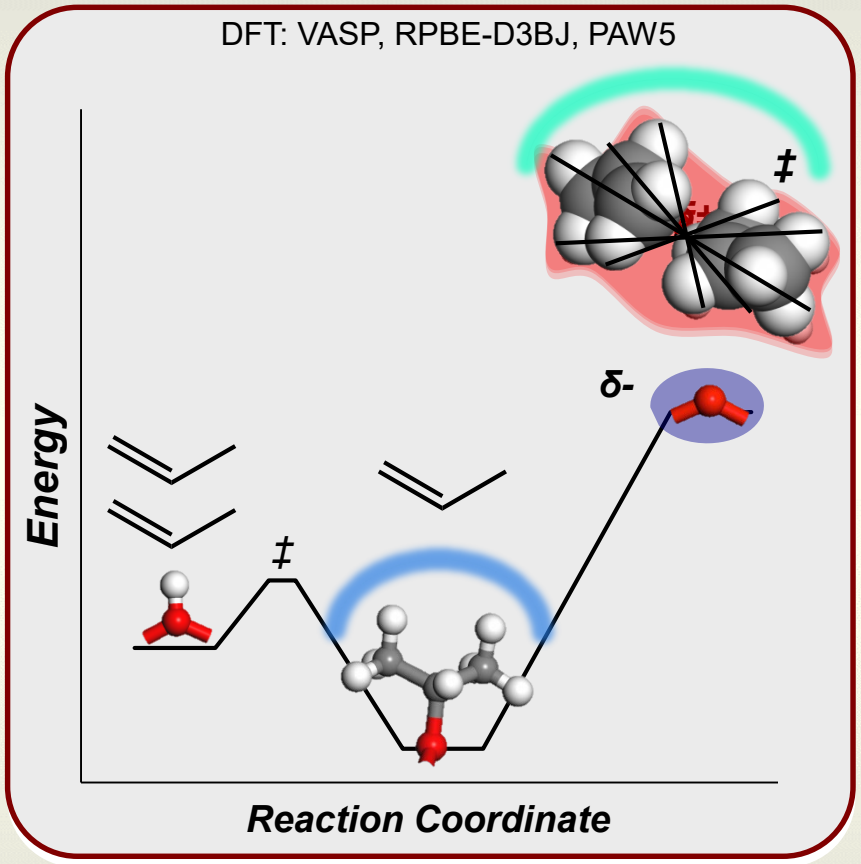
Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$



Things like this will appear throughout …..

Reaction coordinate diagrams

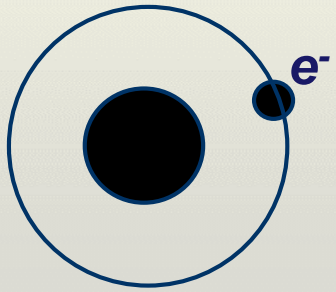


Turnover Rates (per active center)

$$\sim \exp\left(-\Delta G^{\ddagger}/k_B T\right) \cdot f(C_i)$$

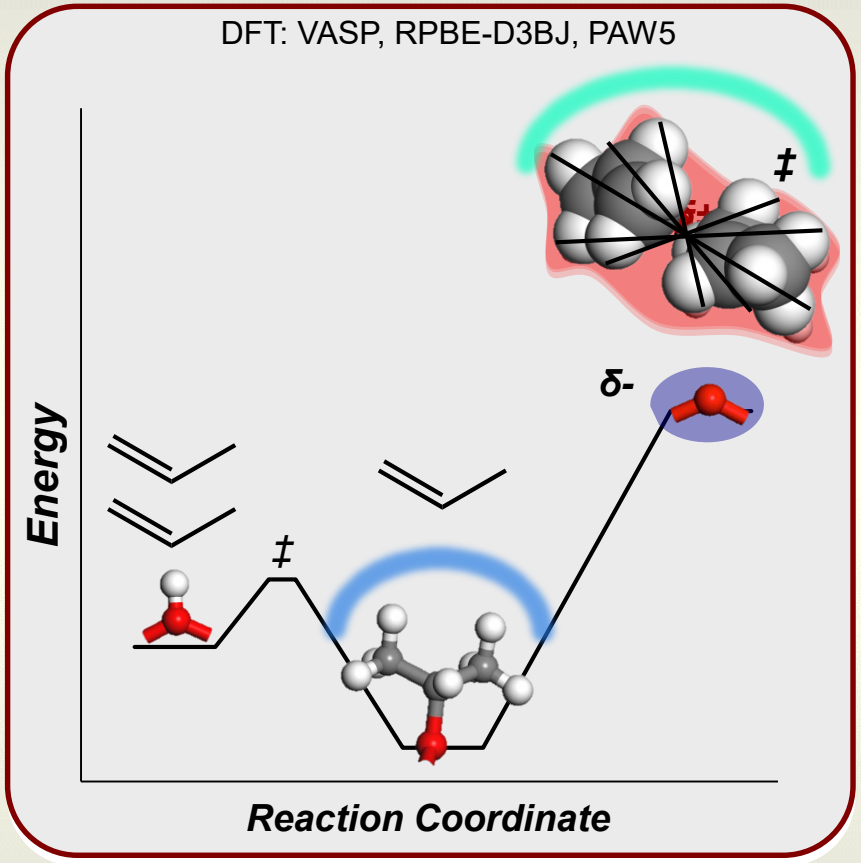
Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$



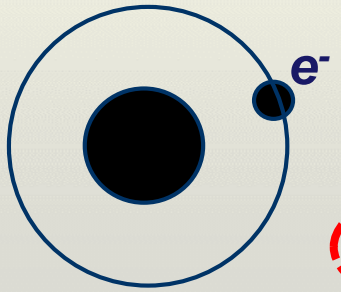
Things like this will appear throughout …..

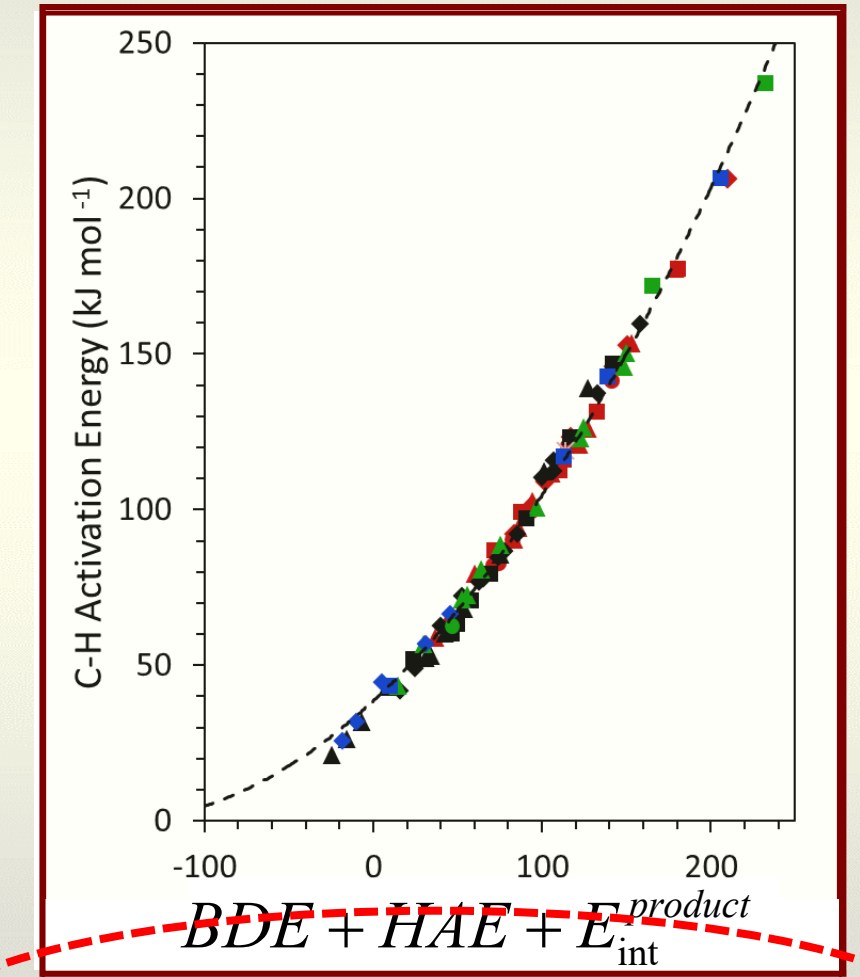
Reaction coordinate diagrams



Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

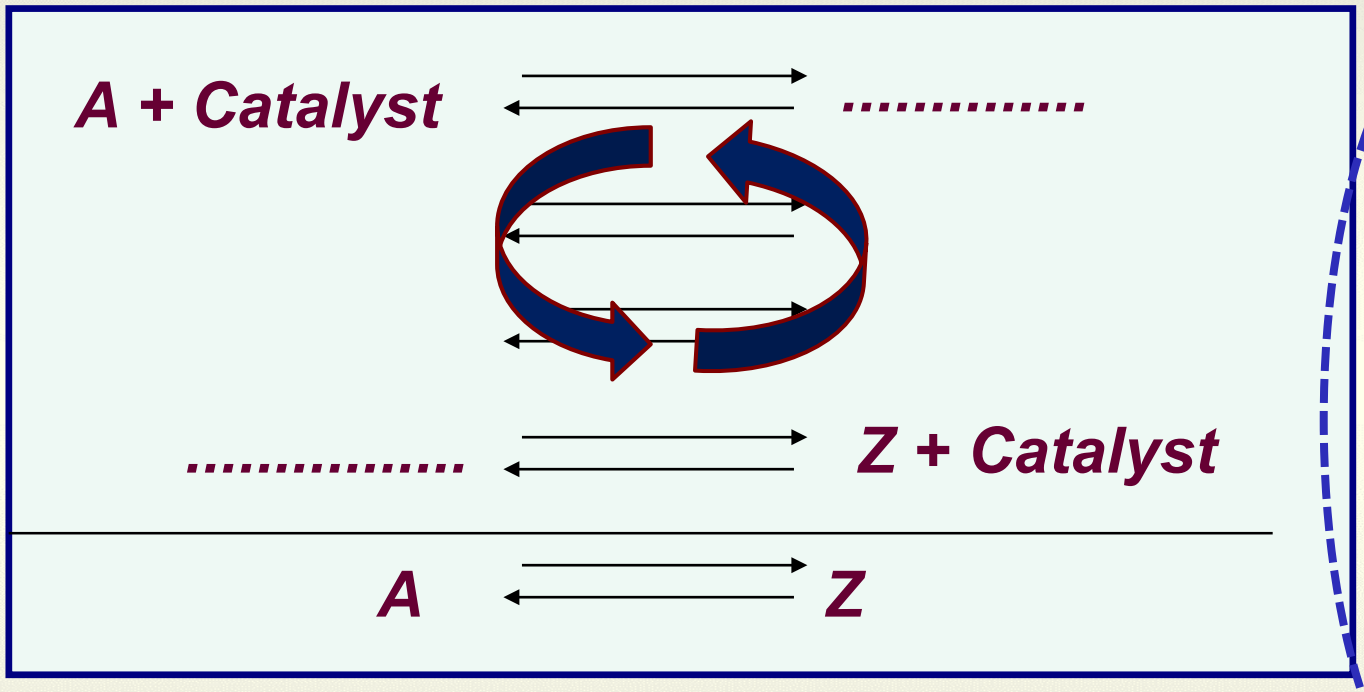


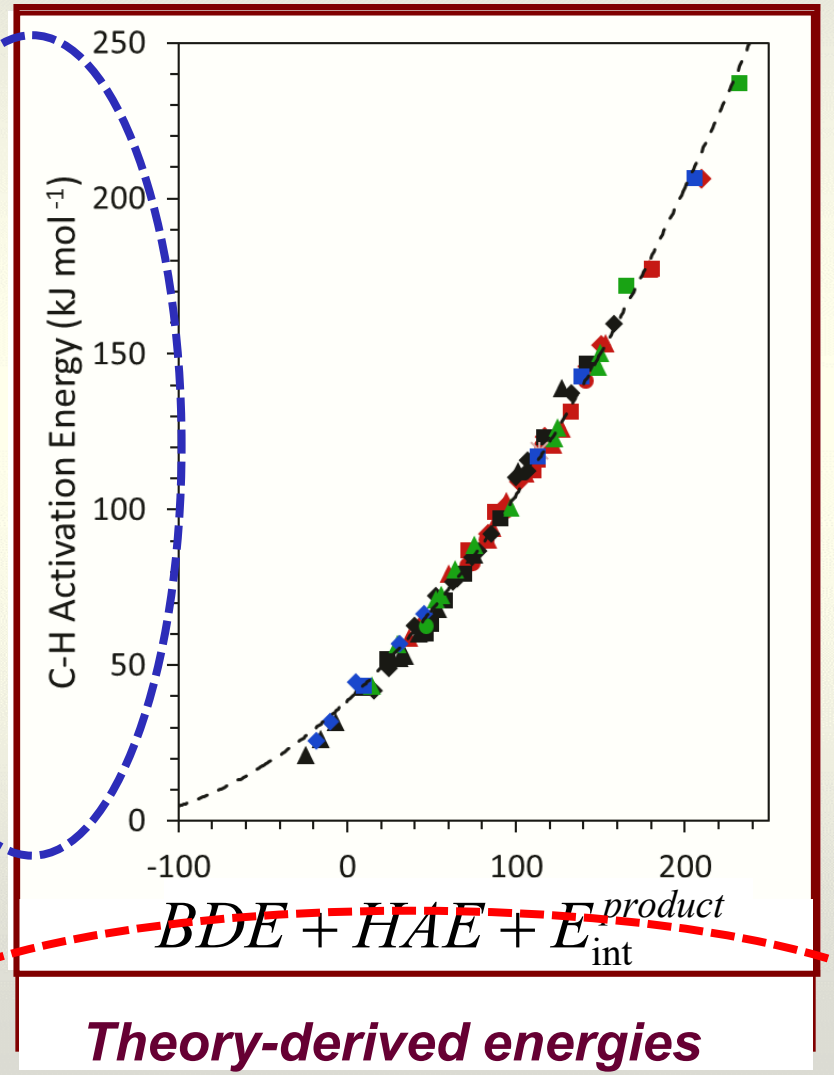


Theory-derived energies

Things like this will appear throughout …..

Experimental inquiries into chemical dynamics ….
and the identity and kinetic relevance of bound species and elementary steps

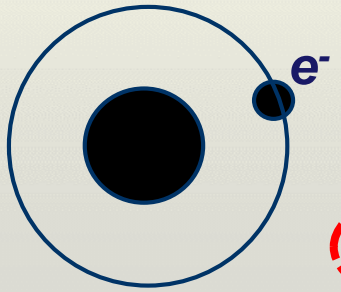




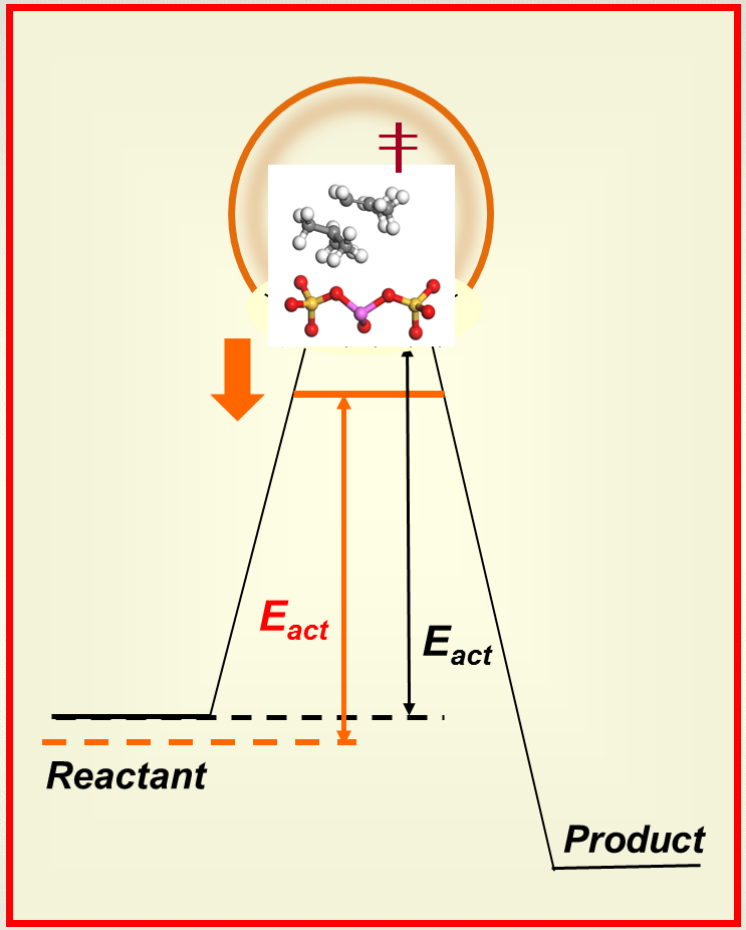
Theory-derived energies

Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$



Surface catalysis …. channeling molecules through energy landscapes



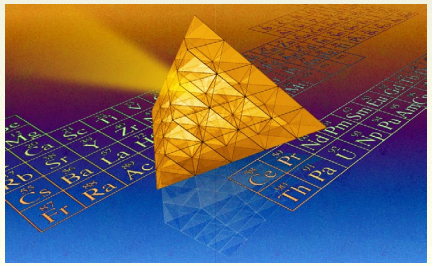
Design and construct binding sites <u>and</u> environments that lower the mountain passes among specific valleys

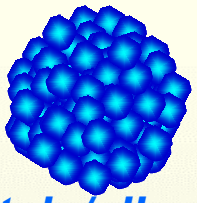
Surface catalysis …. channeling molecules through energy landscapes

Construct and probe specific "binding points"

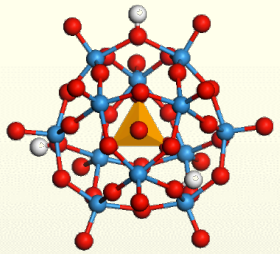
Design solvating environments around "binding points"

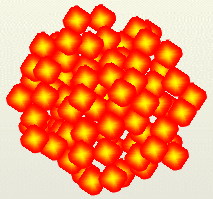
……. the periodic table



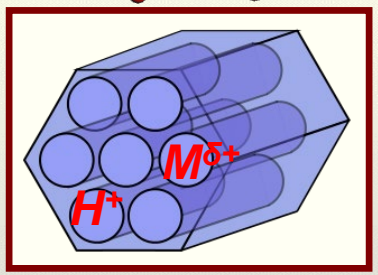


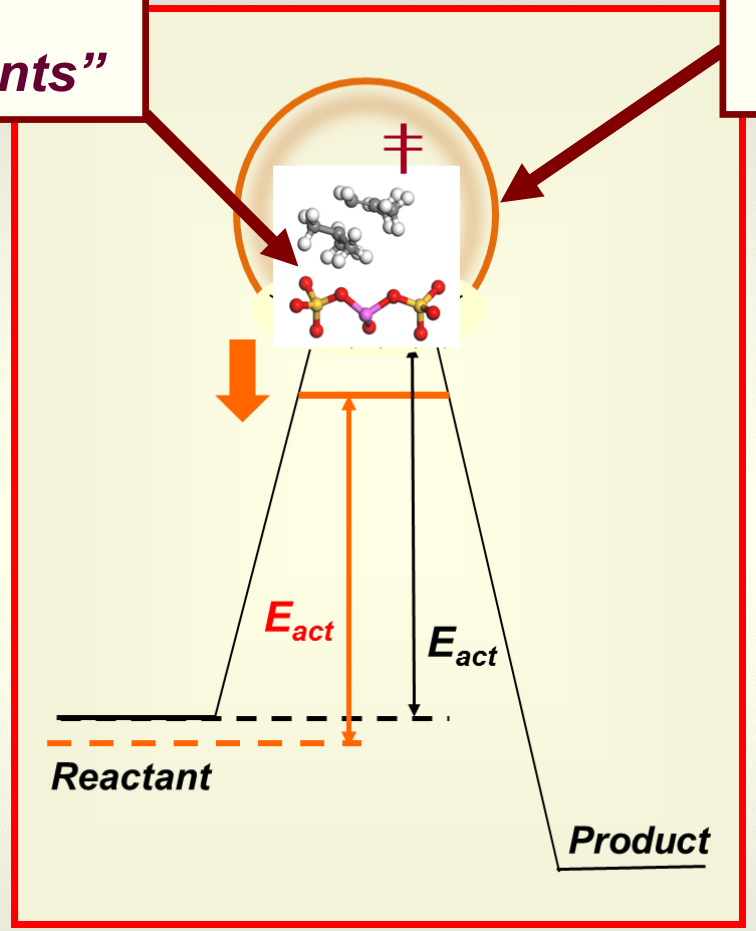
metals/alloys

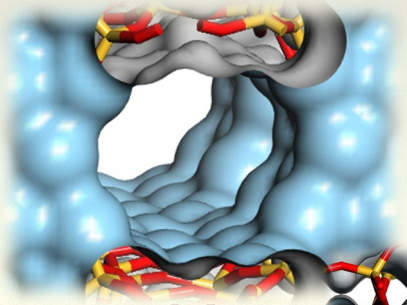




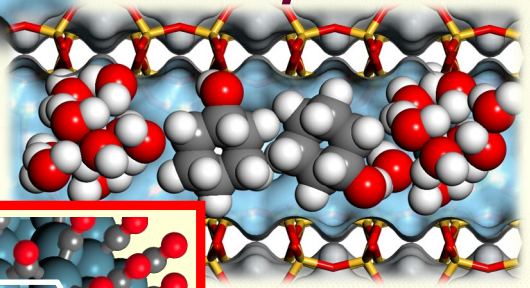
oxides, sulfides ..



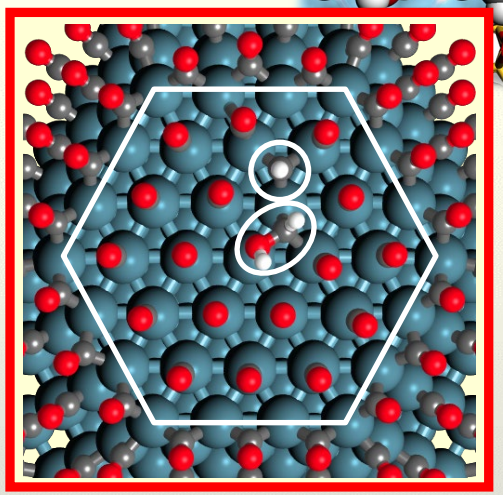




voids



liquids

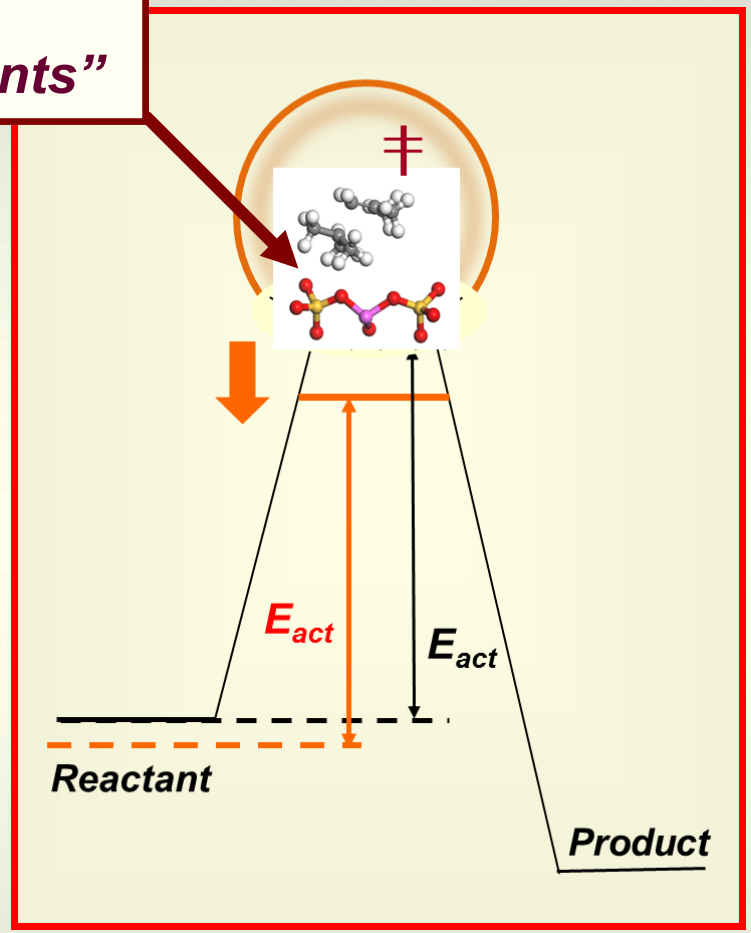


dense adlayers

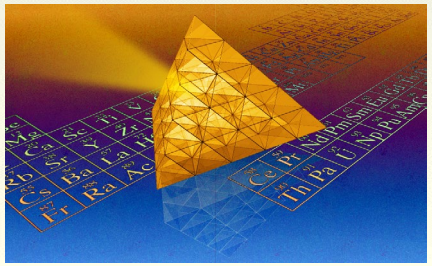
Design and construct binding sites <u>and</u> environments that lower the mountain passes among specific valleys

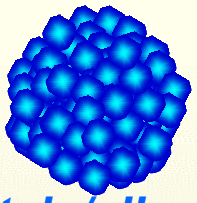
Surface catalysis …. channeling molecules through energy landscapes

Construct and probe specific "binding points"

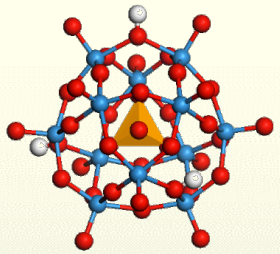


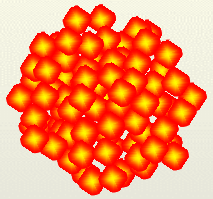
……. the periodic table



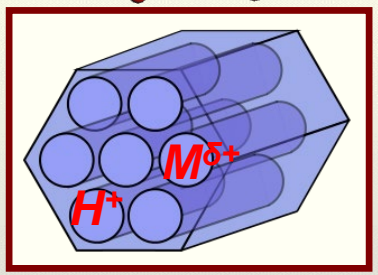


metals/alloys





oxides, sulfides ..

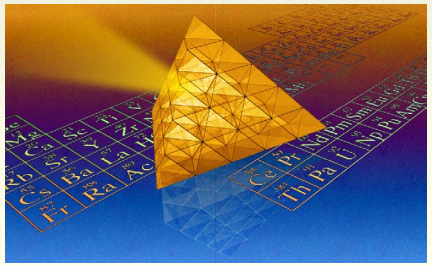


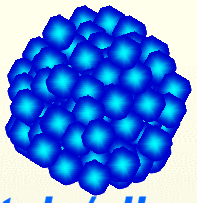
Design and construct binding sites <u>and</u> environments that lower the mountain passes among specific valleys

Surface catalysis …. channeling molecules through energy landscapes

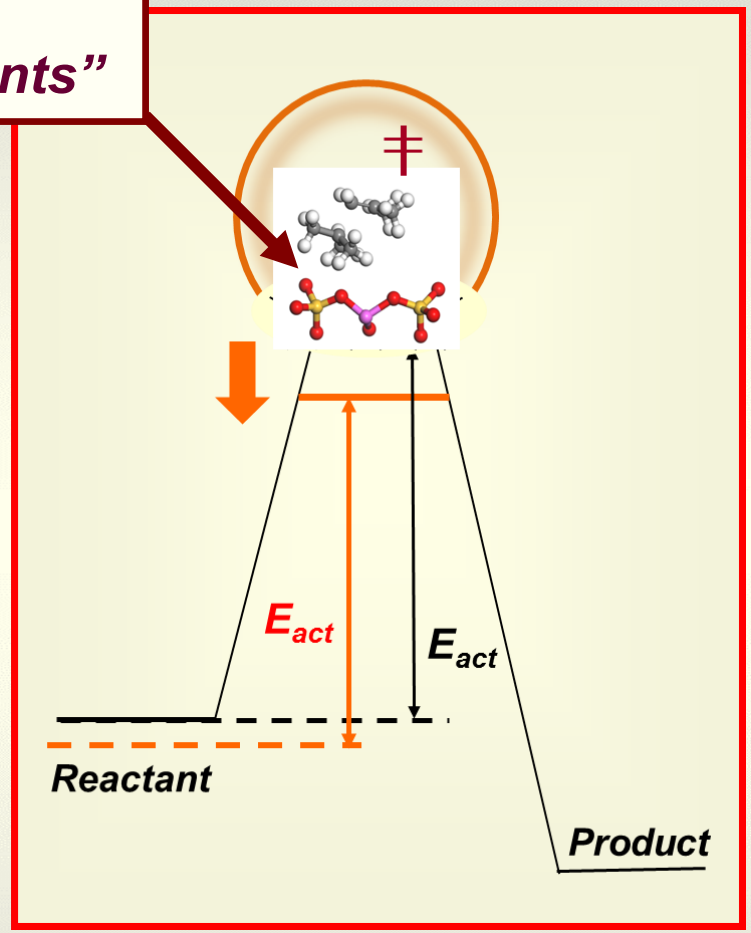
Construct and probe specific "binding points"

……. the periodic table





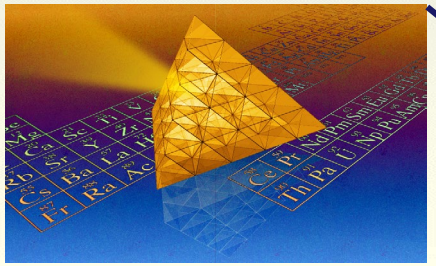
metals/alloys

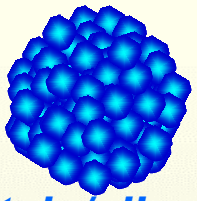


Design and construct binding sites <u>and</u> environments that lower the mountain passes among specific valleys

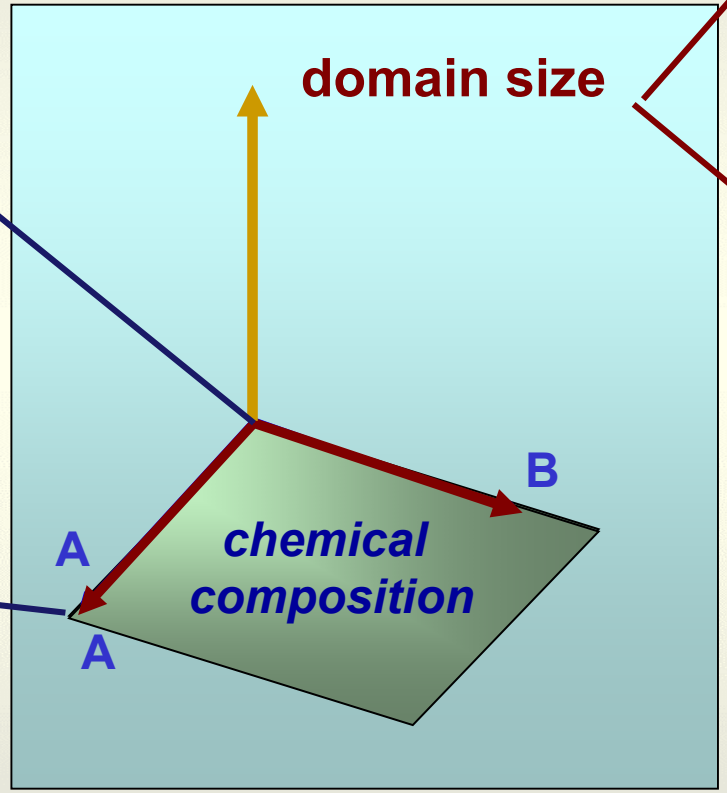
…. metal nanoparticles (and their size) in catalysis……

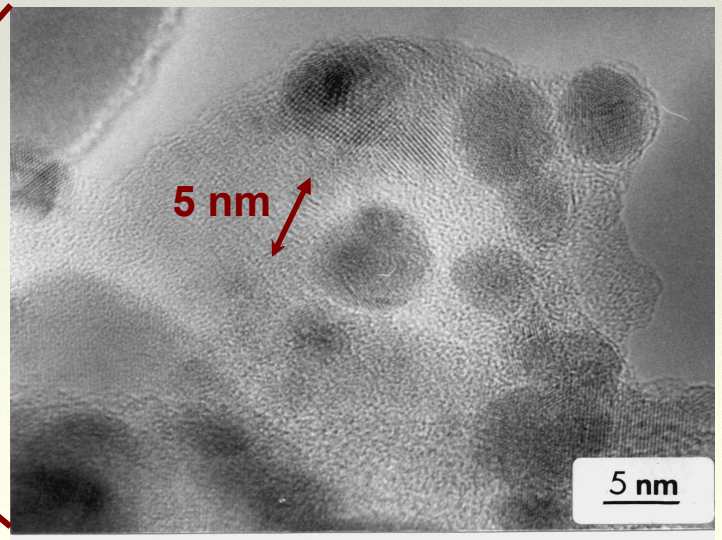
……. the periodic table



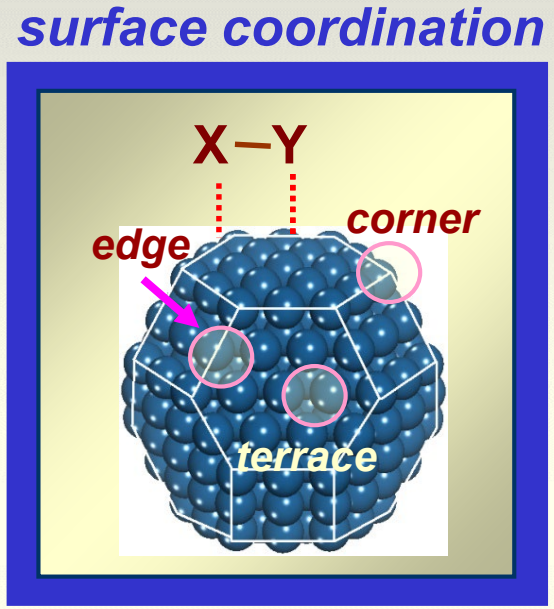


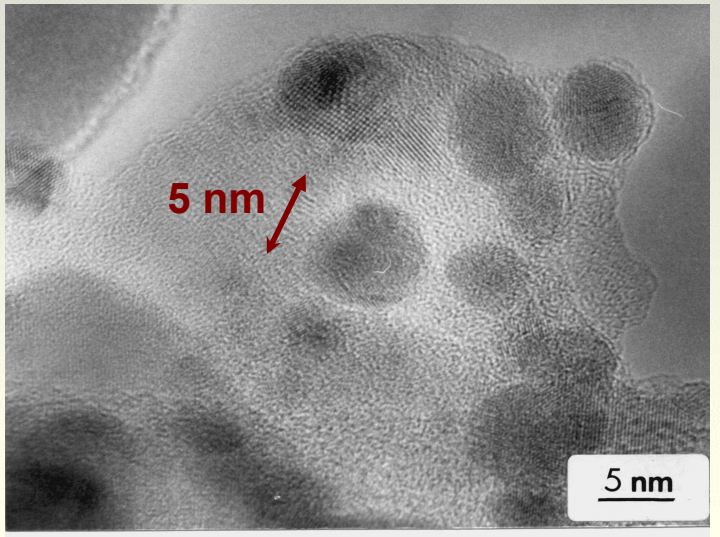
metals/alloys



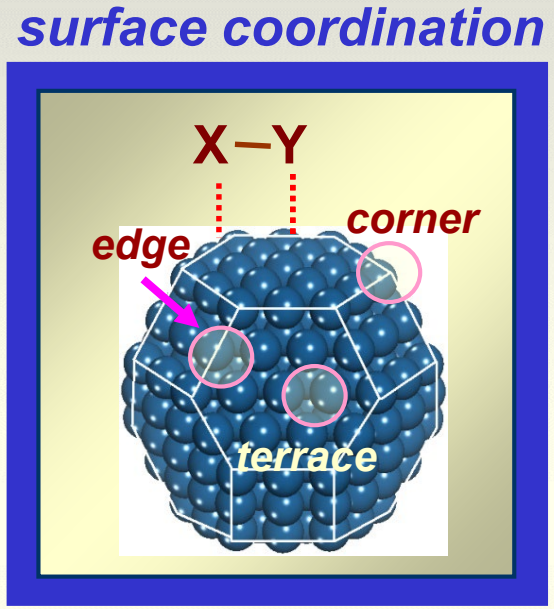


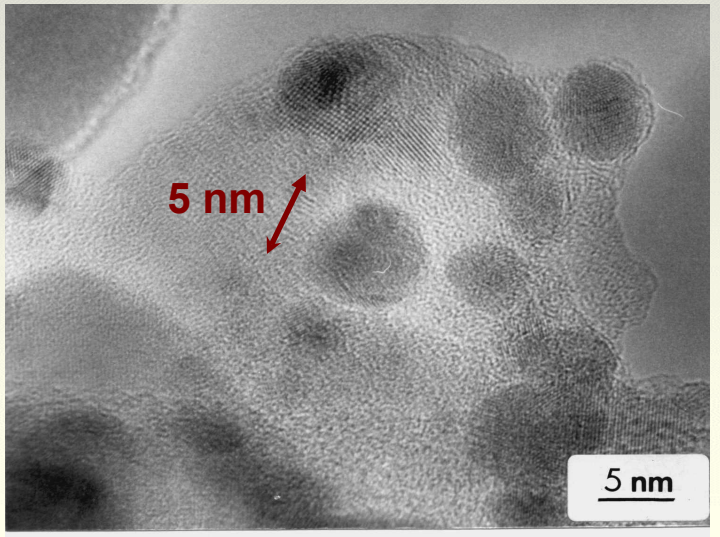
…. metal nanoparticles (and their size) in catalysis……

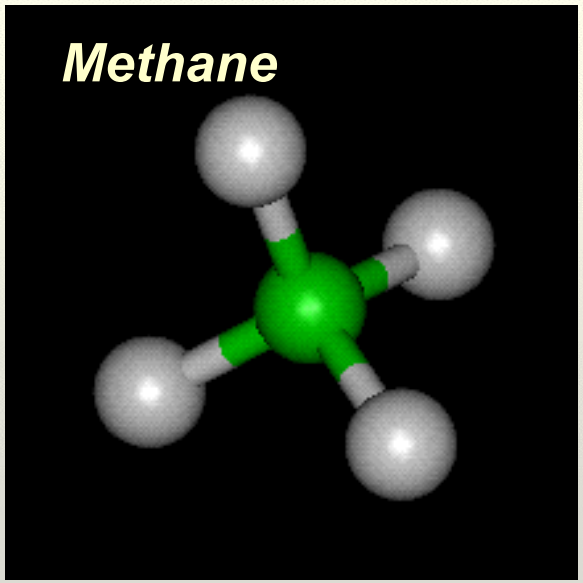




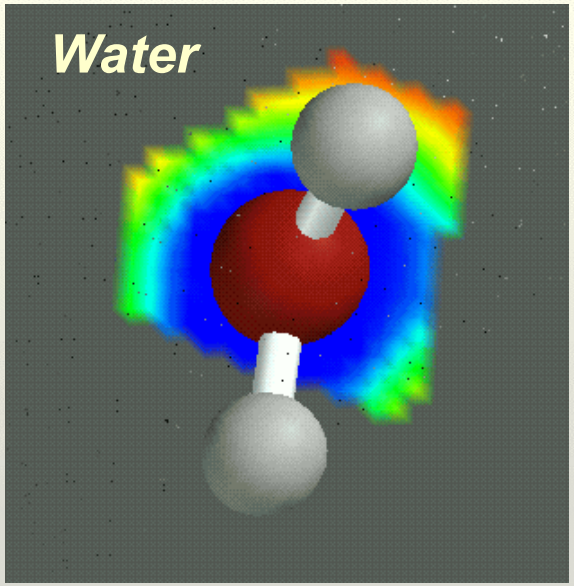
…. metal nanoparticles (and their size) in catalysis……

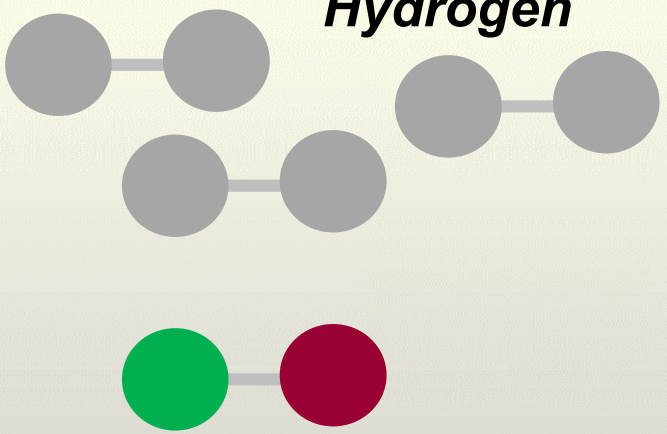






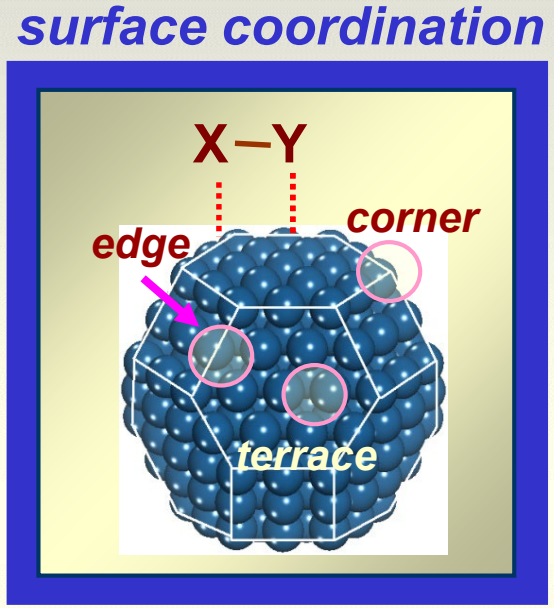
+

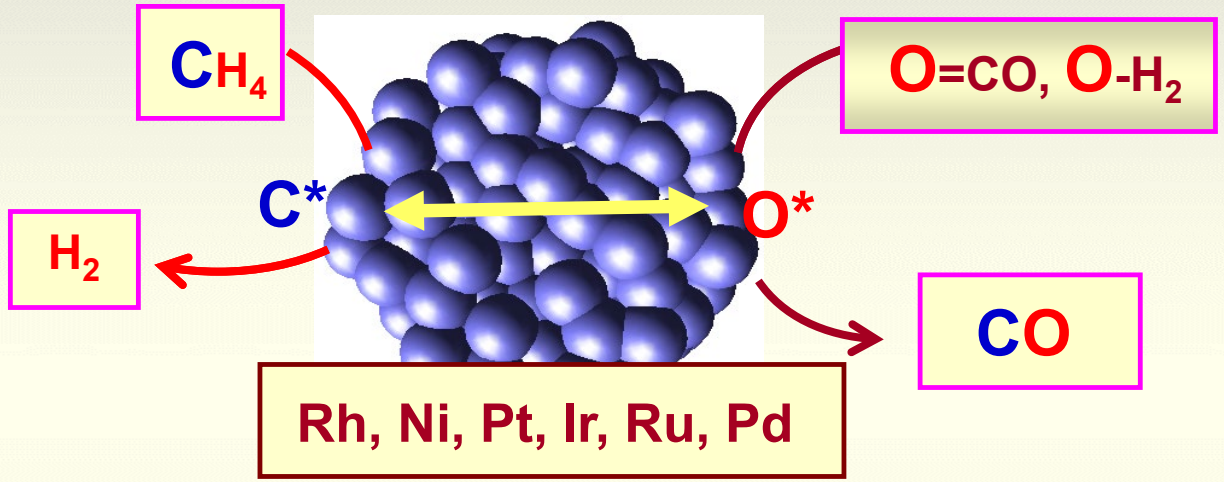


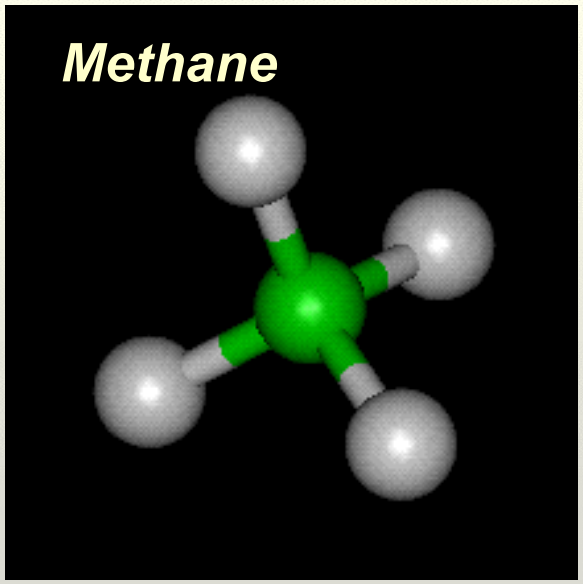


…. metal nanoparticles (and their size) in catalysis……

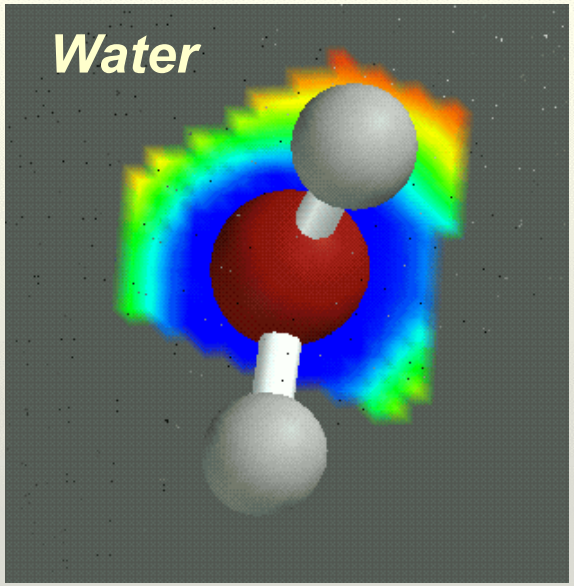
Junmei Wei

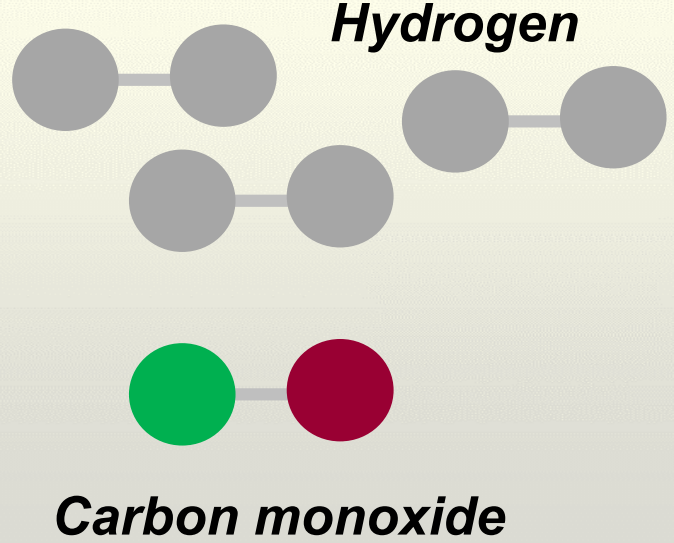






+

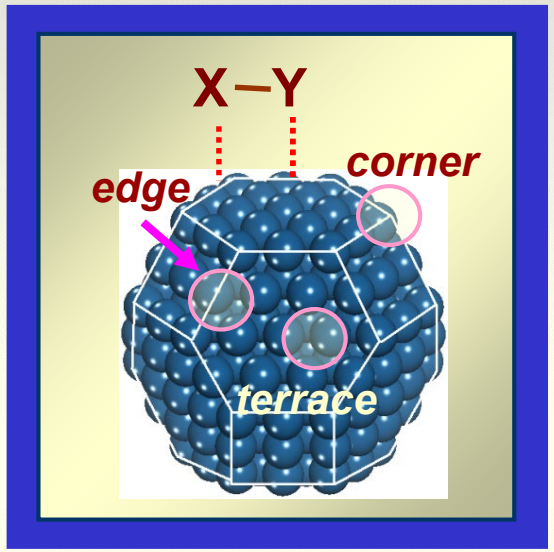




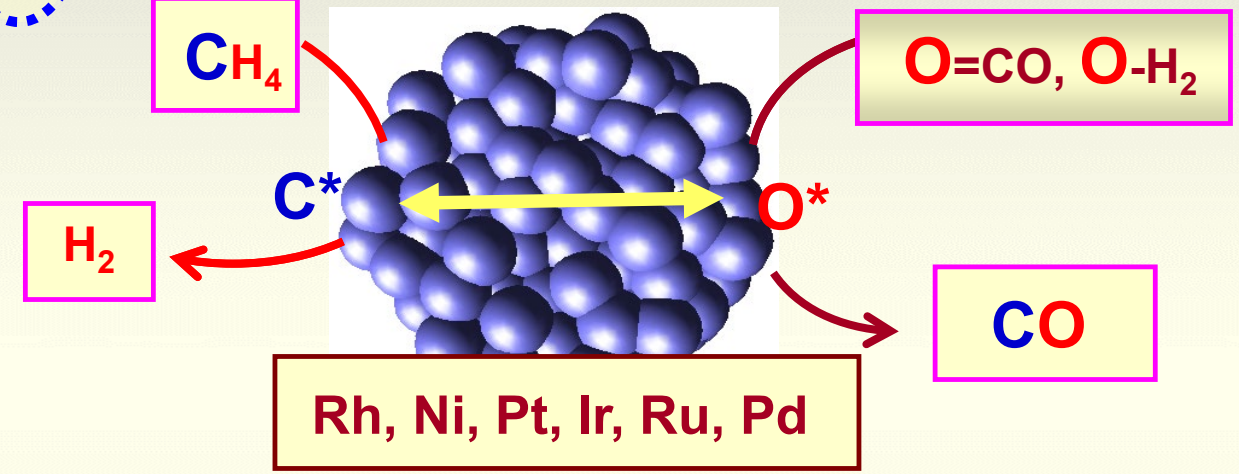
…. metal nanoparticles (and their size) in catalysis……

Junmei Wei

surface coordination



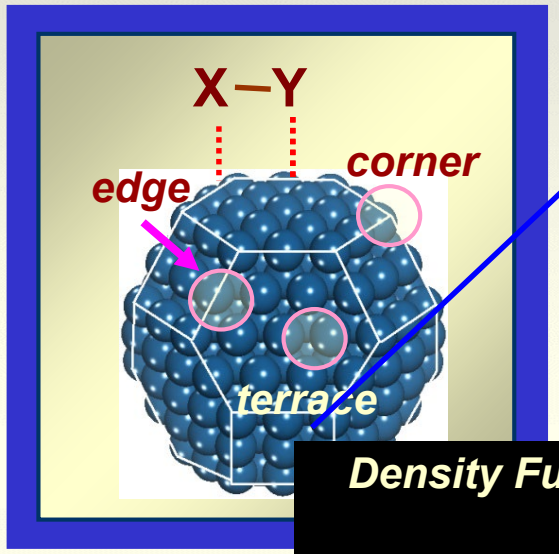
$r = k_{C\text{-}H}(CH_4)$



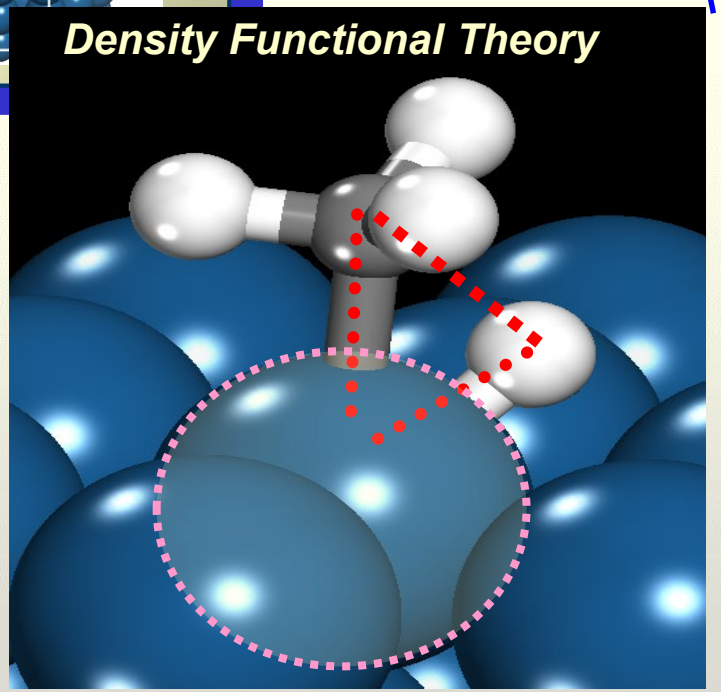
…. metal nanoparticles (and their size) in catalysis……

Junmei Wei

surface coordination

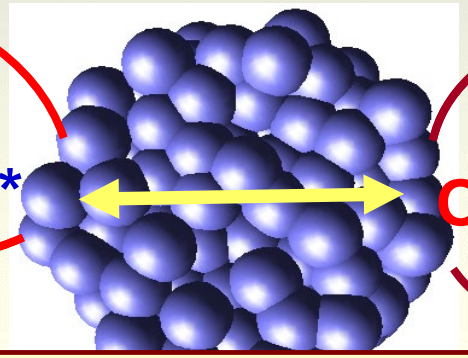


$r = k_{C-H}(CH_4)$



CH_4

H_2



$O{=}CO$, $O{-}H_2$

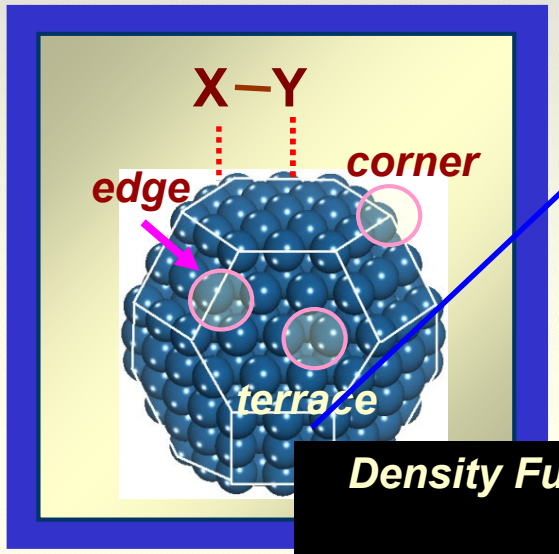
CO

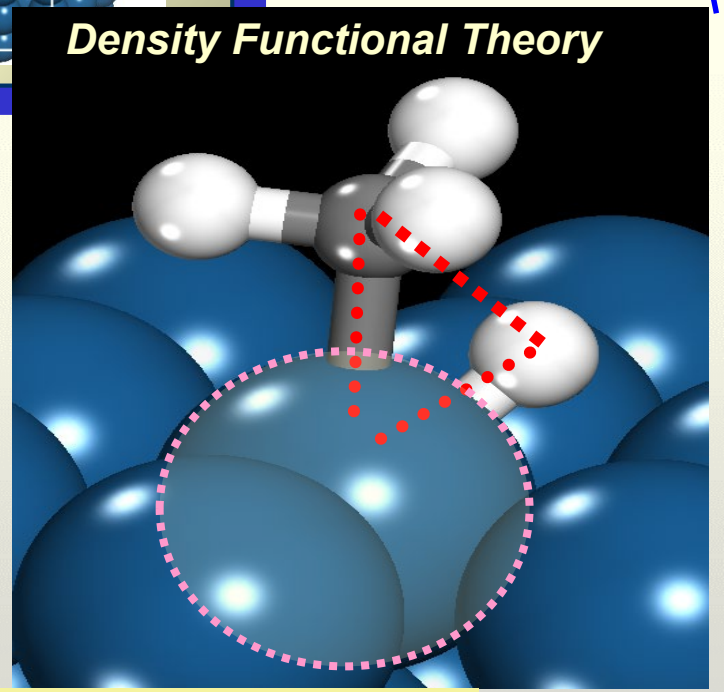
Rh, Ni, Pt, Ir, Ru, Pd

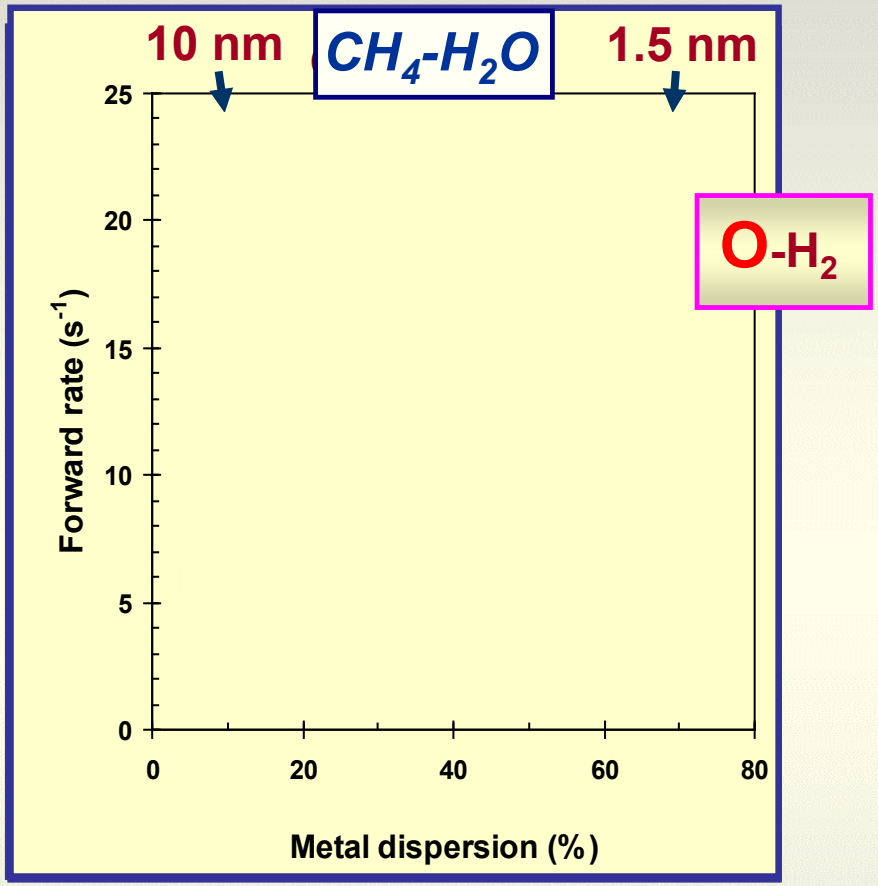
…. metal nanoparticles (and their size) in catalysis……

$r = k_{C\text{-}H}(CH_4)$

surface coordination







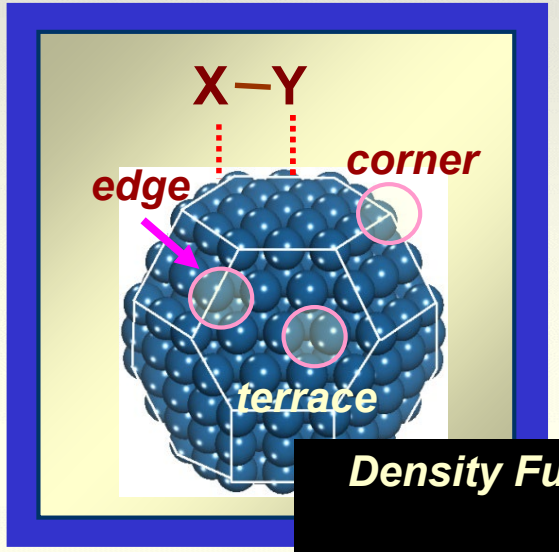
[873 K, 20 kPa CH_4]

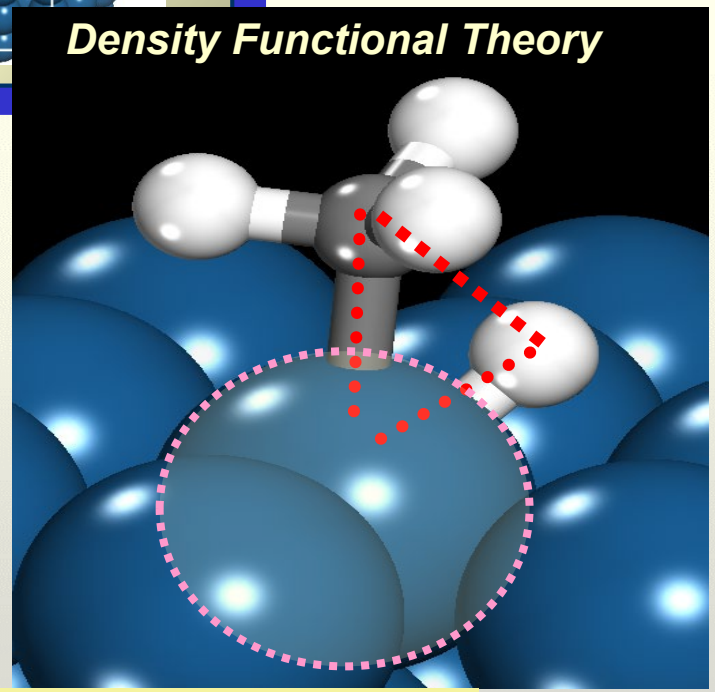
J. Phys. Chem C108 (2004) 4094

Smaller clusters have more (and sharper) edges

.....

surface coordination



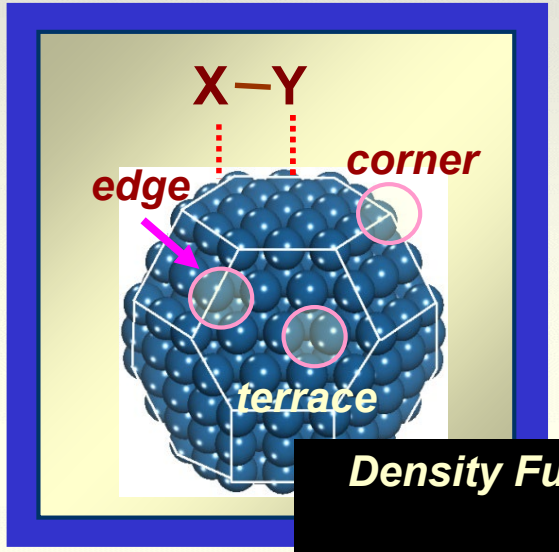


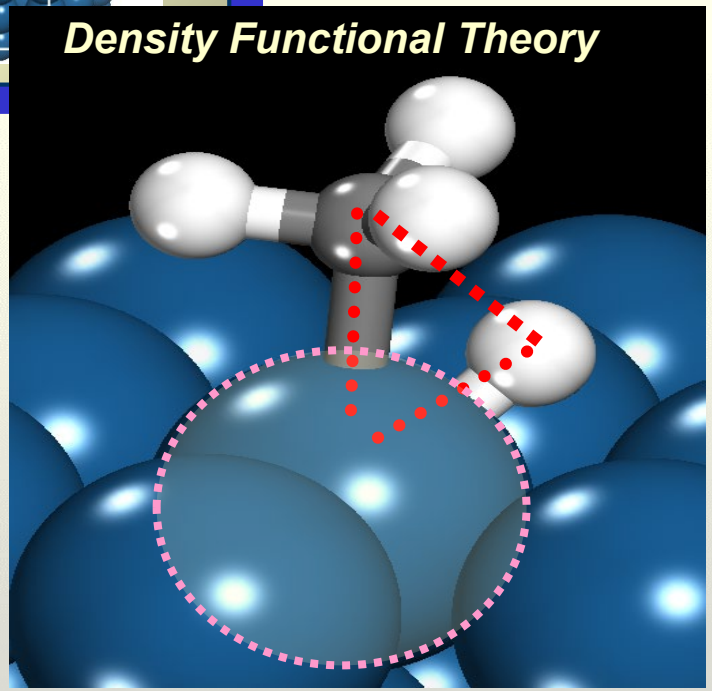
J. Phys. Chem C108 (2004) 4094

Smaller clusters have more (and sharper) edges

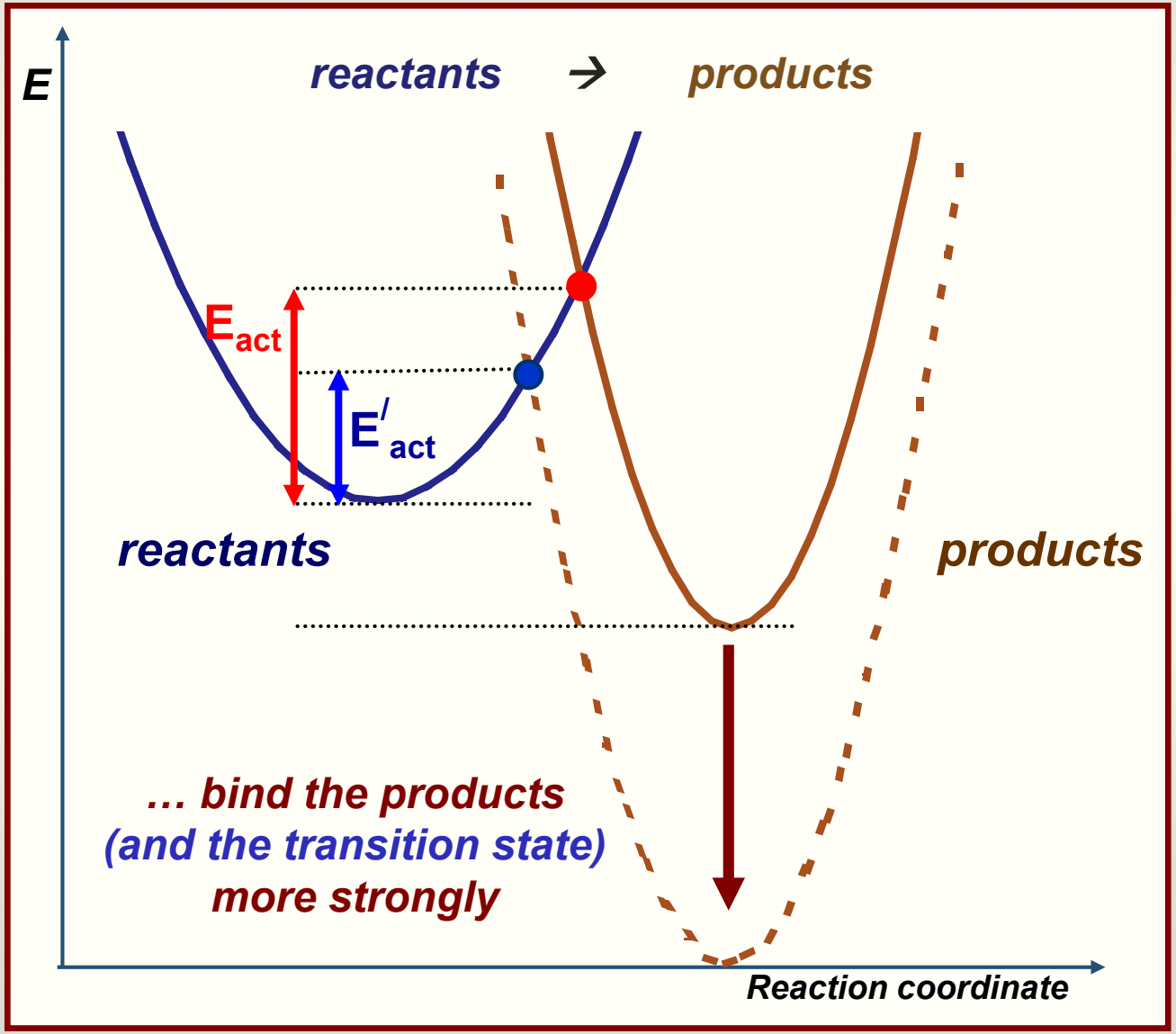
.....

surface coordination



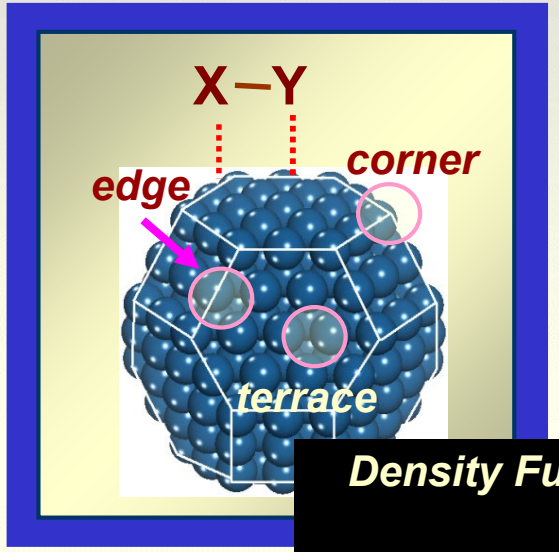


Crossing Potentials "Model"

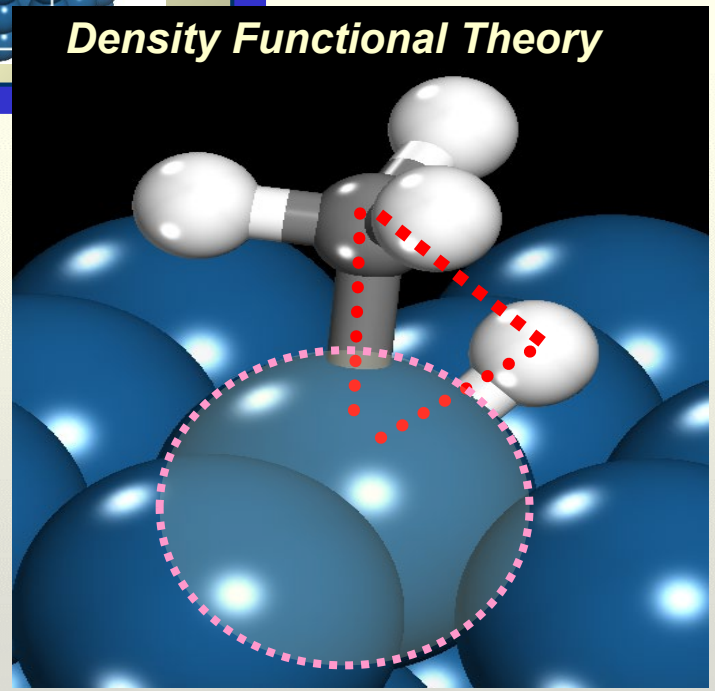


Smaller clusters have more (and sharper) edges

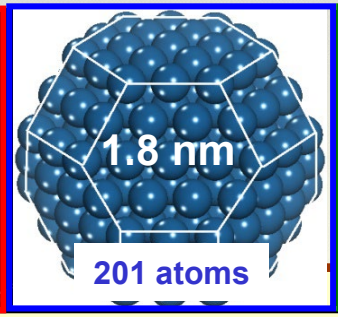
surface coordination

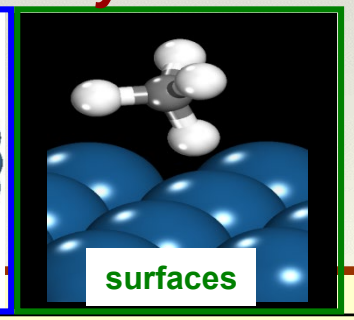


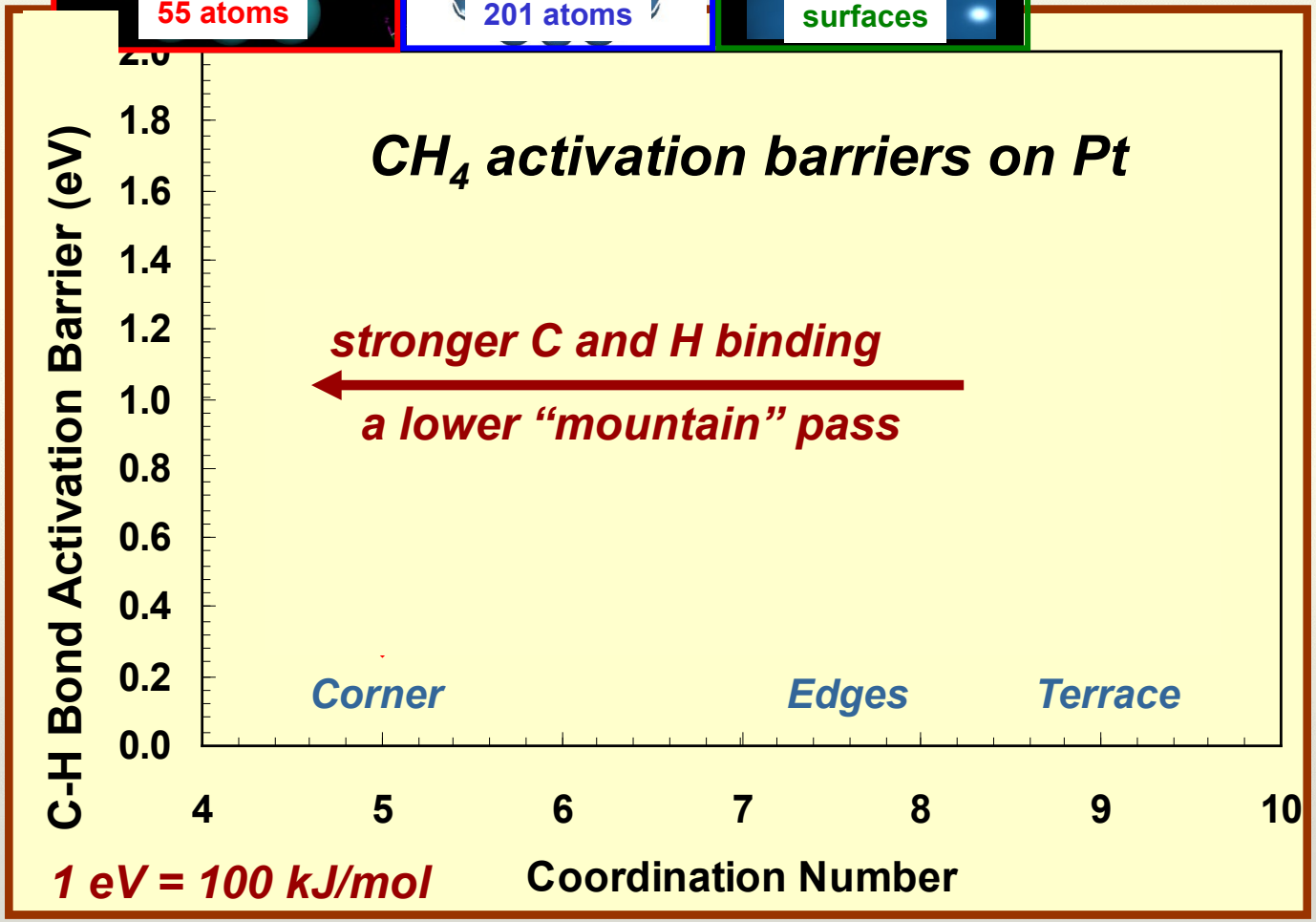
Density Functional Theory



..... Density Functional Theory

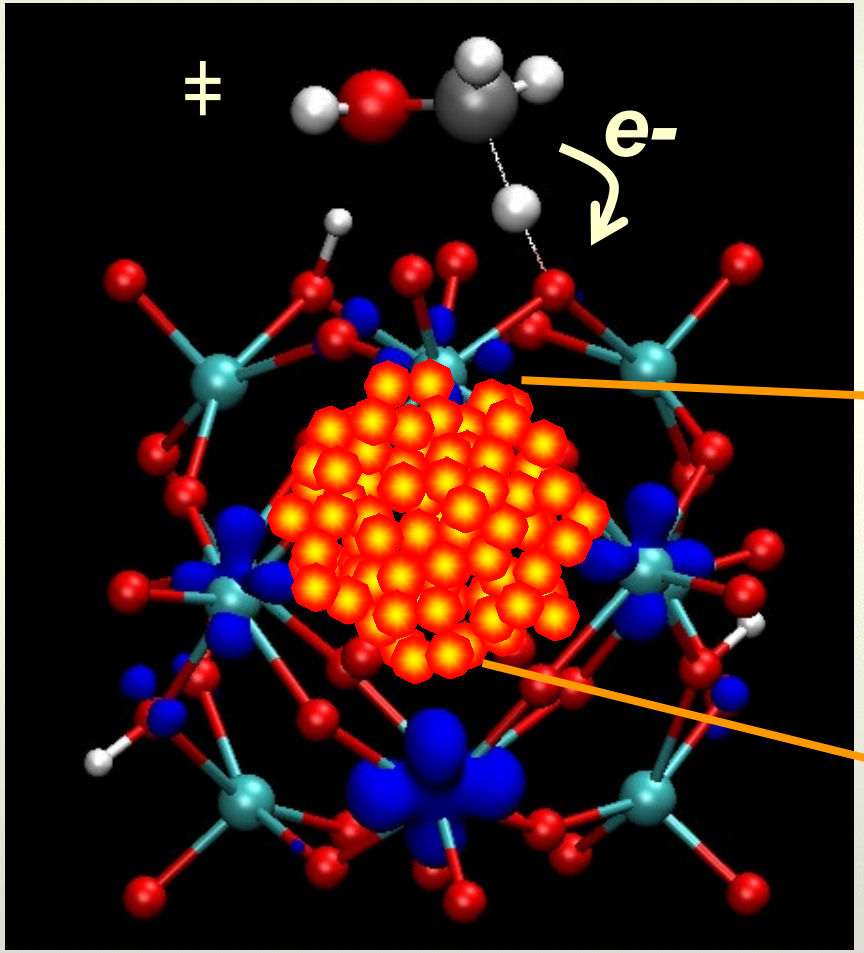




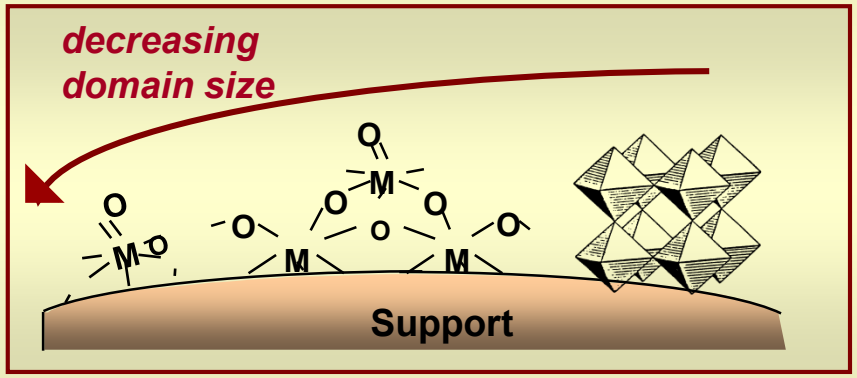


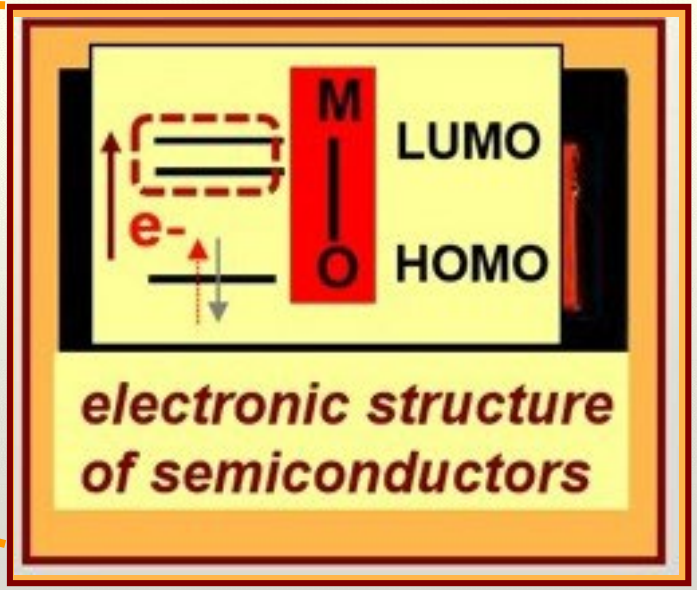
Redox cycles and catalysis on oxide clusters ….
…. relating reactivity to energies (and not just structures)

…. the "energy dialects" of molecules



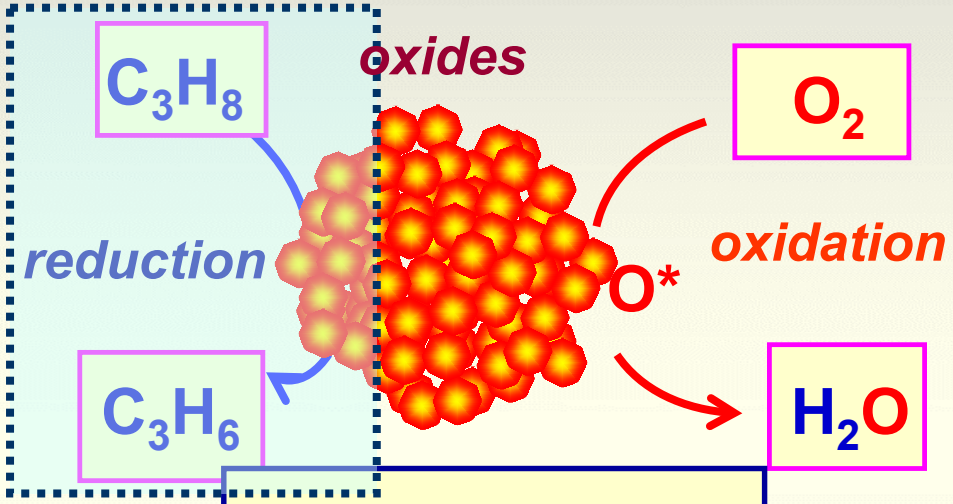
Dispersed oxides (V, Mo, Nb, W, ..)



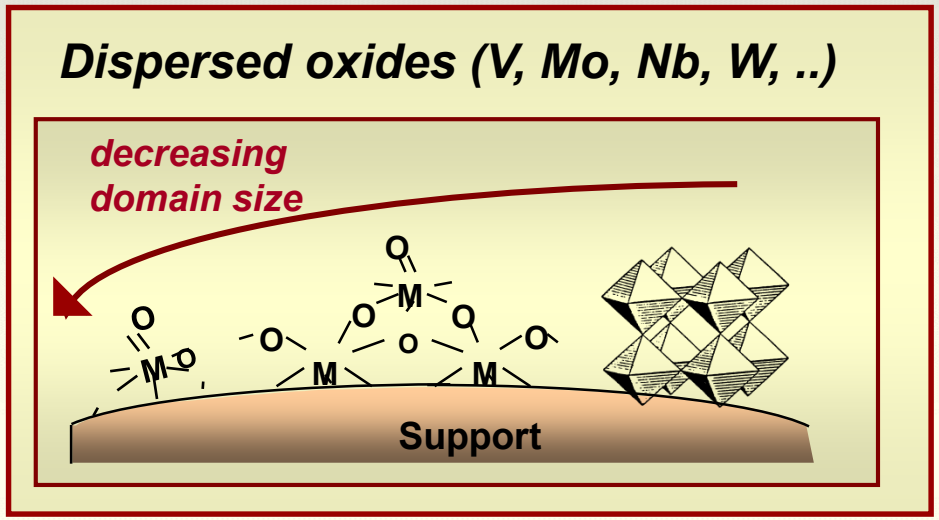


Redox cycles and catalysis on oxide clusters ….
…. relating reactivity to energies (and not just structures)

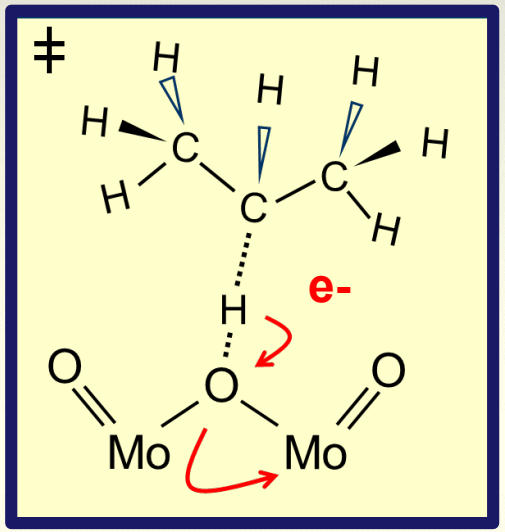
Oxidative dehydrogenation

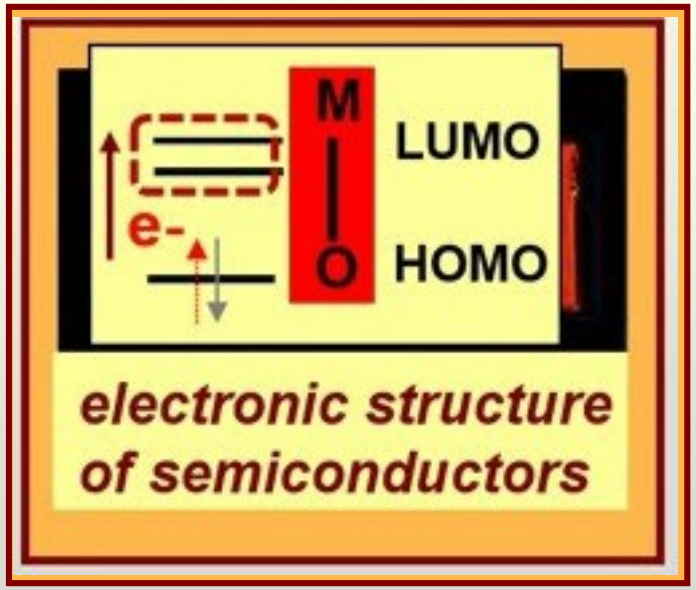


$r = k_1 (C_3H_8)$



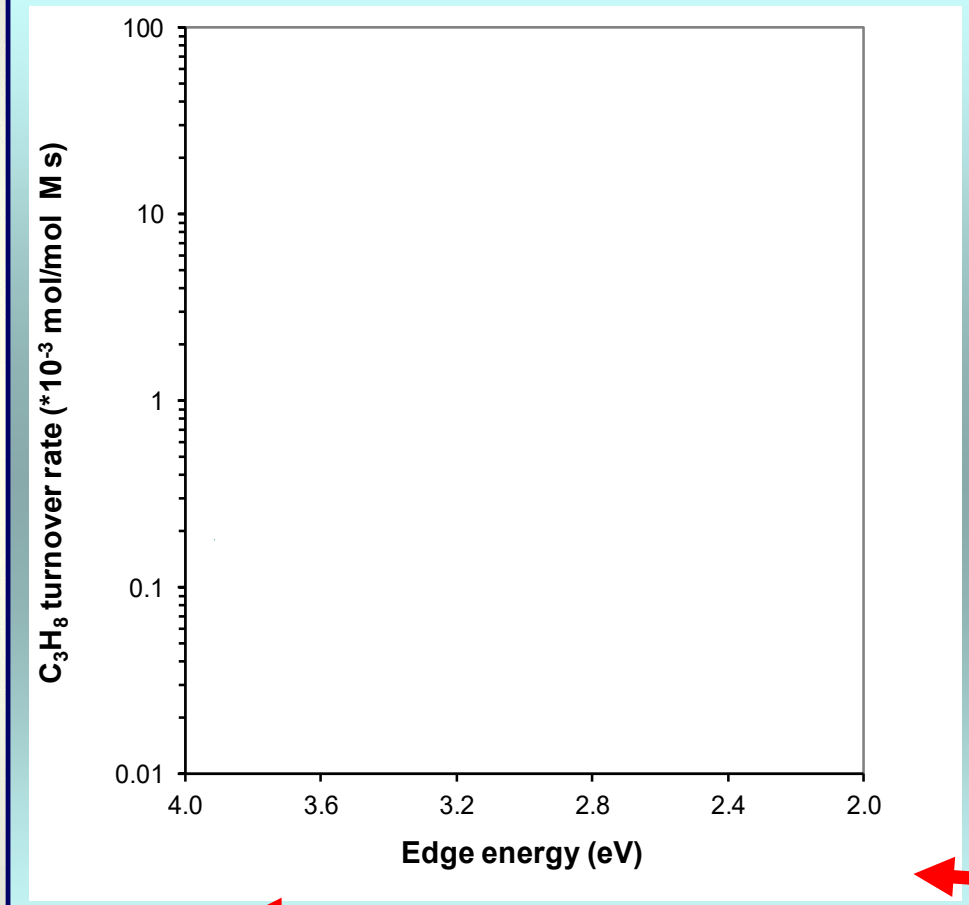
Transition state





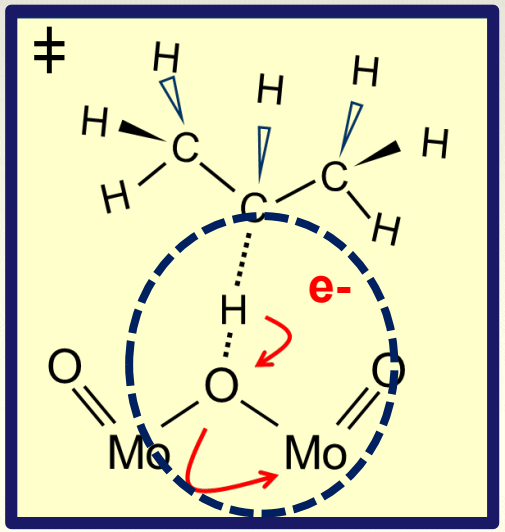
Redox cycles and catalysis on oxide clusters ….
…. relating reactivity to energies (and not just structures)

Propane ODH Turnover Rates

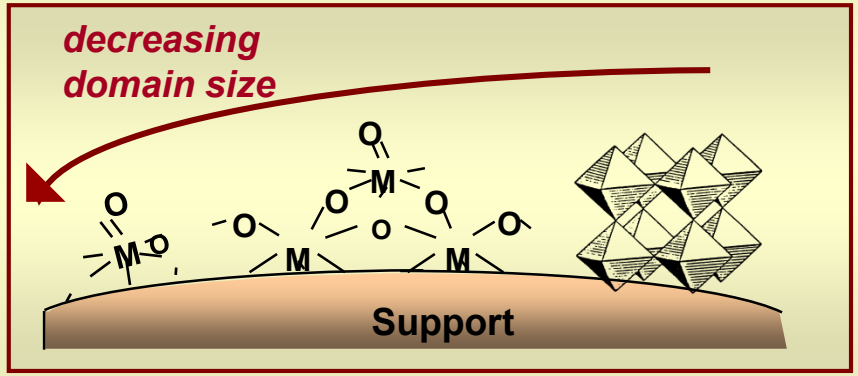


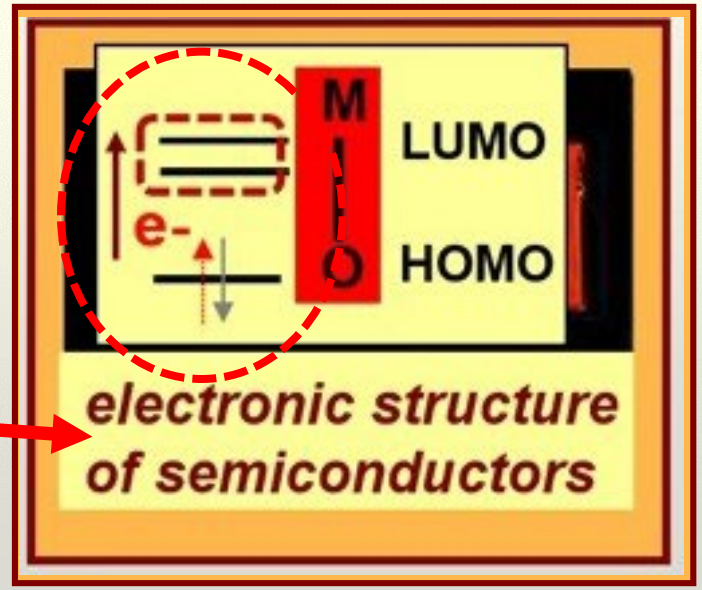
smaller domains

Transition state



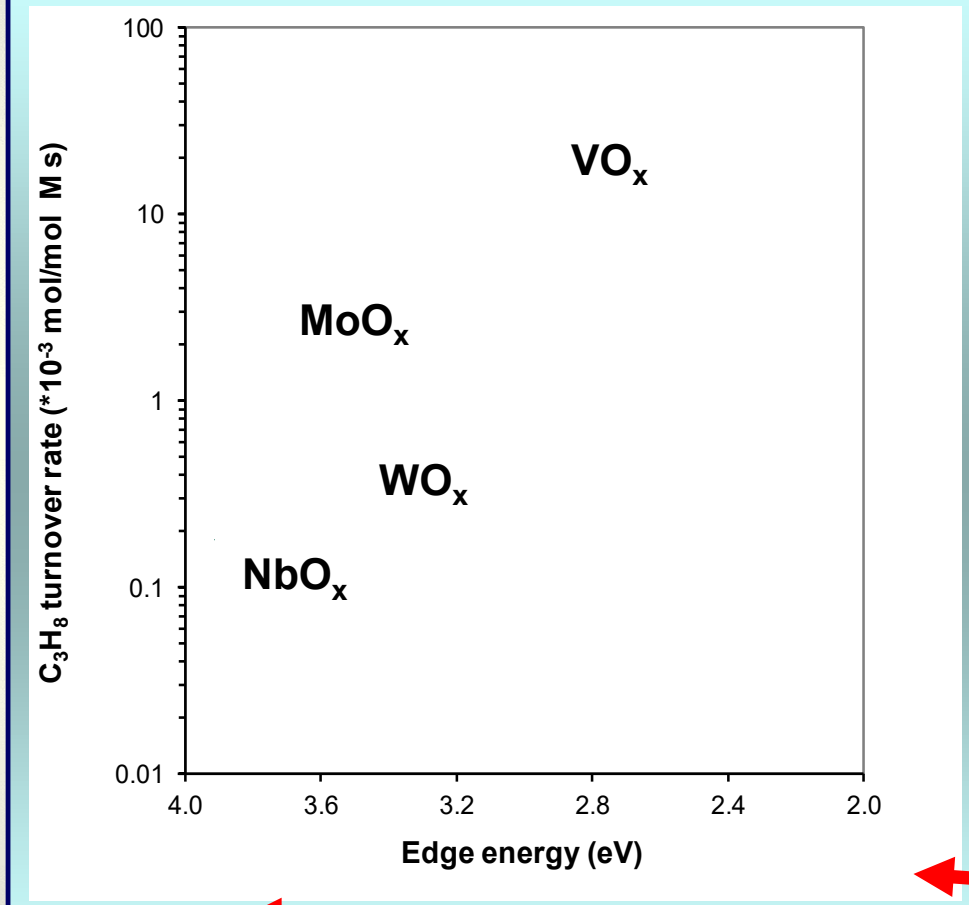
Dispersed oxides (V, Mo, Nb, W, ..)





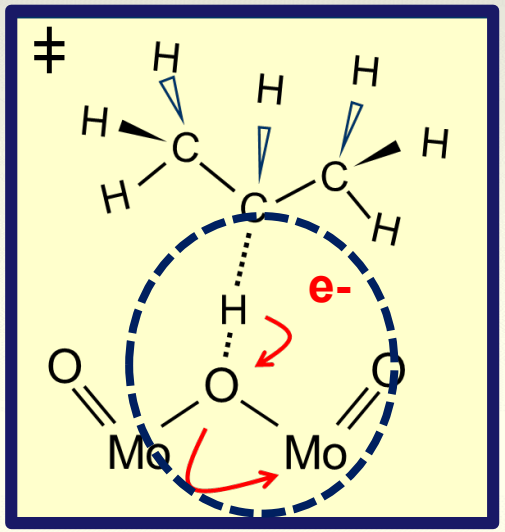
Redox cycles and catalysis on oxide clusters ….
…. relating reactivity to energies (and not just structures)

Propane ODH Turnover Rates

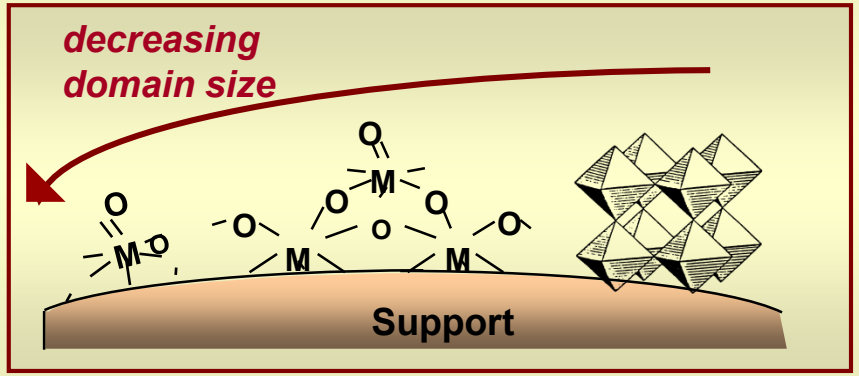


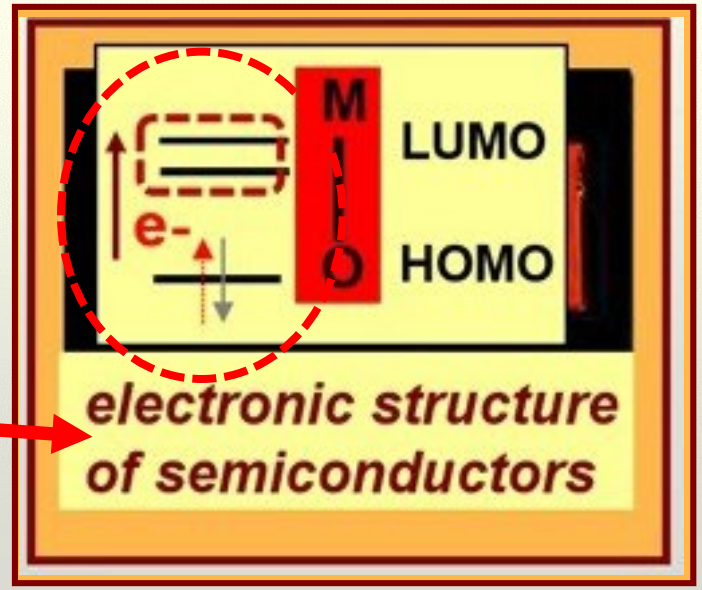
smaller domains

Transition state



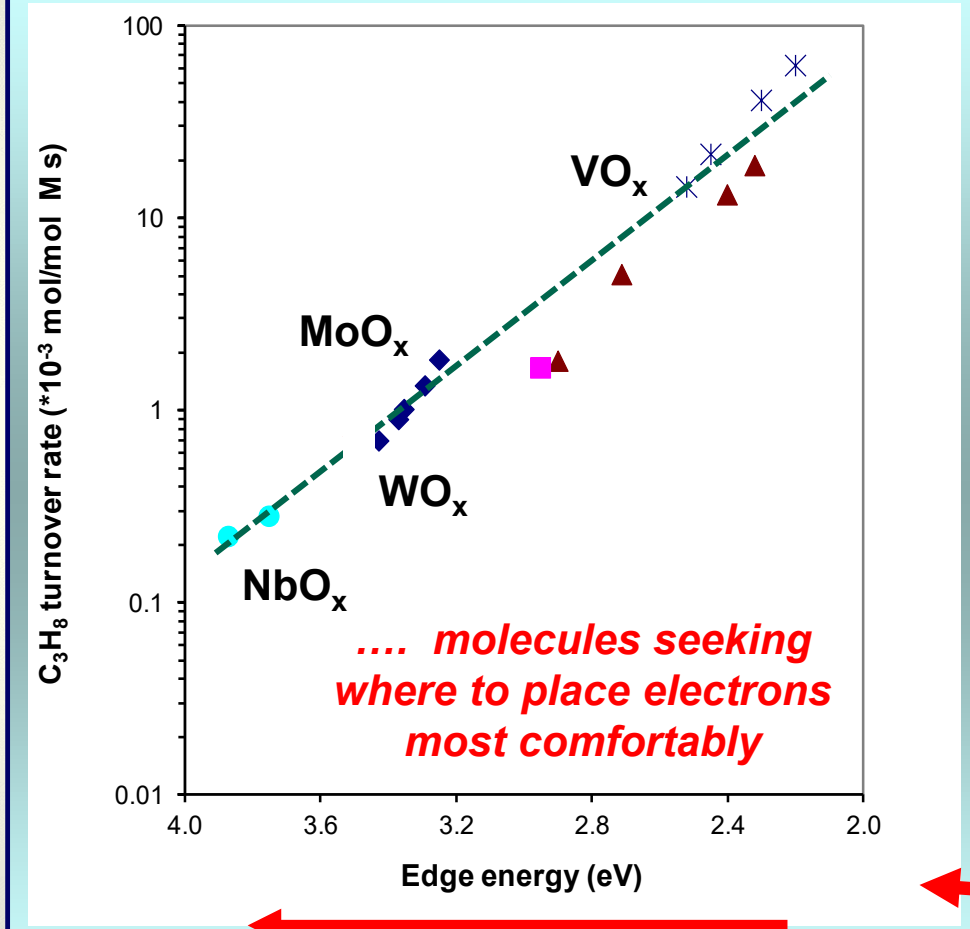
Dispersed oxides (V, Mo, Nb, W, ..)





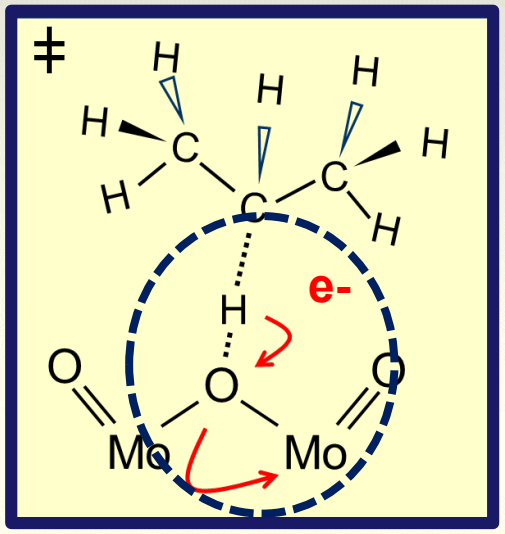
Redox cycles and catalysis on oxide clusters ….
…. relating reactivity to energies (and not just structures)

Propane ODH Turnover Rates

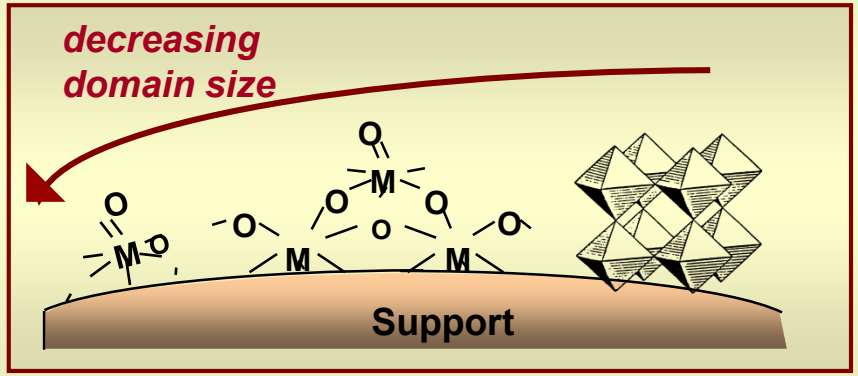


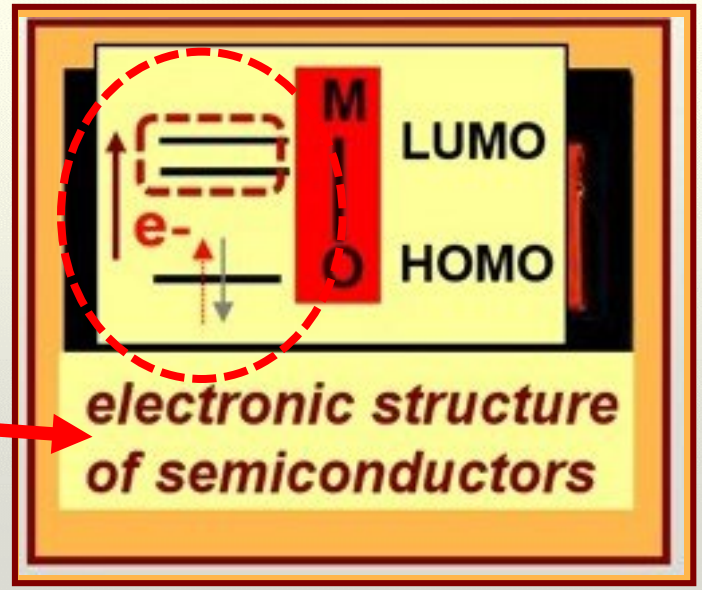
smaller domains

Transition state

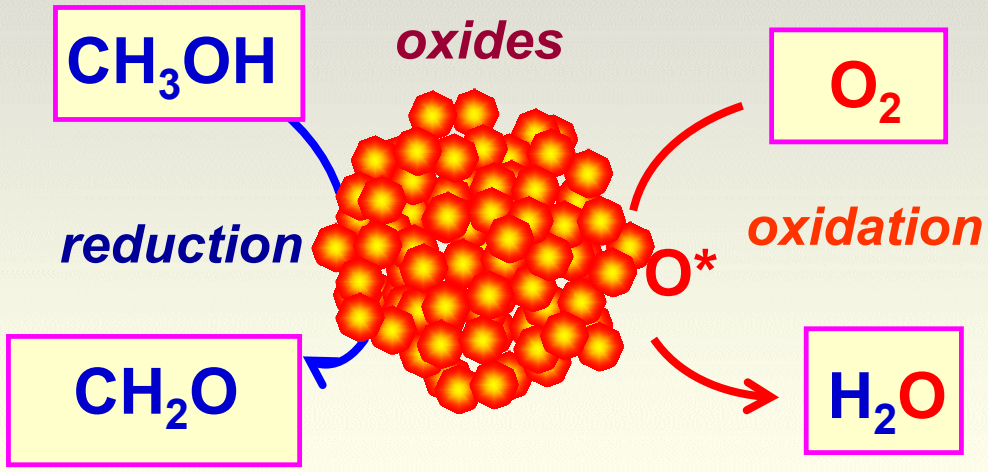


Dispersed oxides (V, Mo, Nb, W, ..)

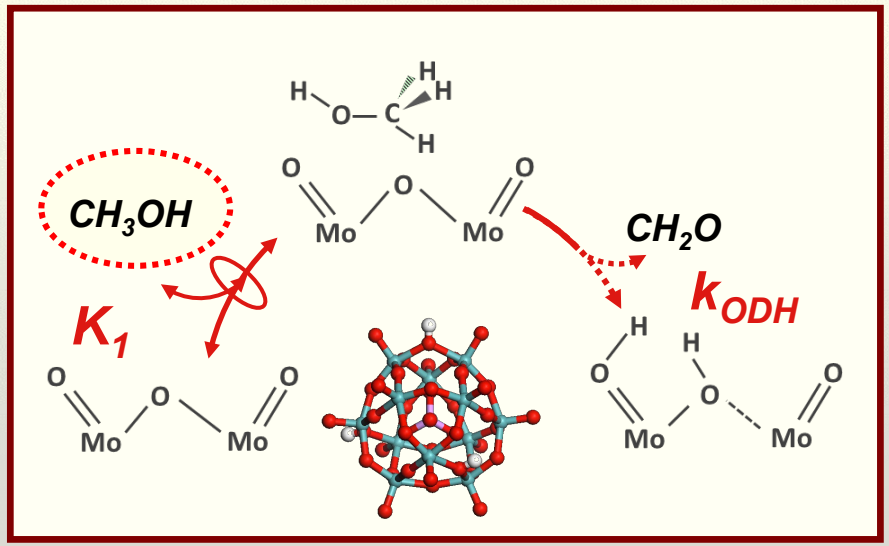




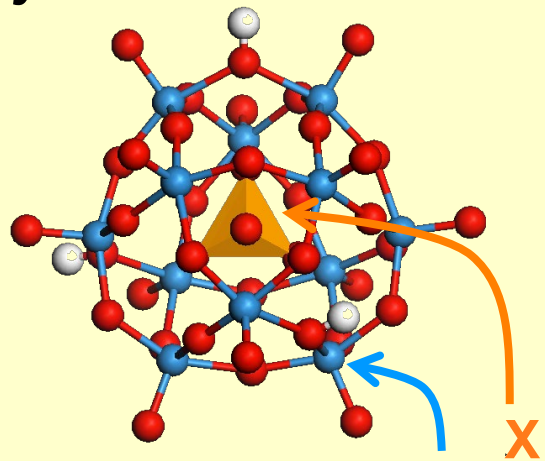
Exploiting solids with known structure … and descriptors of reactivity



methanol to formaldehyde



Polyoxometalate clusters



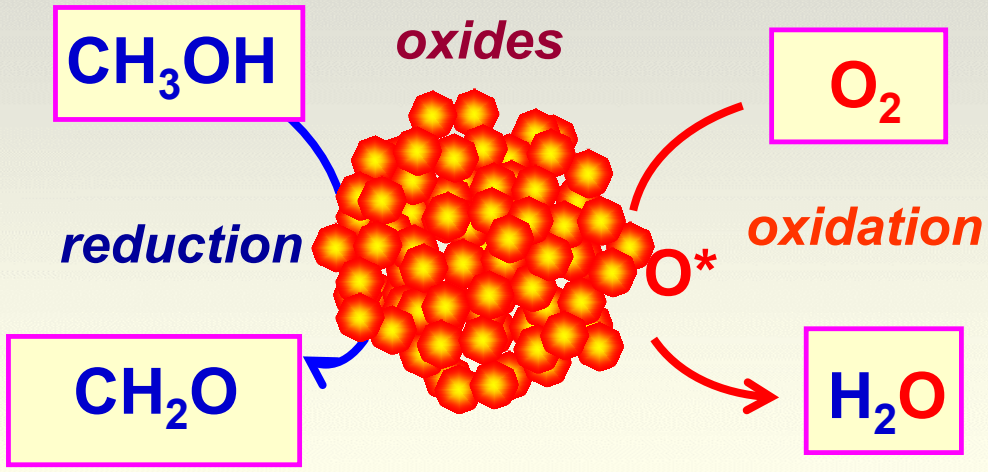
$H_{8-n}X^{n+}M_{12}O_{40}$

M = W, Mo, V X = P, Si

… compositional diversity
… similar and known structures

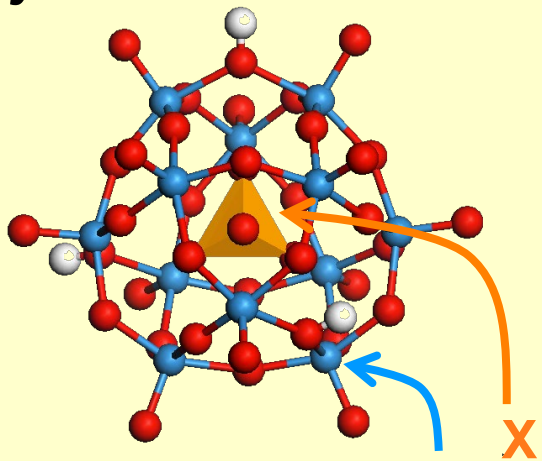
Prashant Deshlahra
Stephanie Kwon

Exploiting solids with known structure … and descriptors of reactivity



methanol to formaldehyde

Polyoxometalate clusters

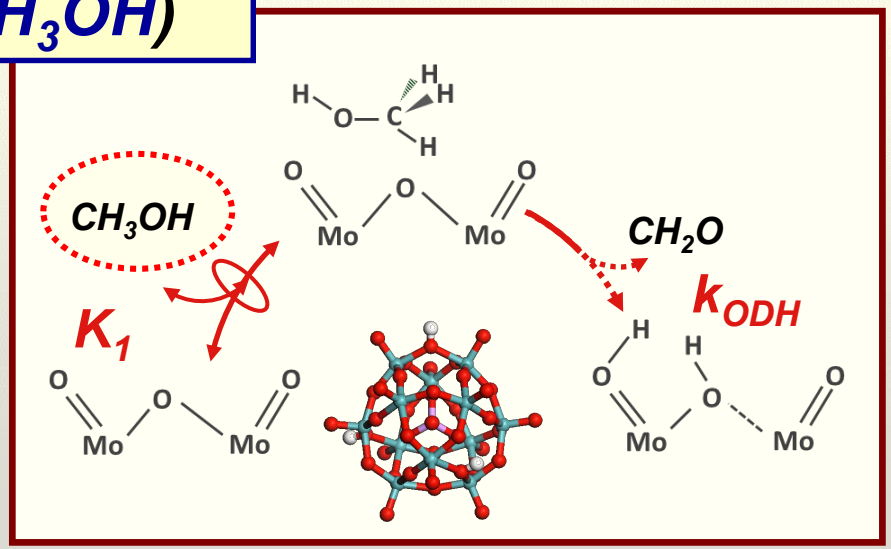


$H_{8-n}X^{n+}M_{12}O_{40}$

M = W, Mo, V X = P, Si

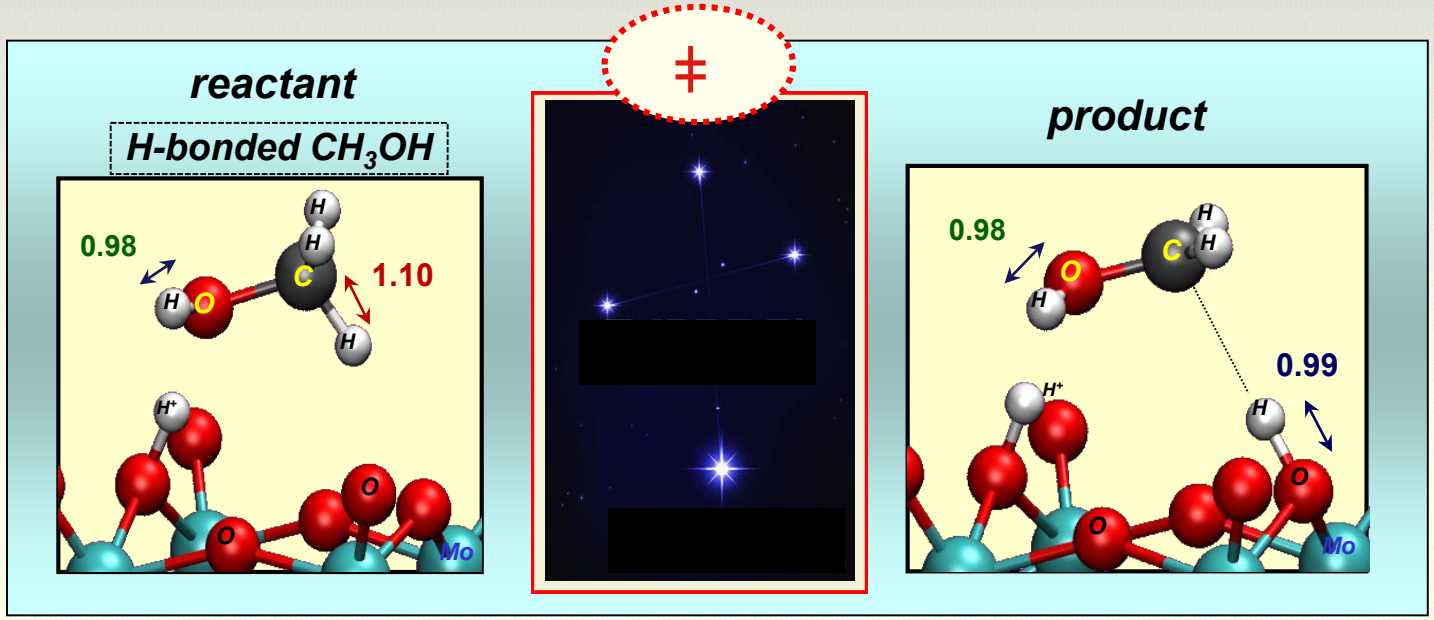
… compositional diversity
… similar and known structures

$r = k_{ODH}(CH_3OH)$

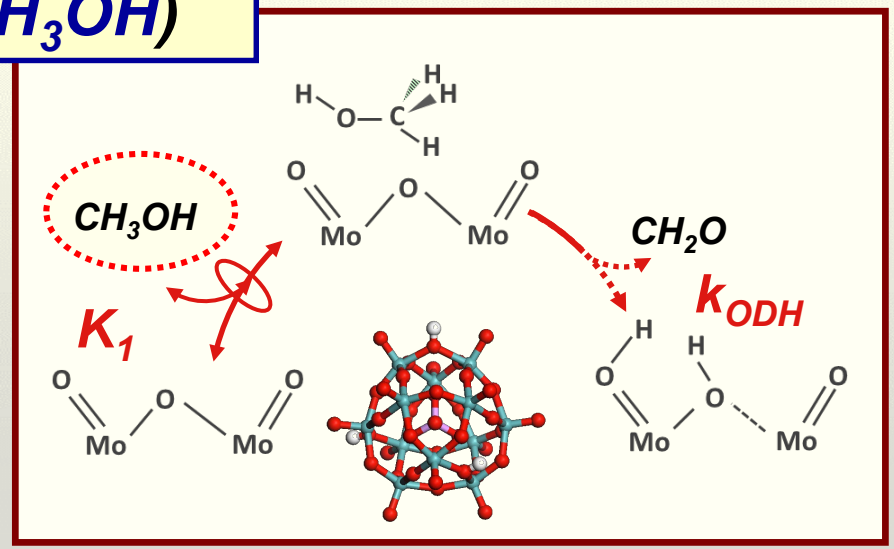


Prashant Deshlahra
Stephanie Kwon

Exploiting solids with known structure … and descriptors of reactivity

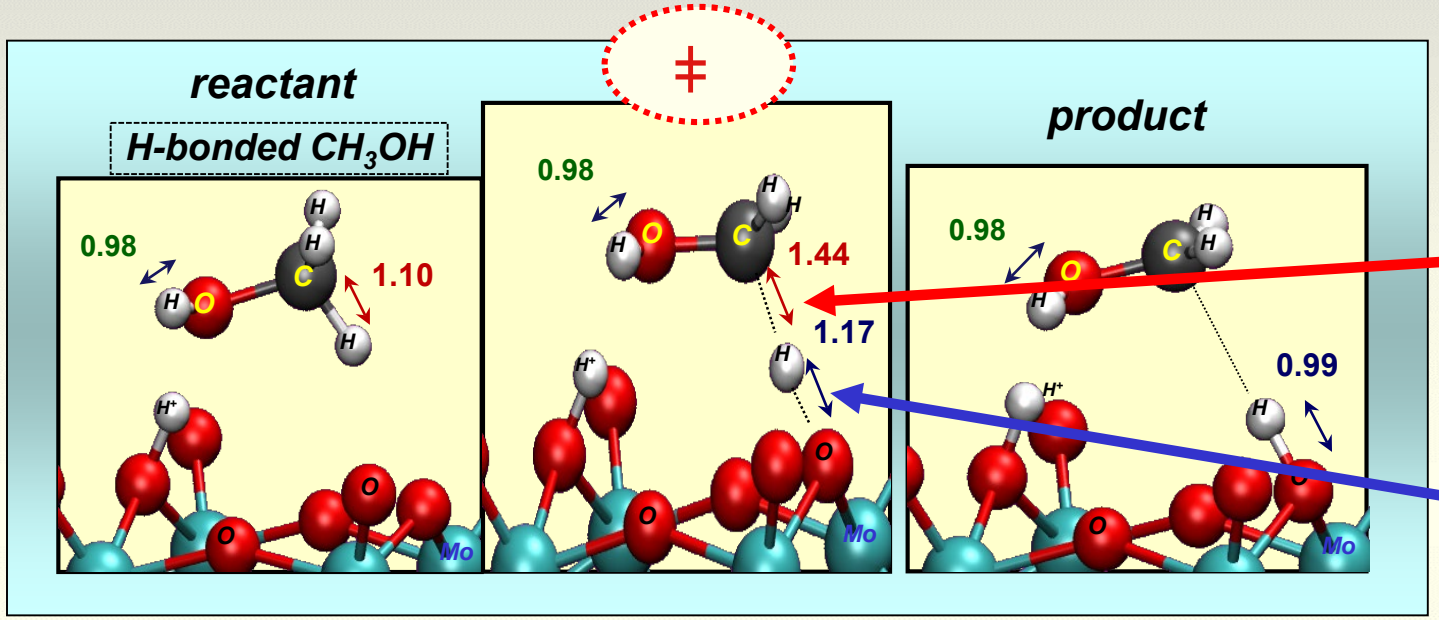


$$r = k_{ODH}(CH_3OH)$$



Exploiting solids with known structure … and descriptors of reactivity

… a molecular property



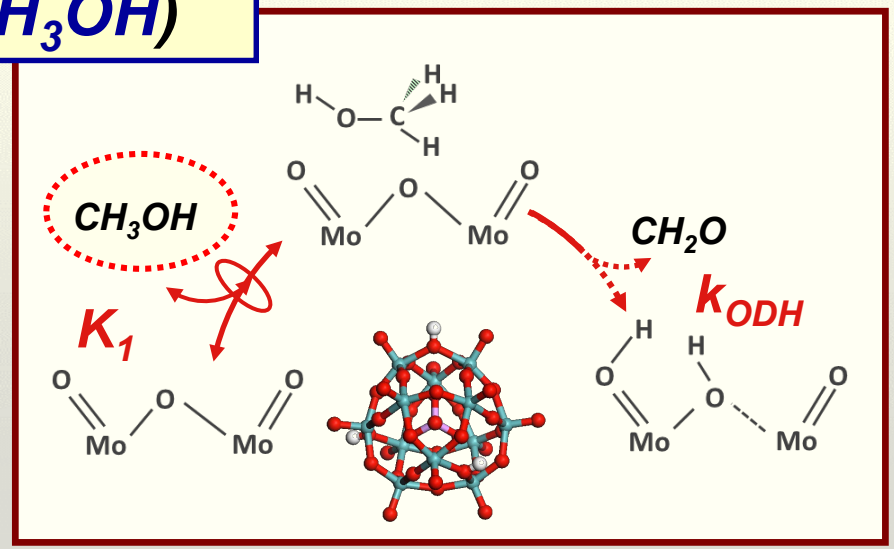
C-H dissociation energy

C-H bond nearly cleaved

O-H bond nearly formed

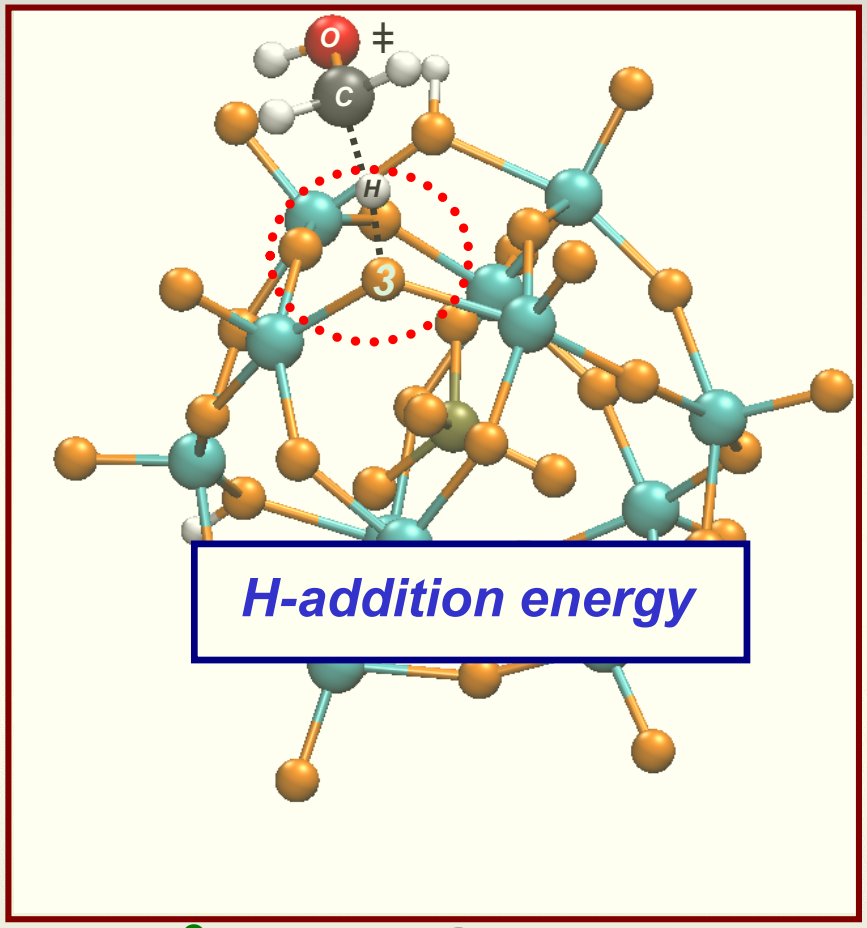
H-addition energy

$r = k_{ODH}(CH_3OH)$

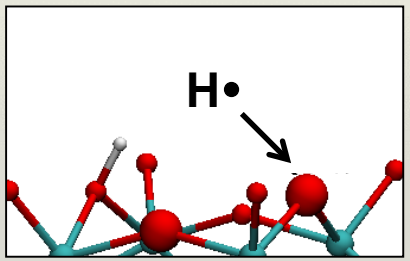


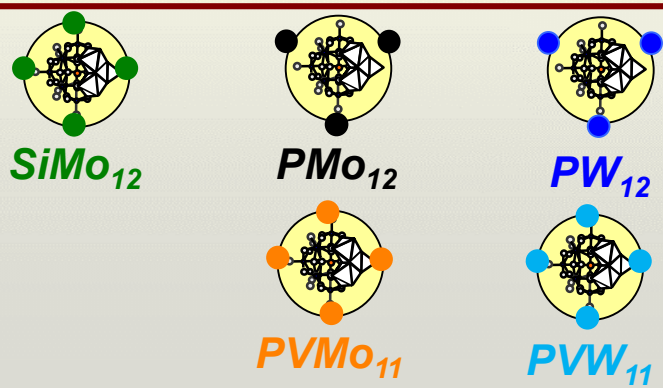
…. a catalyst property

Reactivity …. and "chemical proxies" for composition



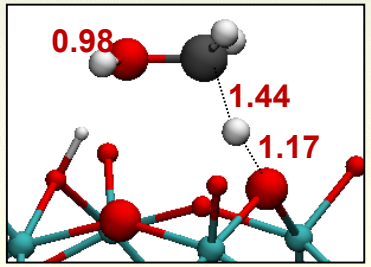
HAE

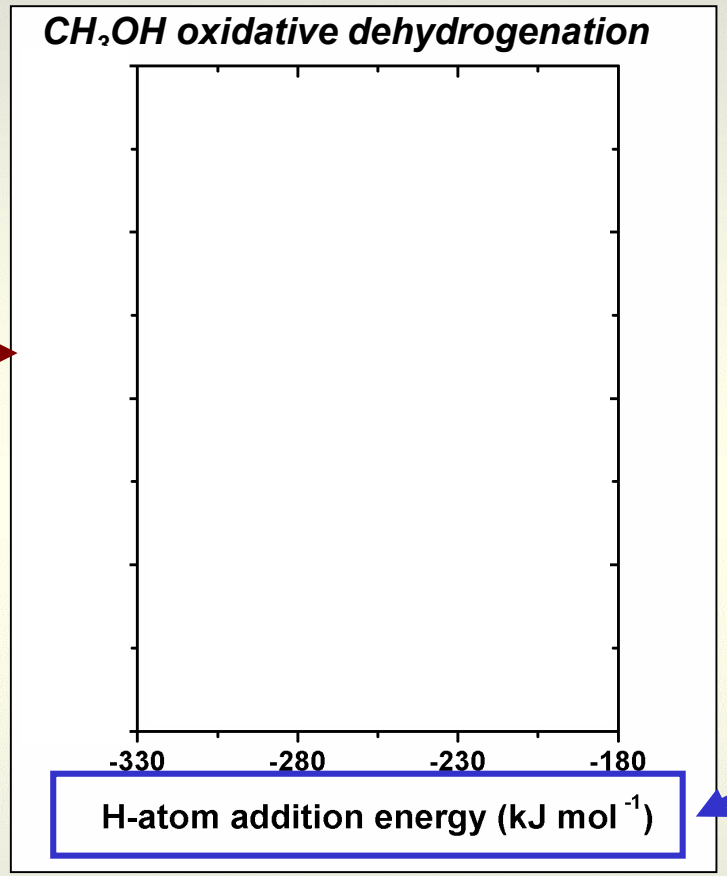




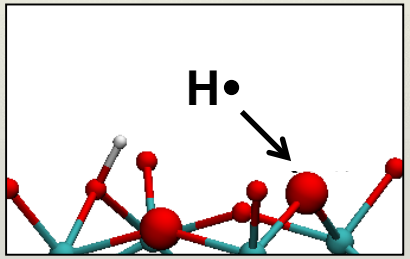
Reactivity …. and “chemical proxies” for composition

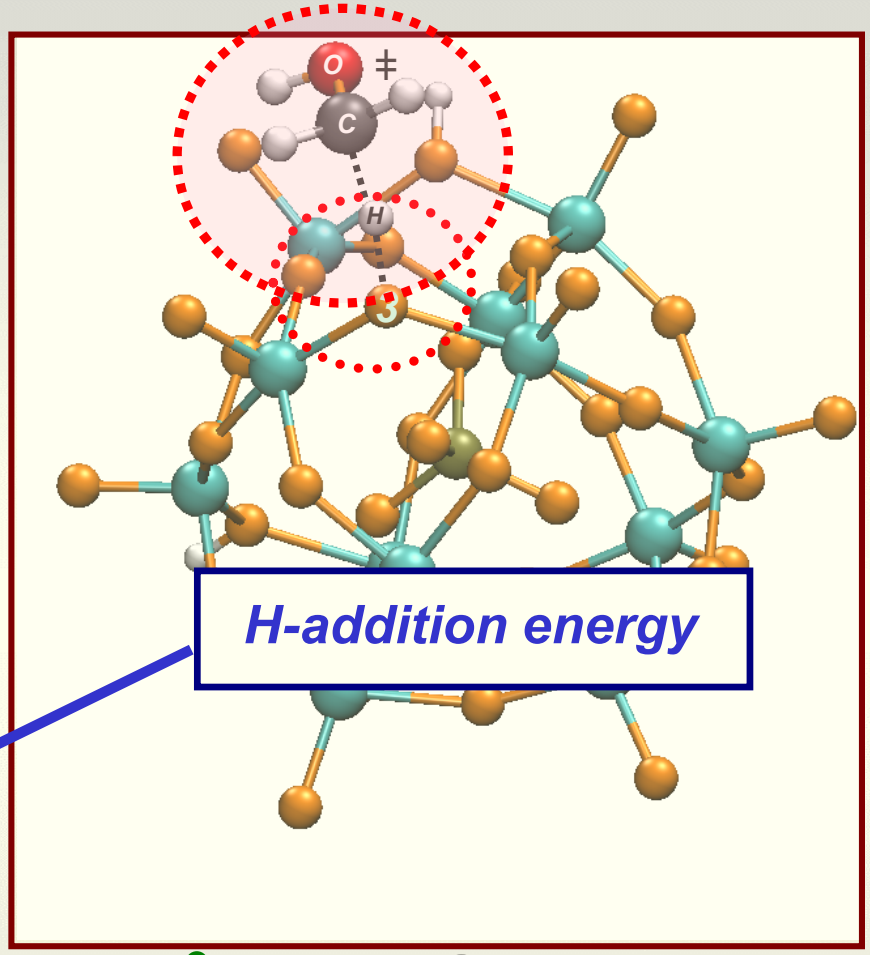
H-abstraction TS

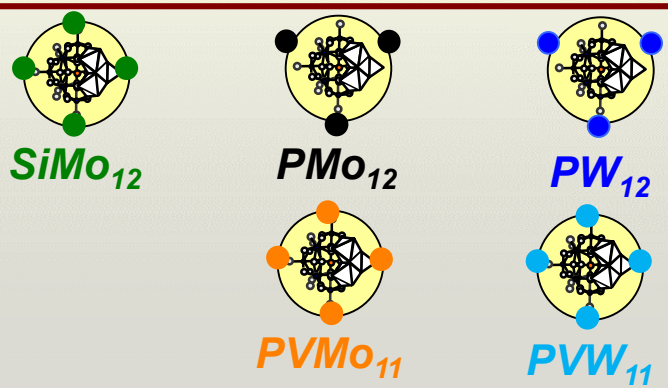




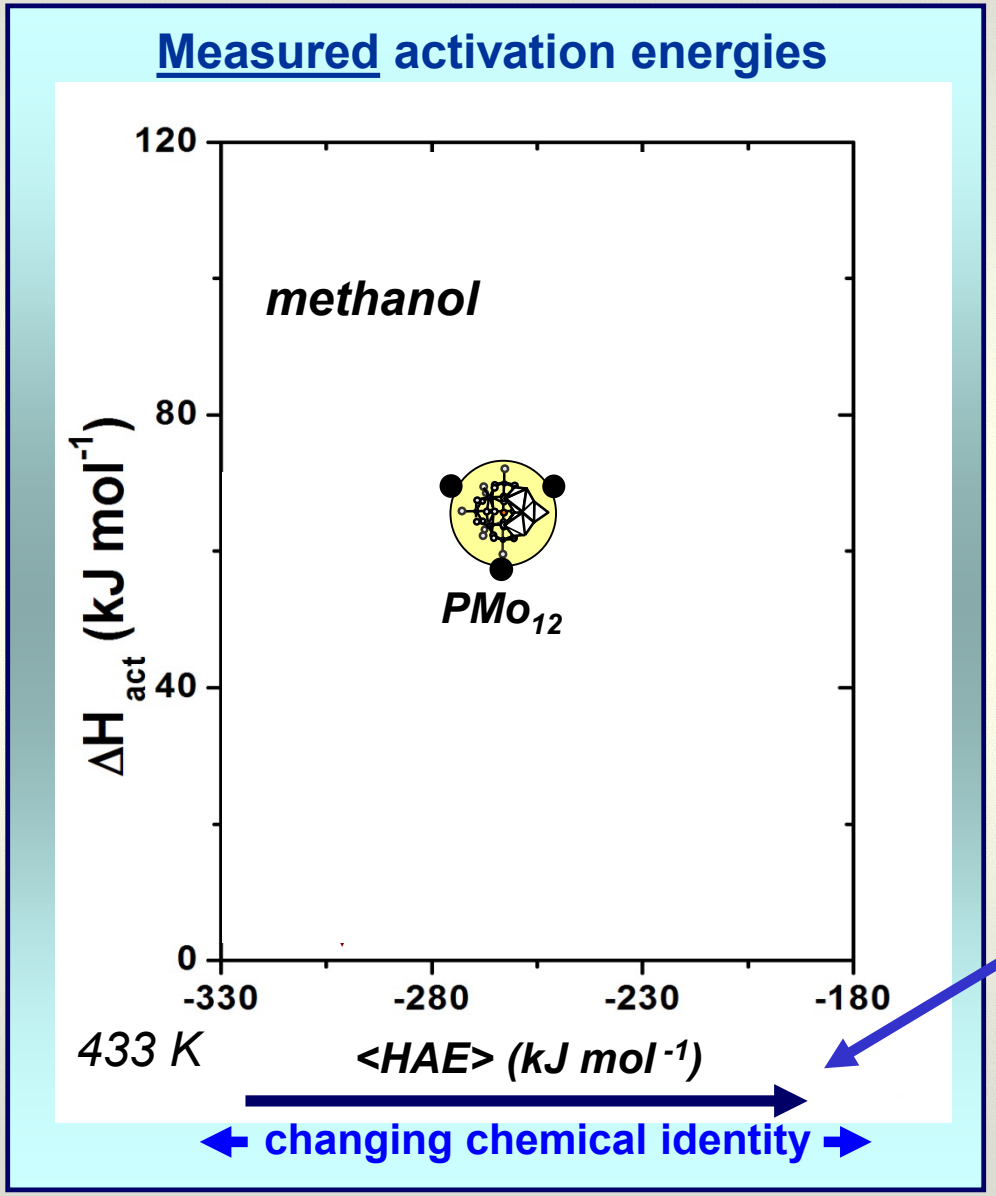
HAE

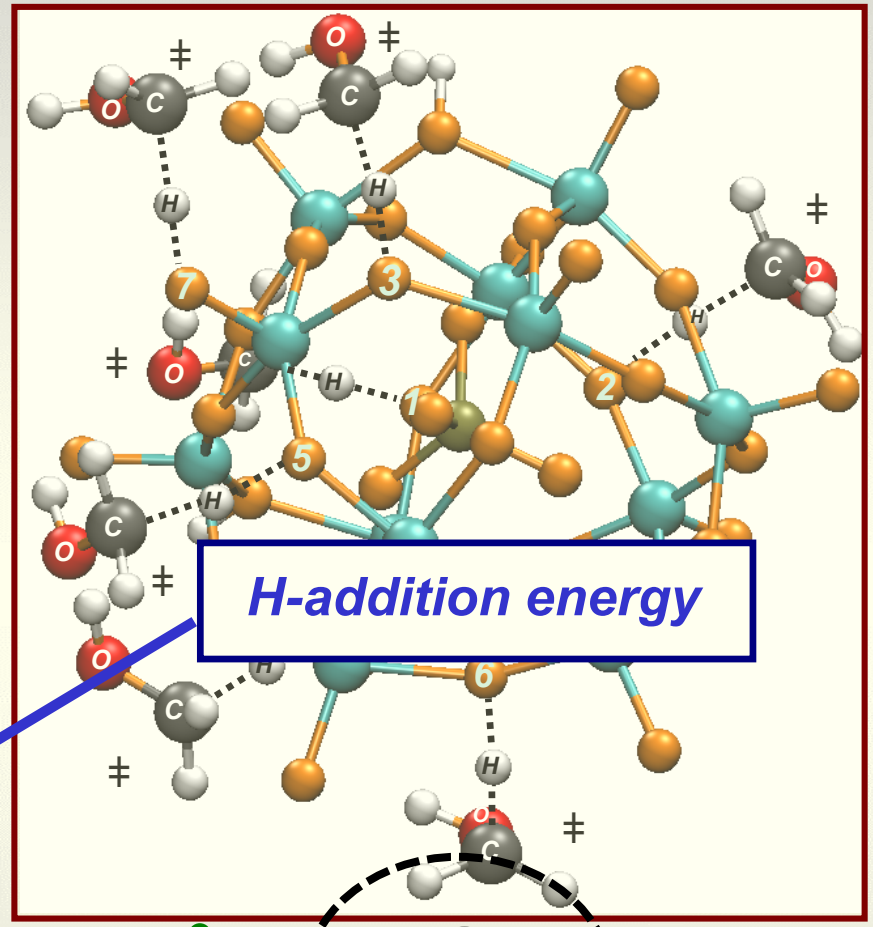




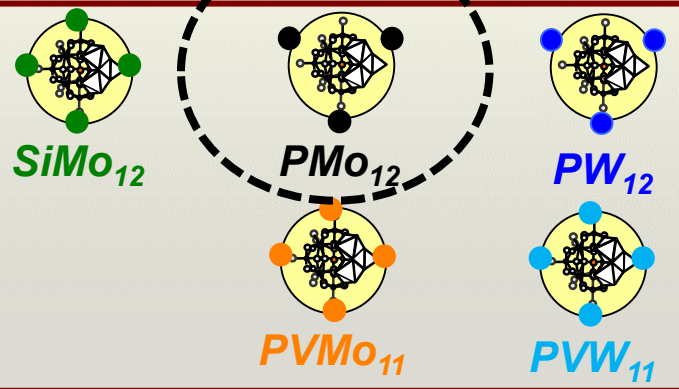


Reactivity …. and "chemical proxies" for composition

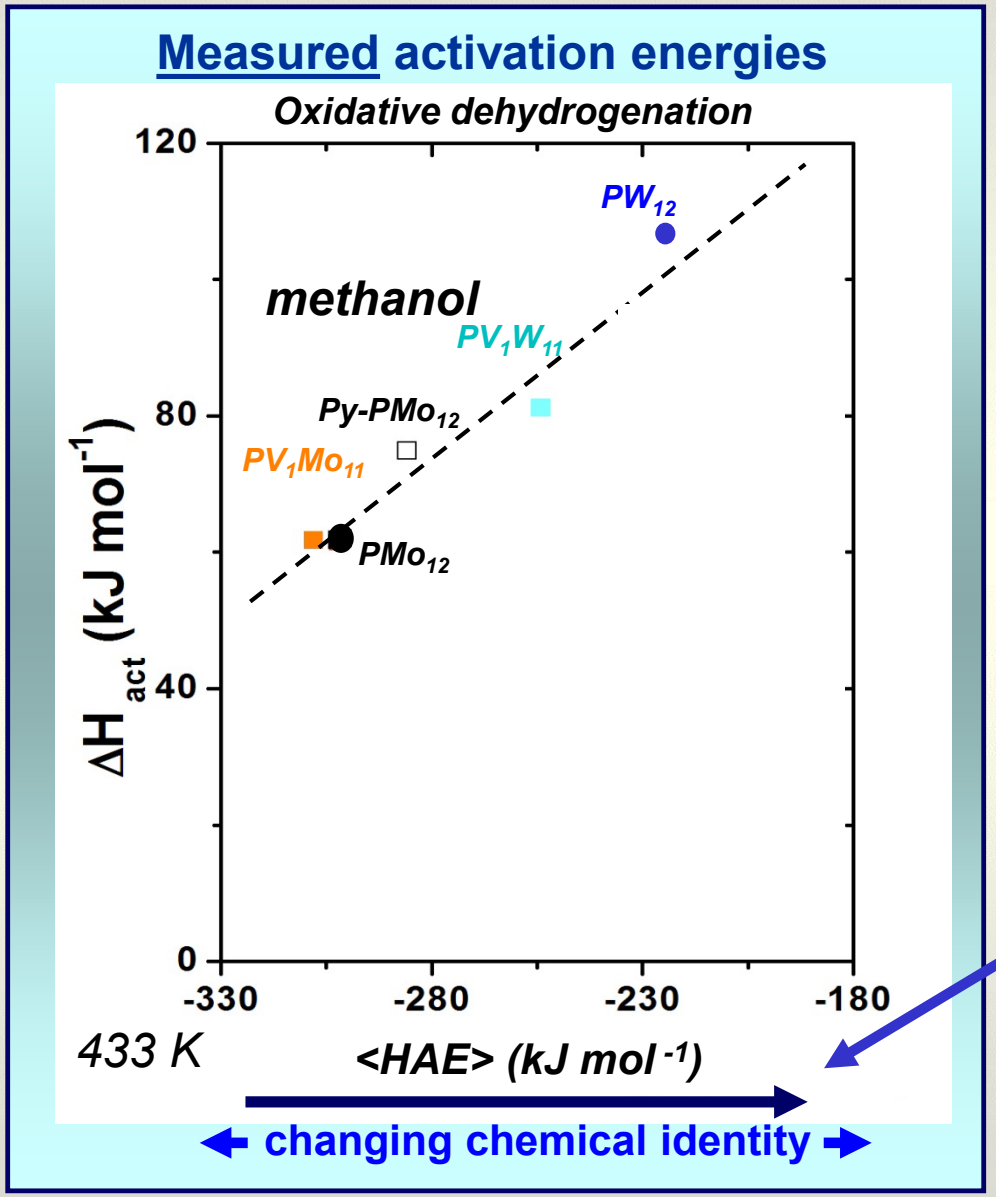


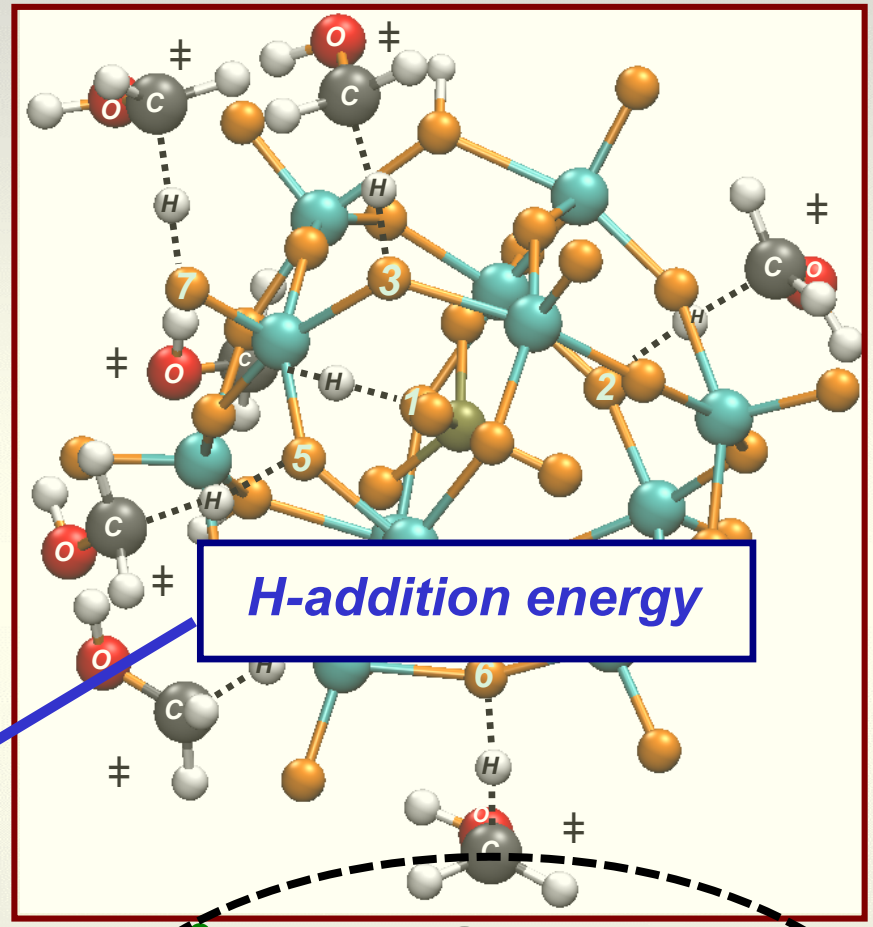

H-addition energy

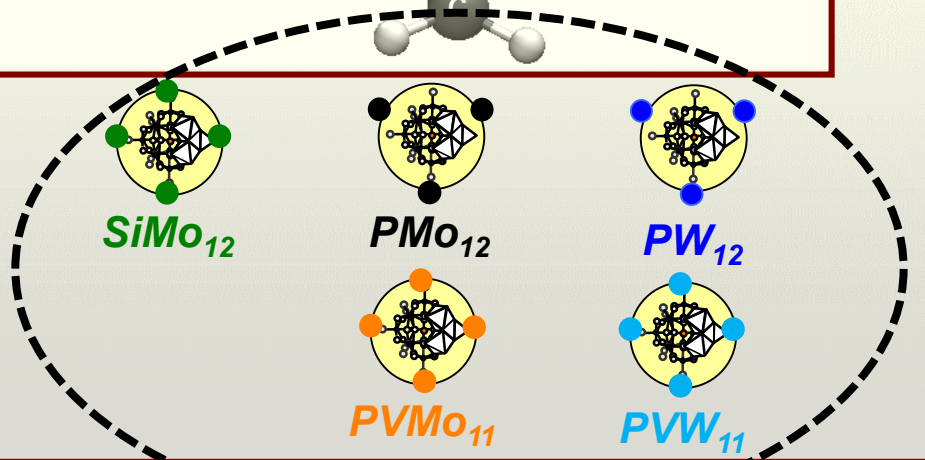
Ensemble average
<HAE> = -302



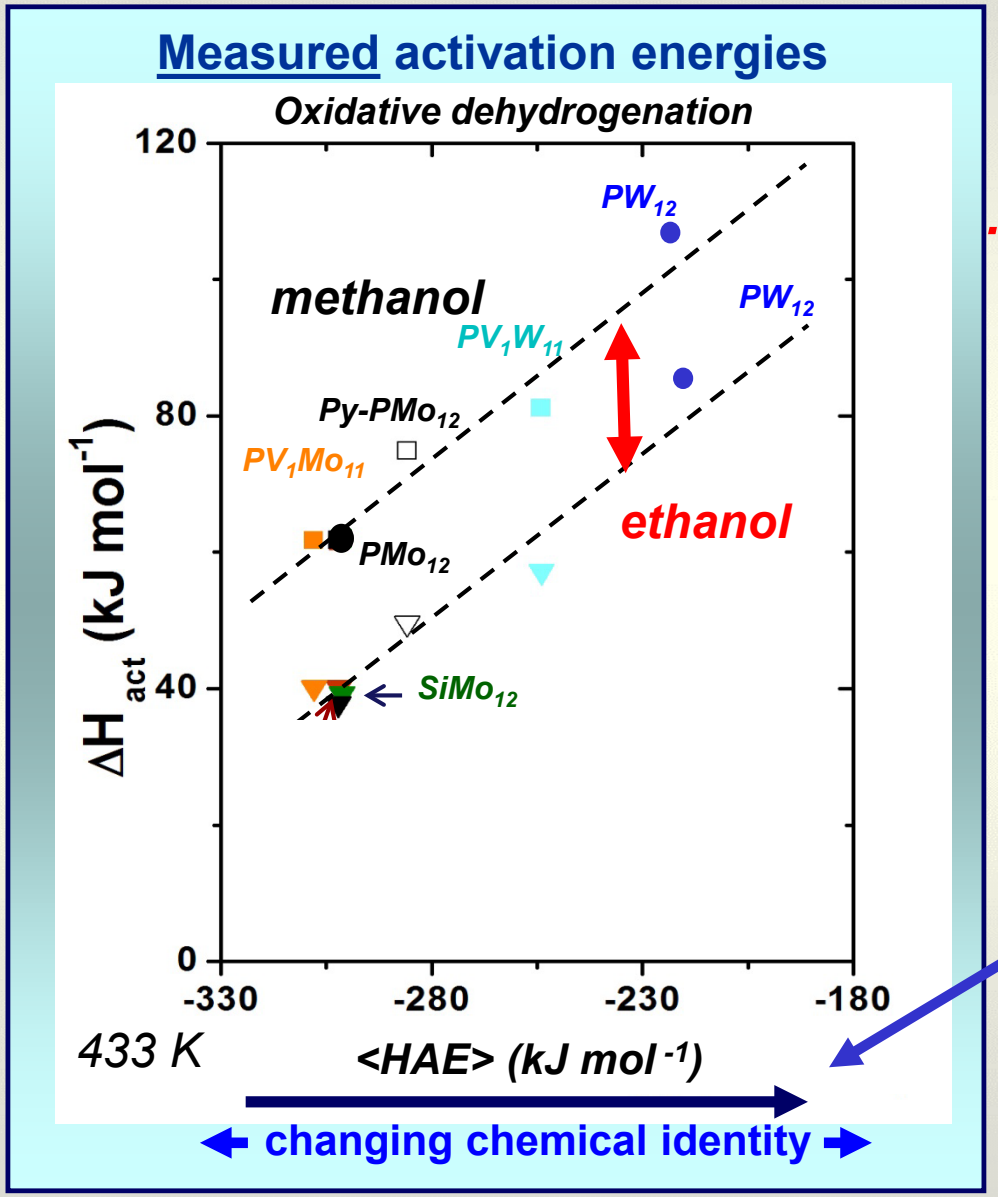
Reactivity …. and "chemical proxies" for composition



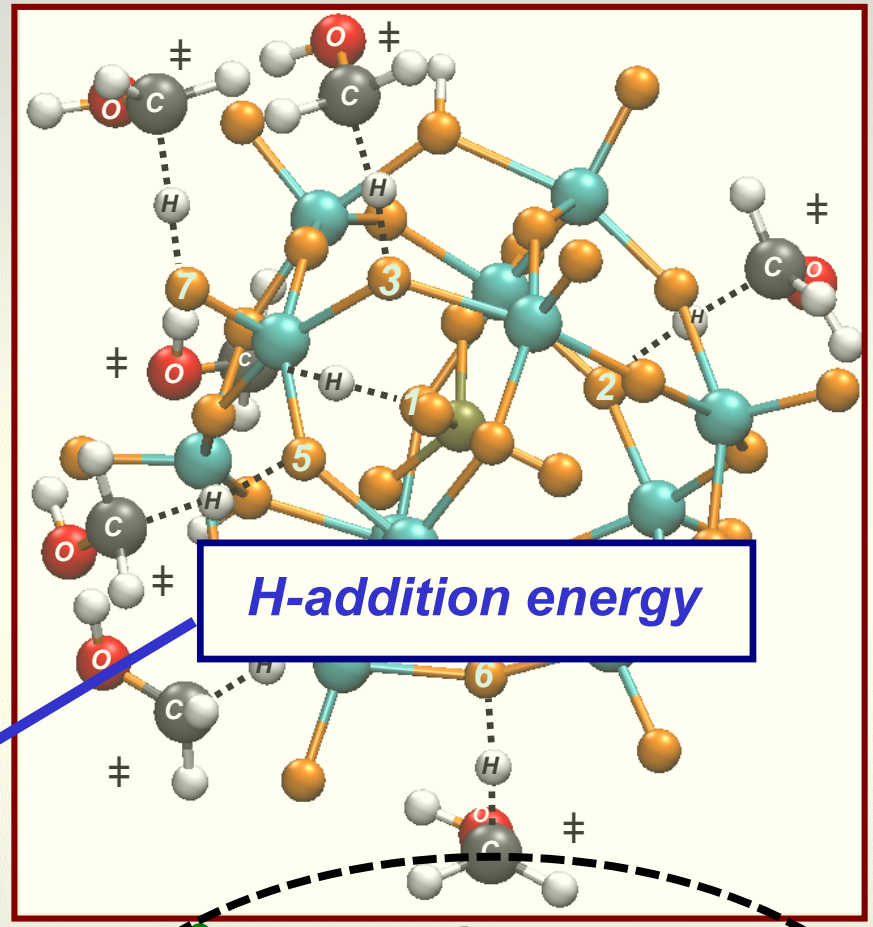


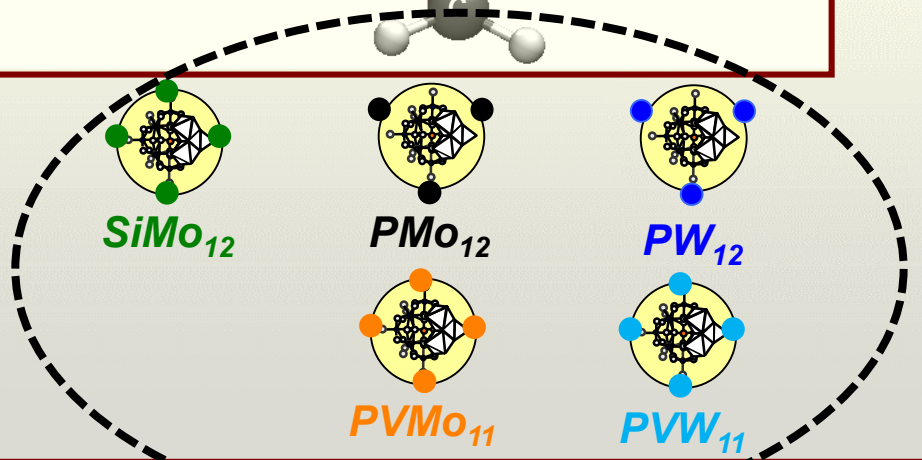


Reactivity …. and "chemical proxies" for composition



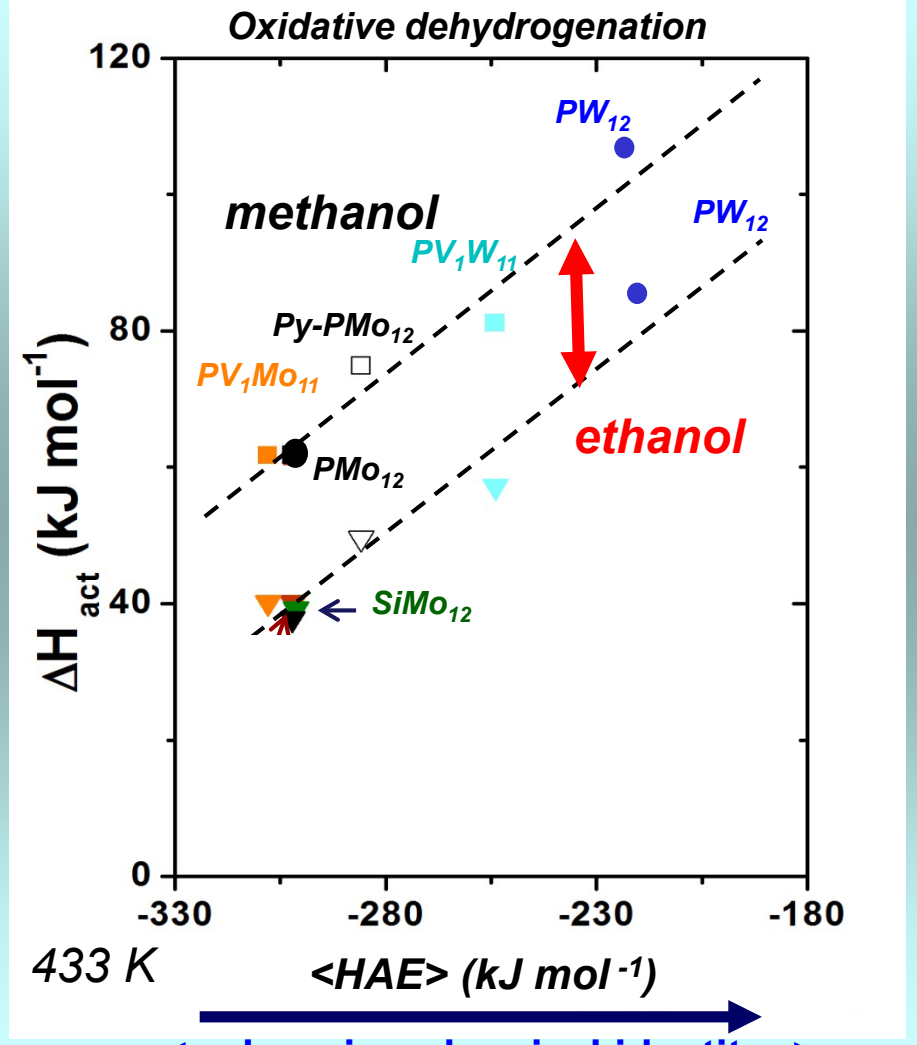
… the weaker C-H bond in ethanol



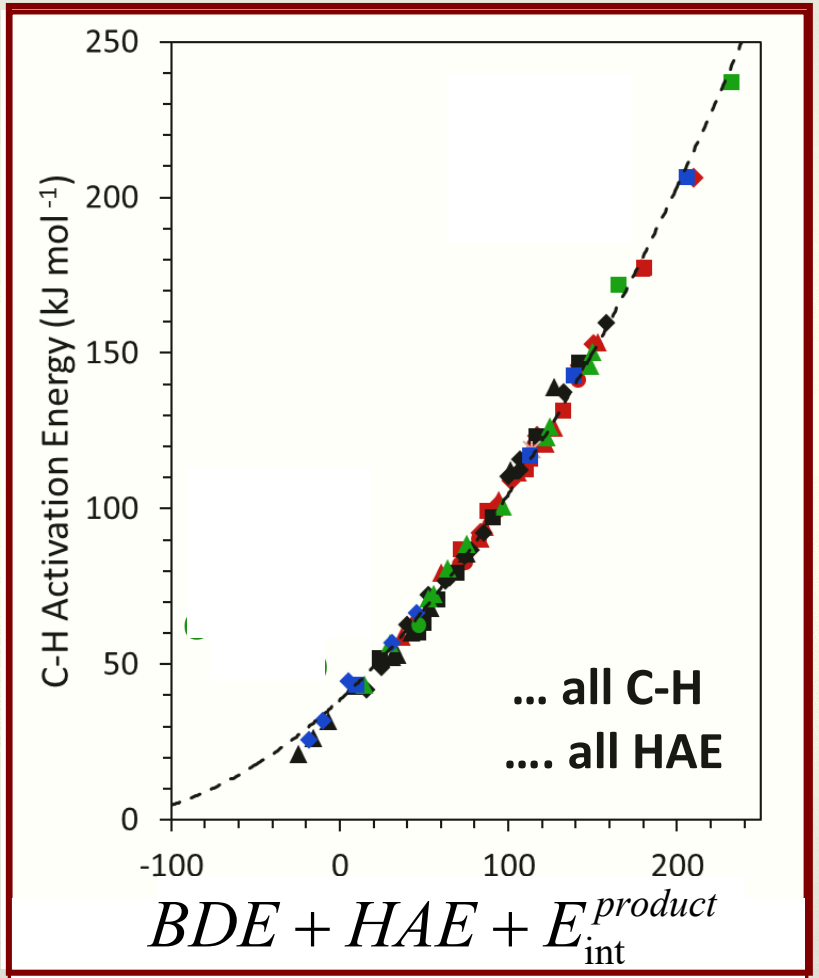


Reactivity …. and "chemical proxies" for composition

Measured activation energies



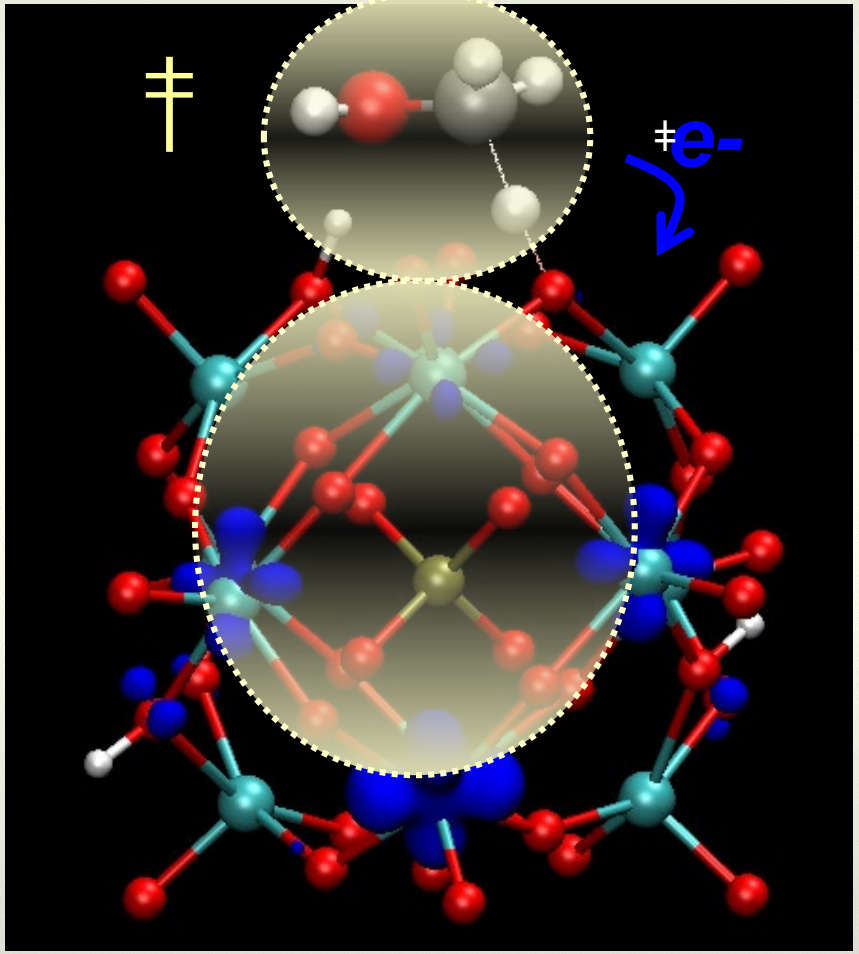
DFT-derived C-H bond activation barriers
(alcohols, paraffins, olefins, ketones,…)



VASP - PW91 - PAW

Reactivity Descriptors as Energies: Oxidation Catalysis

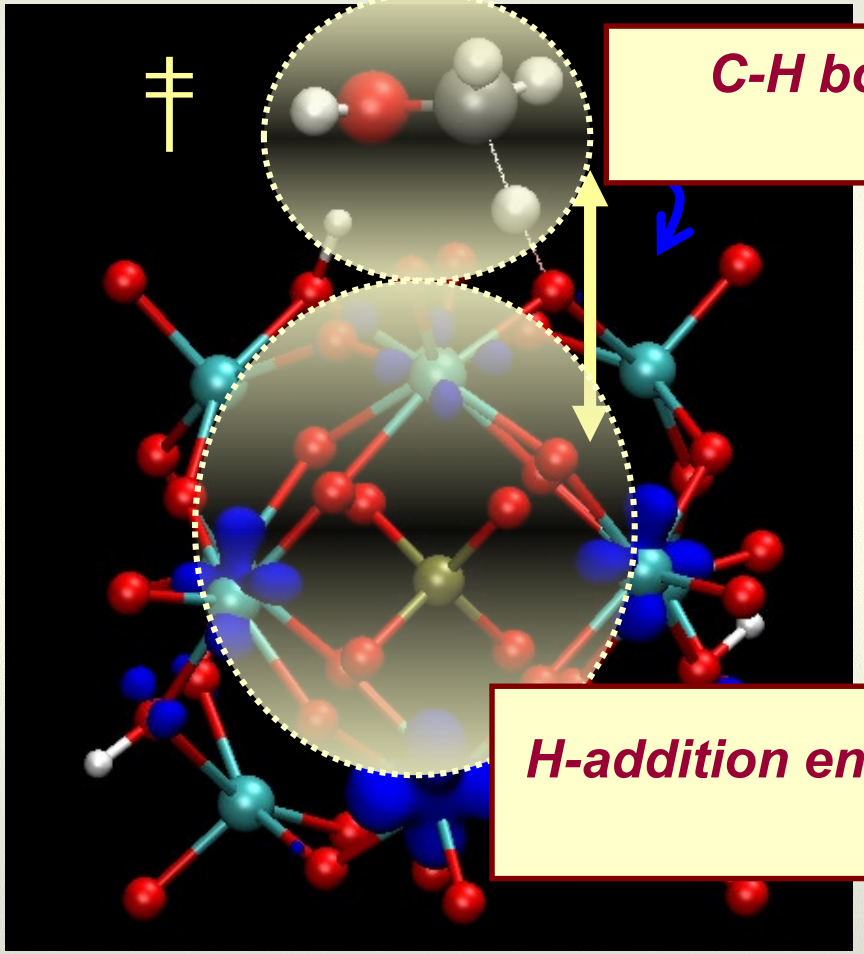
redox-active oxides
(H-atom transfer)



… "late" transition states with respect to transfer of H (to catalyst)

Reactivity Descriptors as Energies: Oxidation Catalysis

redox-active oxides
(H-atom transfer)



C-H bond energy

molecule

H-addition energy

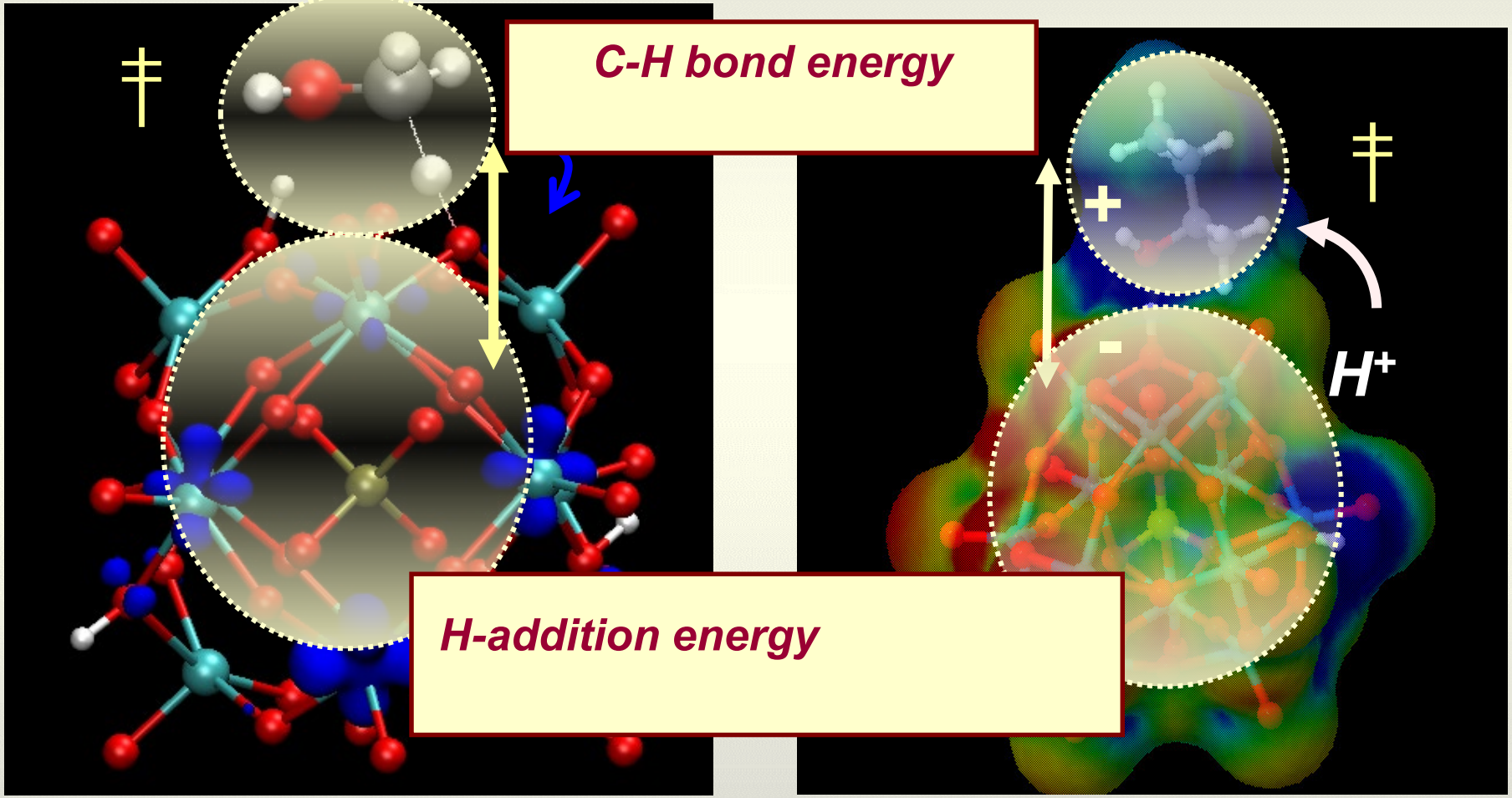
catalyst

… "late" transition states with respect to transfer of H (to catalyst)

Reactivity Descriptors as Energies: Catalysis on Solid Acids

redox-active oxides (H-atom transfer)

solid Brønsted acids (proton transfer)



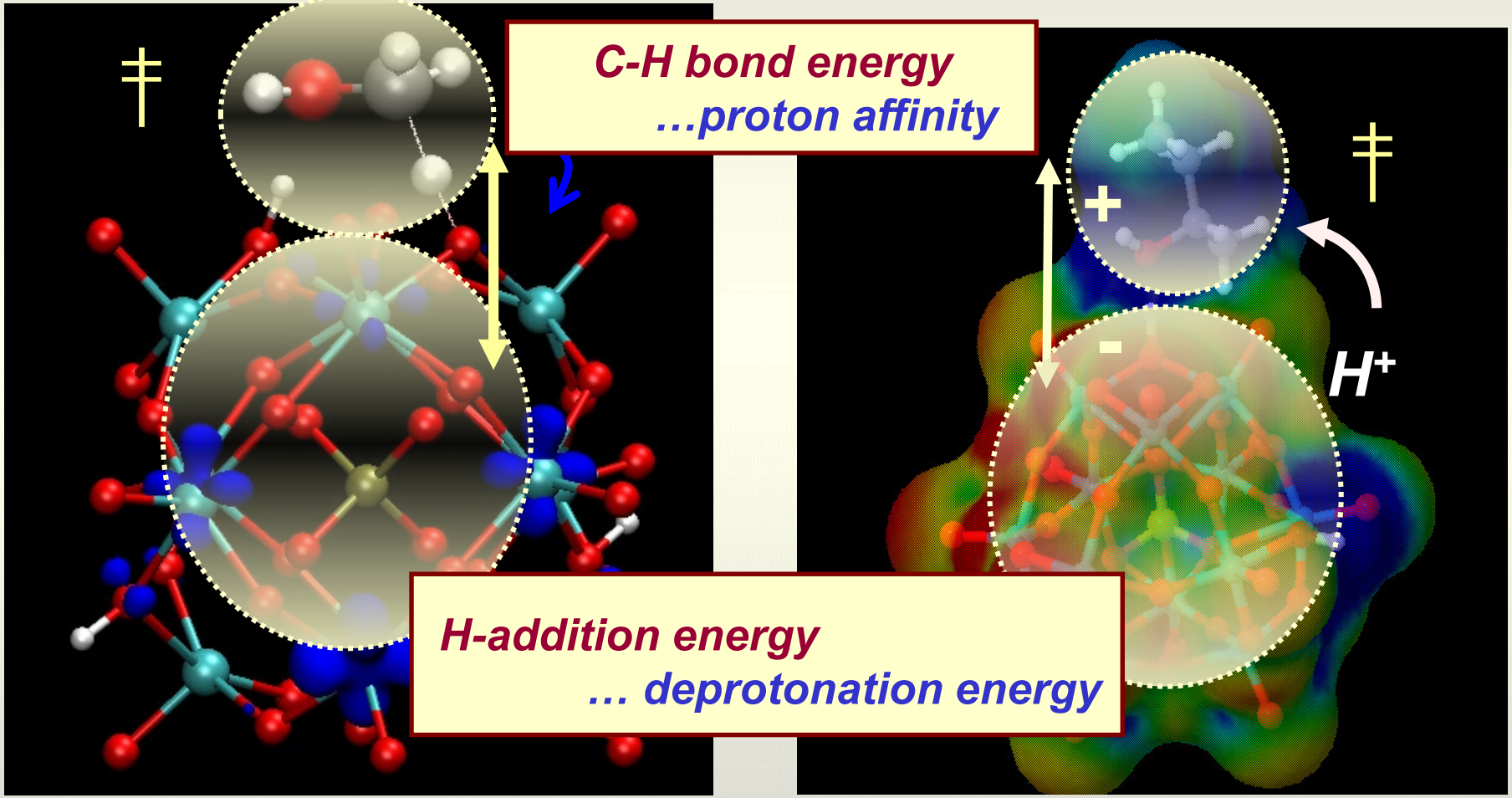
… "late" transition states with respect to transfer of H (to catalyst)

H^+ (from catalyst)

Reactivity Descriptors as Energies: Catalysis on Solid Acids

redox-active oxides (H-atom transfer)

solid Brønsted acids (proton transfer)



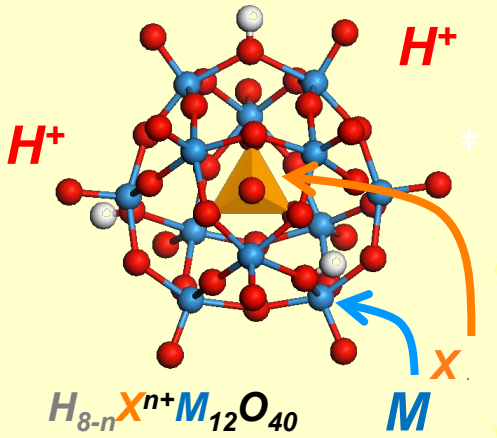
… "late" transition states with respect to transfer of H (to catalyst)

H^+ (from catalyst)

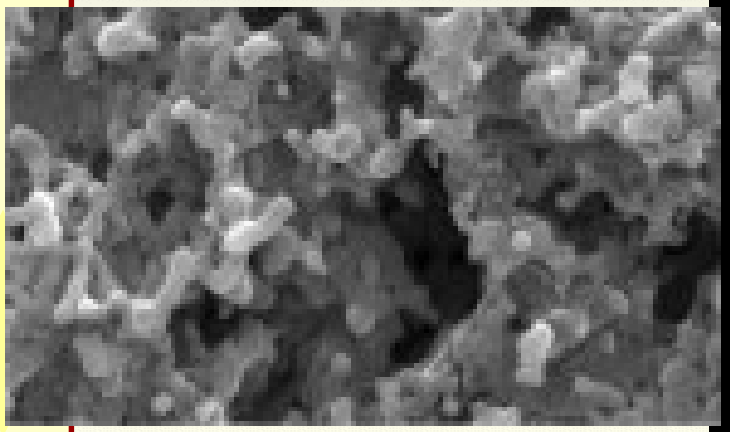
Reactivity Descriptors as Energies: Catalysis on Solid Acids

solid acids with known structure

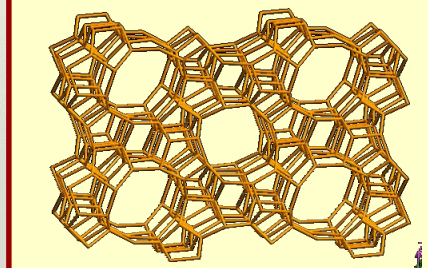
polyoxometalates

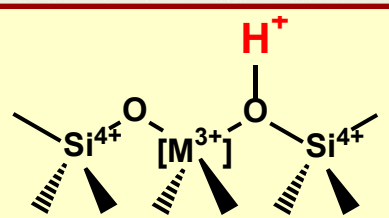


M = W X = P, Si, Co, Al



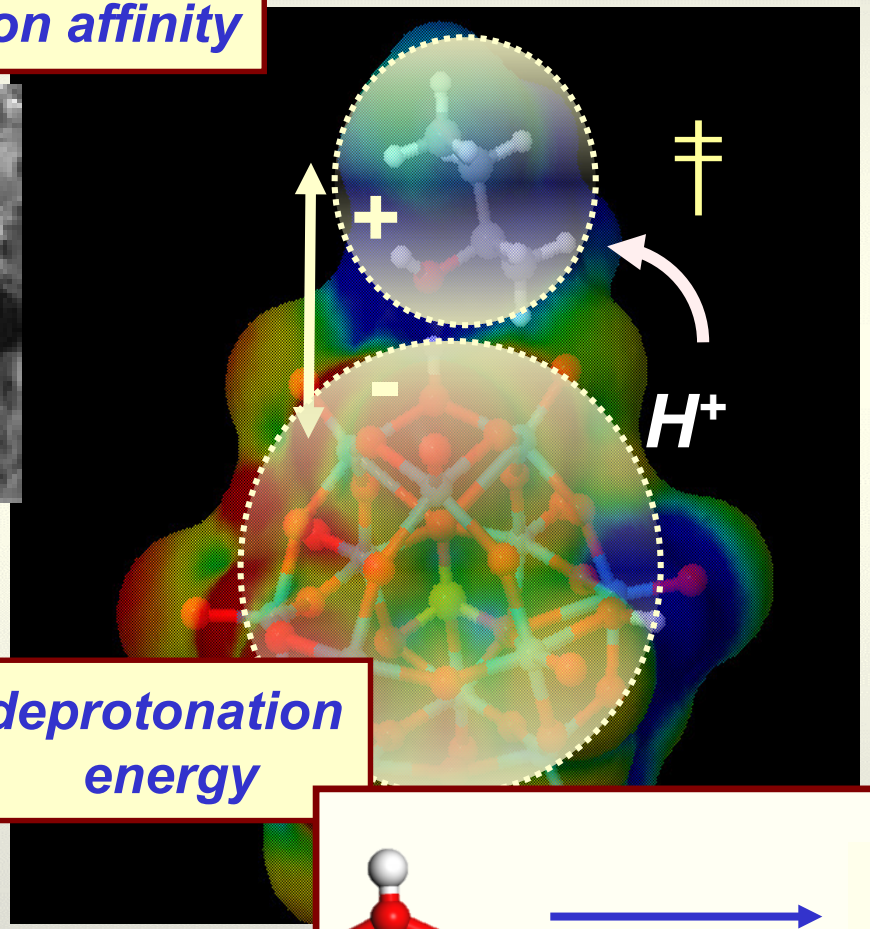
Crystalline/amorphous heterosilicates



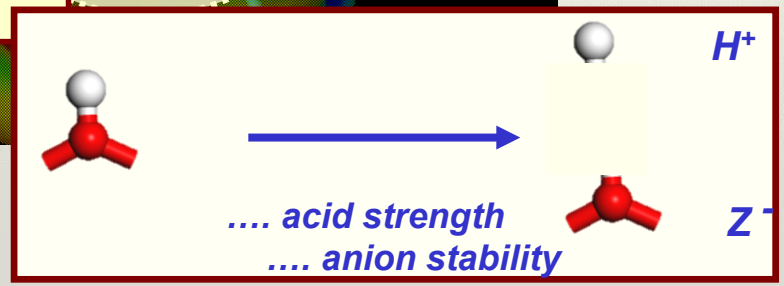


M = Al, Fe, Ga, B

proton affinity

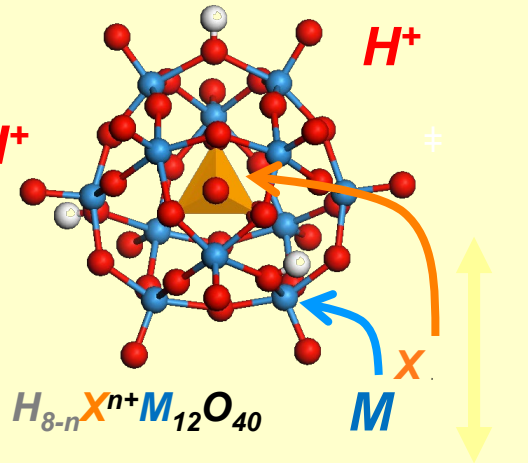


deprotonation energy



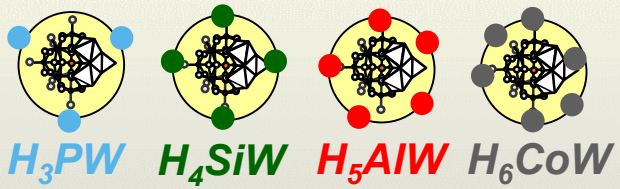
Reactivity Descriptors as Energies: Catalysis on Solid Acids

polyoxometalates

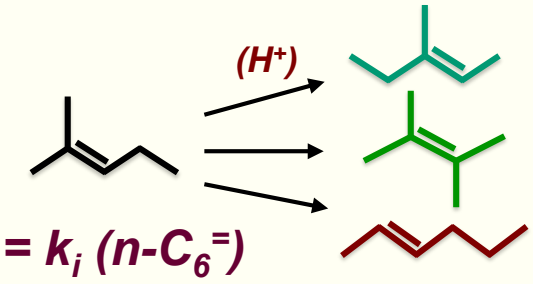


$H_{8-n}X^{n+}M_{12}O_{40}$

M = W X = P, Si, Co, Al



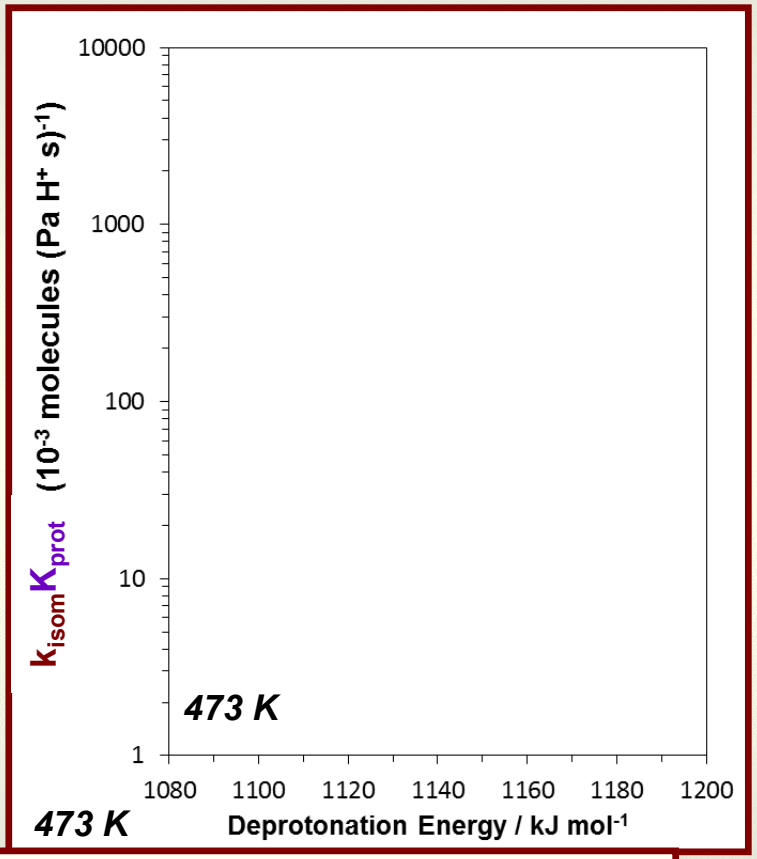
Skeletal rearrangements



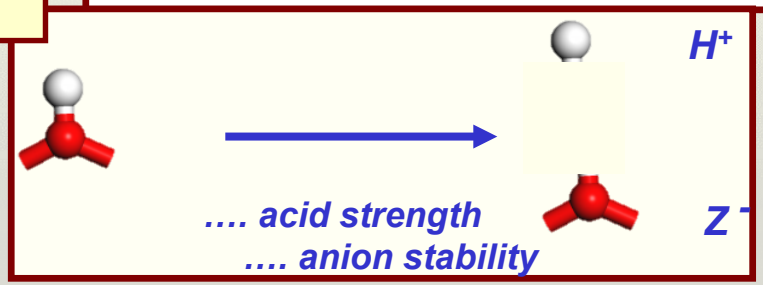
$r_i = k_i\ (n\text{-}C_6^=)$

$k = k_{isom}\ K_{ptrot}$

Reaction rate constant



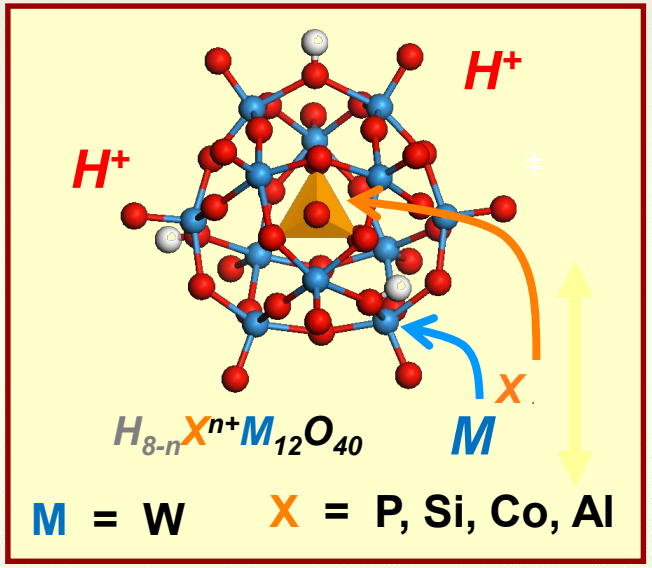
deprotonation energy

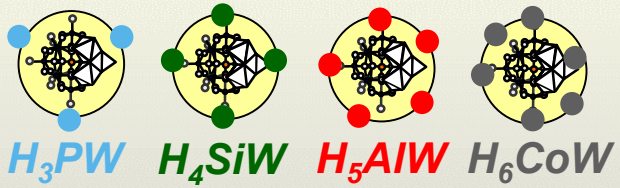


Will Knaeble

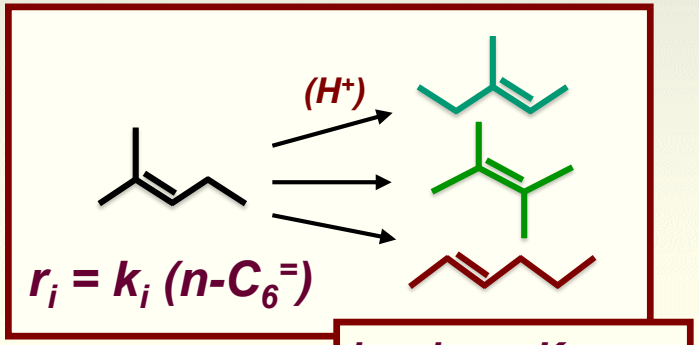
Reactivity Descriptors as Energies: Catalysis on Solid Acids

polyoxometalates

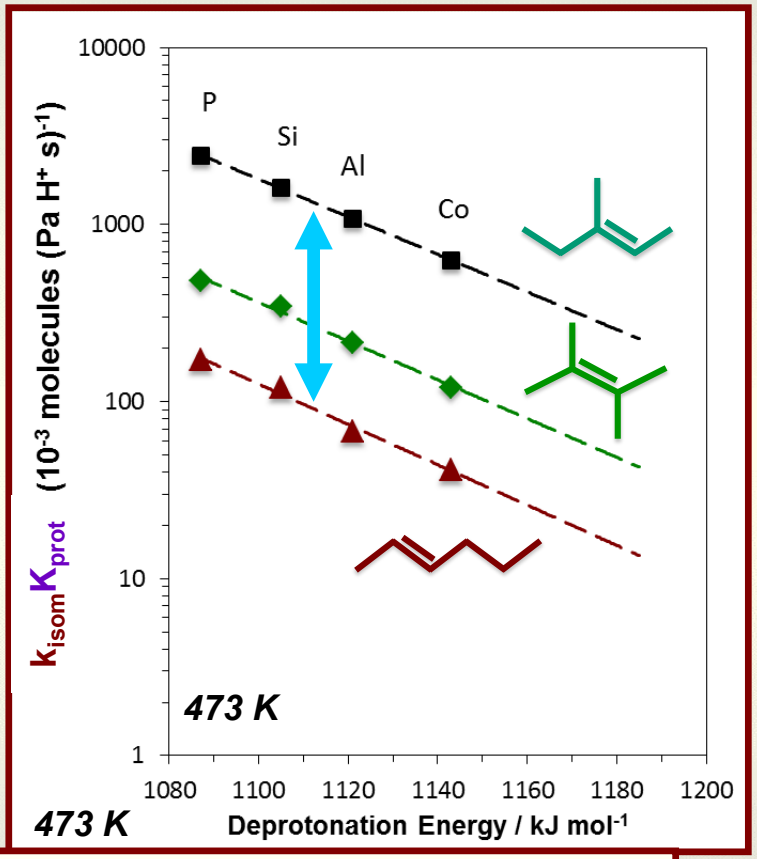




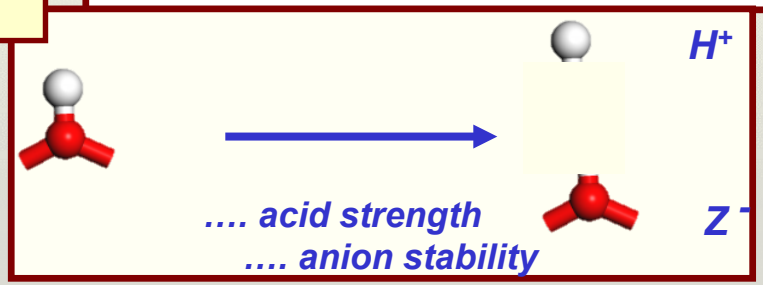
Skeletal rearrangements



Reaction rate constant

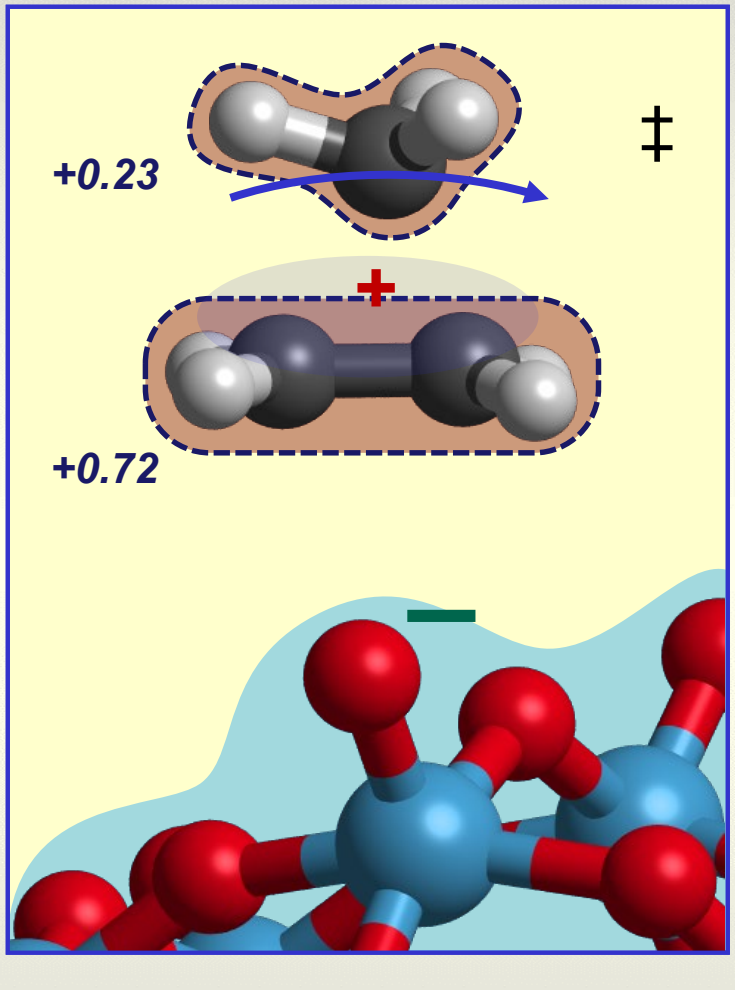


deprotonation energy

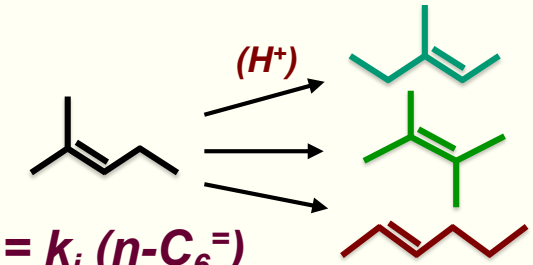


Will Knaeble

Reactivity Descriptors as Energies: Catalysis on Solid Acids



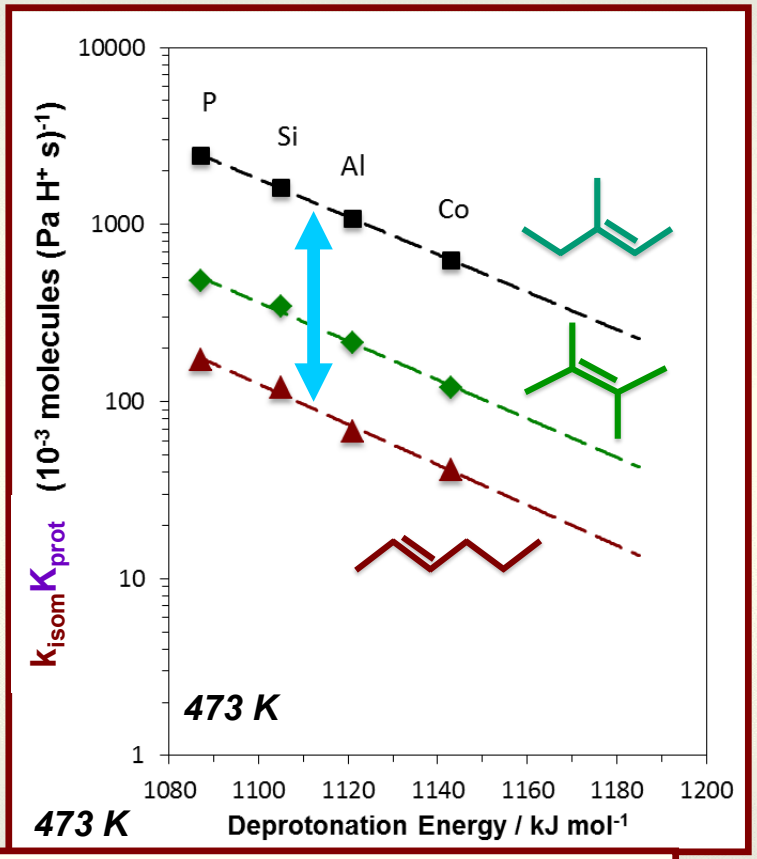
Skeletal rearrangements



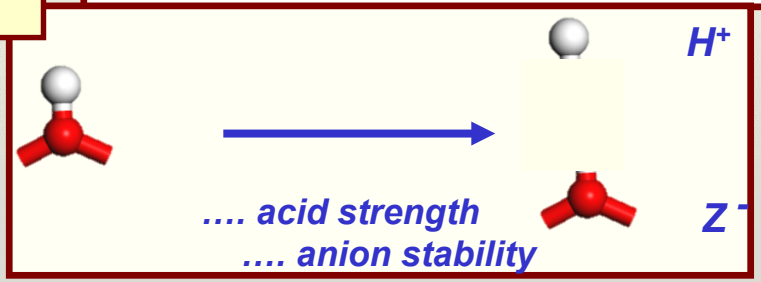
$r_i = k_i\ (n\text{-}C_6^=)$

$k = k_{isom}\ K_{ptrot}$

Reaction rate constant

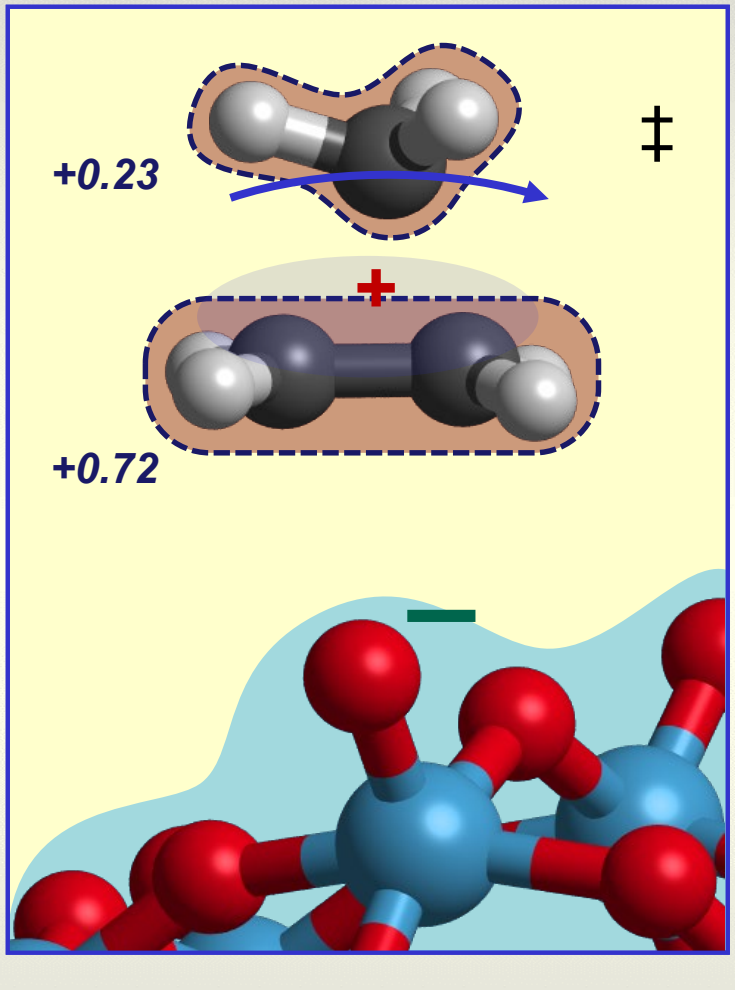


deprotonation energy



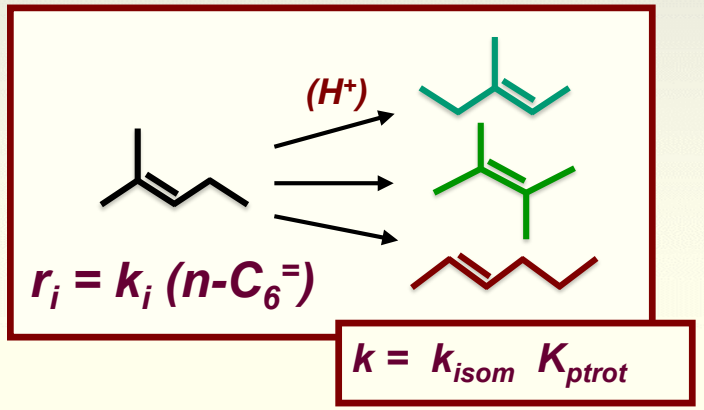
Will Knaeble

Reactivity Descriptors as Energies: Catalysis on Solid Acids

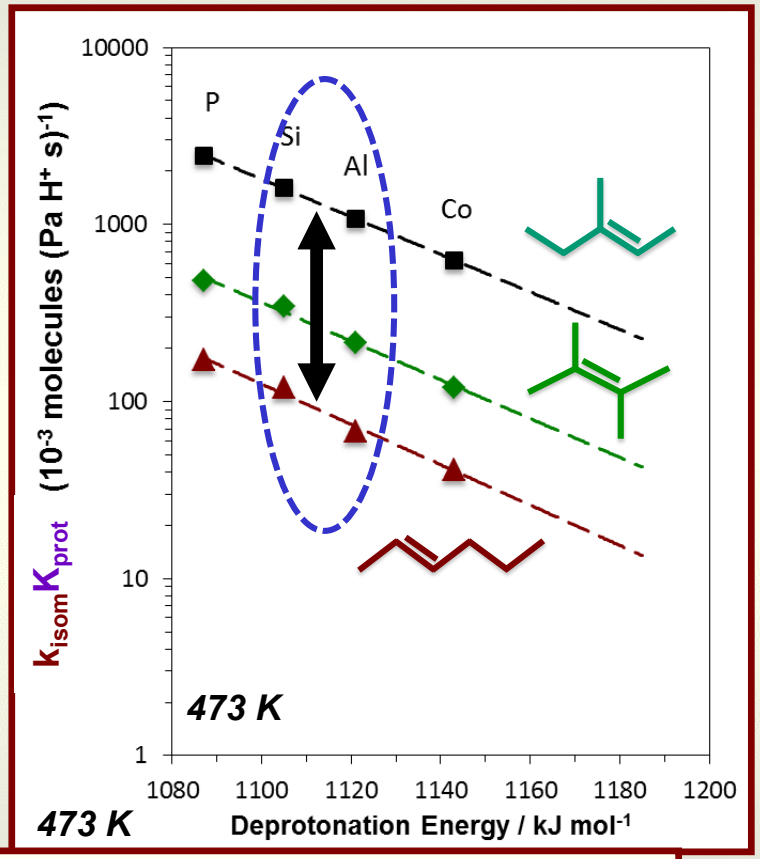


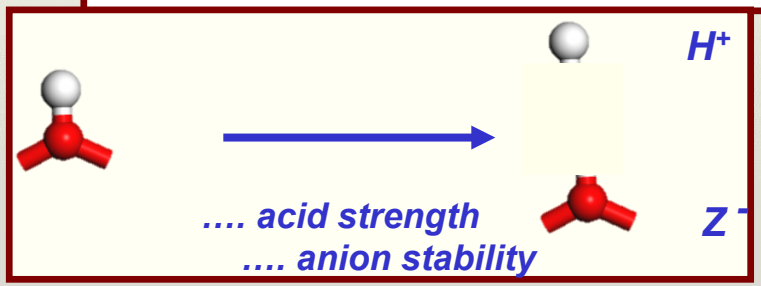
Will Knaeble

Skeletal rearrangements



Reaction rate constant



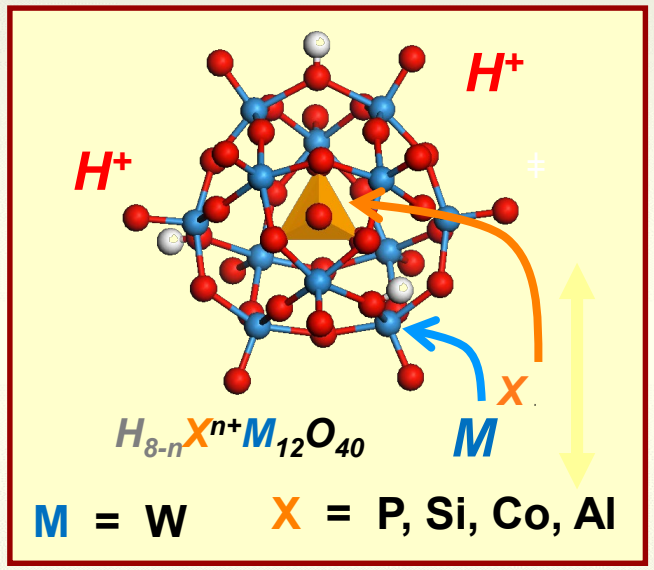


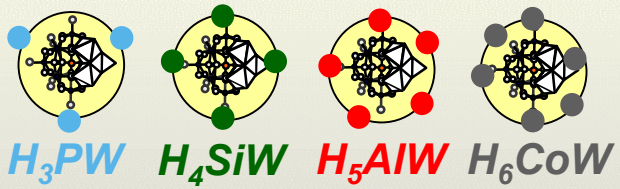
Combining the binding point and its environment ……

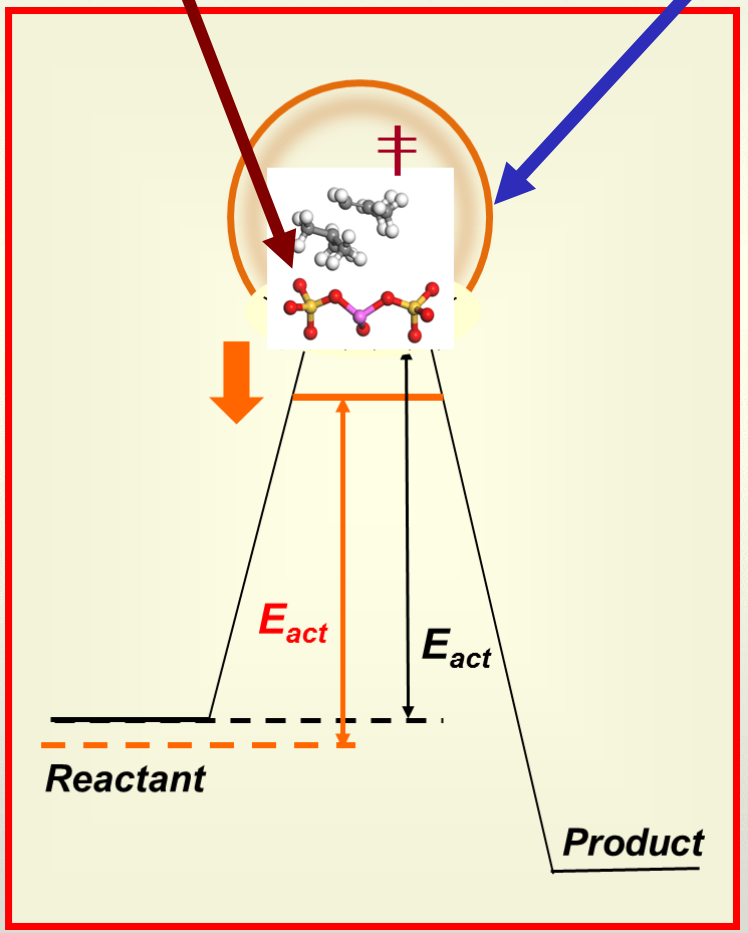
Construct and probe specific "binding points"

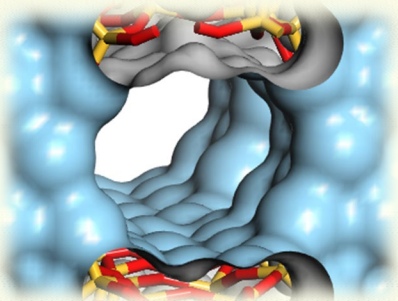
Design solvating environments around "binding points"

polyoxometalates









voids

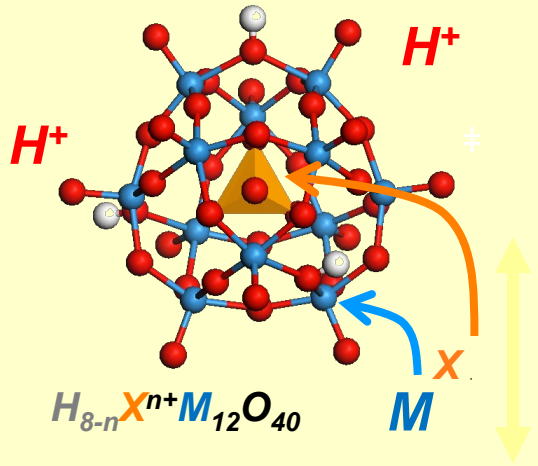
Combining the binding point and its environment ……

Michele Sarazen

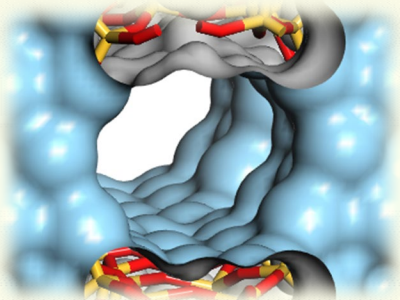
Construct and probe specific "binding points"

Design solvating environments around "binding points"

polyoxometalates

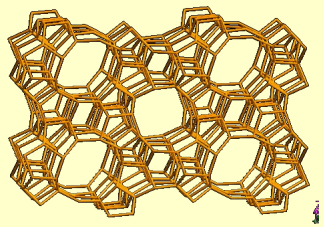


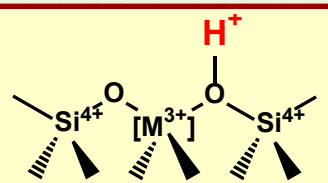
M = W X = P, Si, Co, Al



voids

crystalline heterosilicates



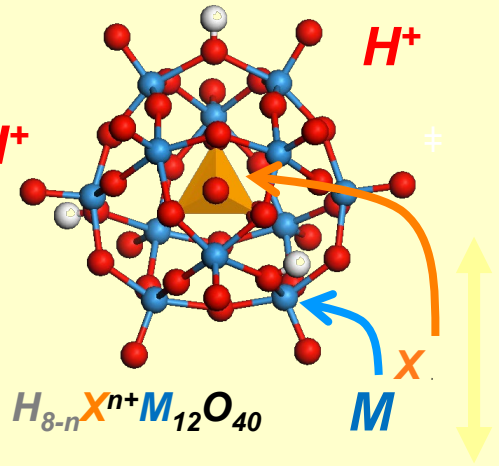


M= Al,Fe,Ga,B

Forming new carbon-carbon bonds on solid acid catalysts …….

Michele Sarazen

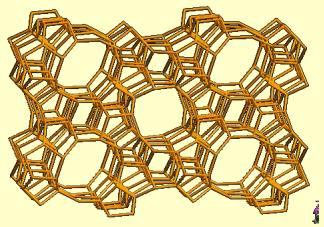
polyoxometalates

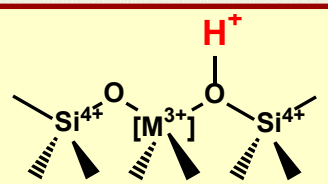


$H_{8-n}X^{n+}M_{12}O_{40}$

M = W X = P, Si, Co, Al

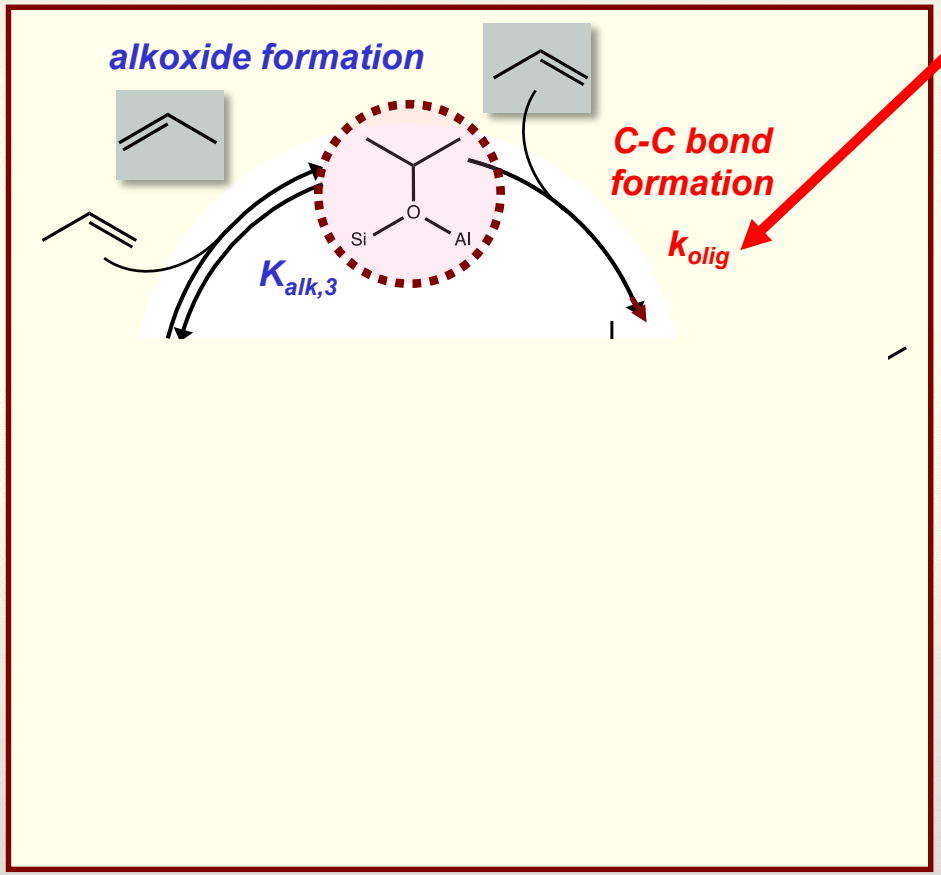
crystalline heterosilicates





M= Al,Fe,Ga,B

alkene dimerization on solid acids

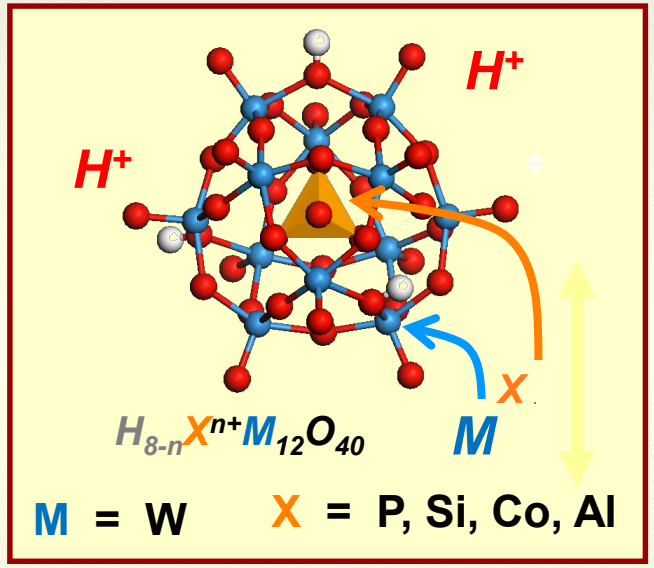


$r_{olig} = k_{oliig}$ (propene)

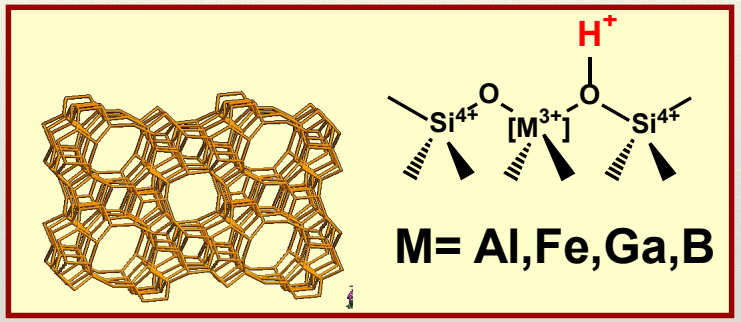
Forming new carbon-carbon bonds on solid acid catalysts …….

Michele Sarazen

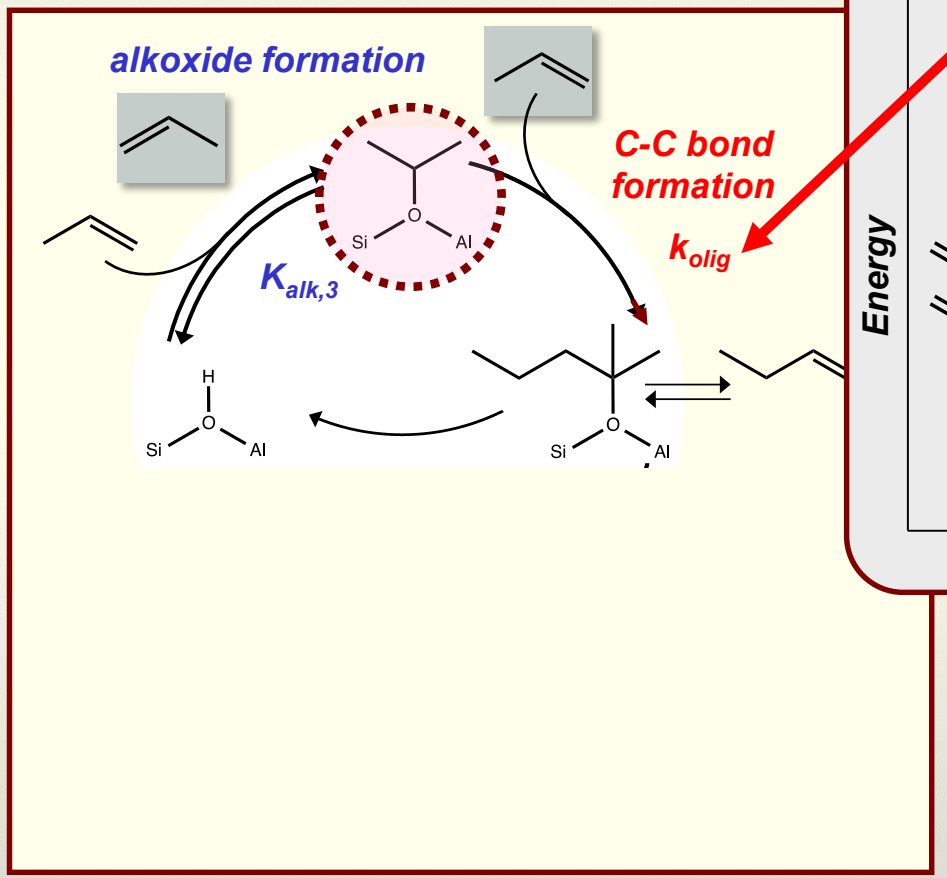
polyoxometalates



crystalline heterosilicates

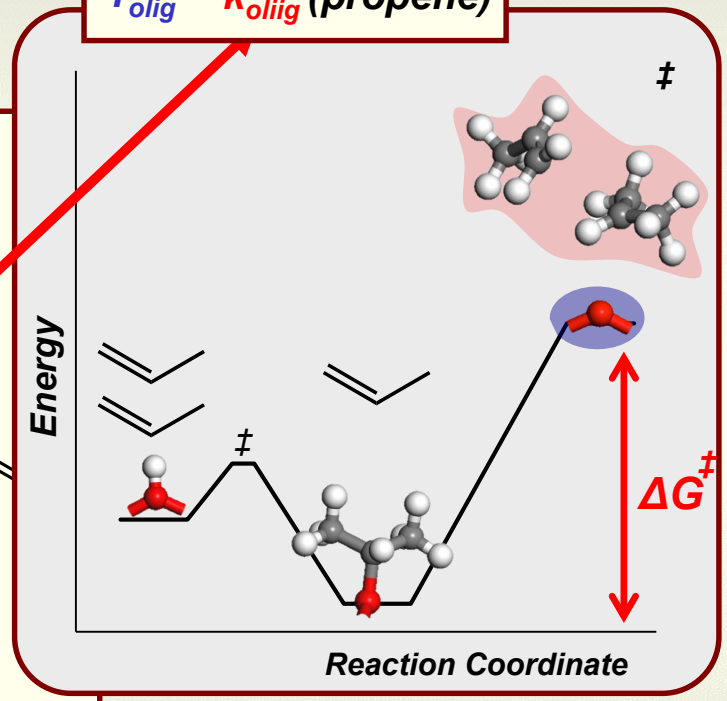


alkene dimerization on solid acids



$k_{olig} \sim exp(-\Delta G^{\ddagger}/RT)$

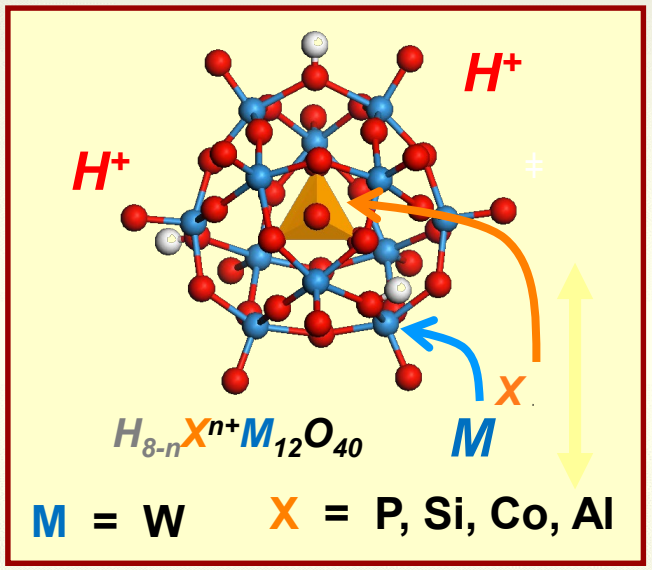
$r_{olig} = k_{oliig}$ (propene)



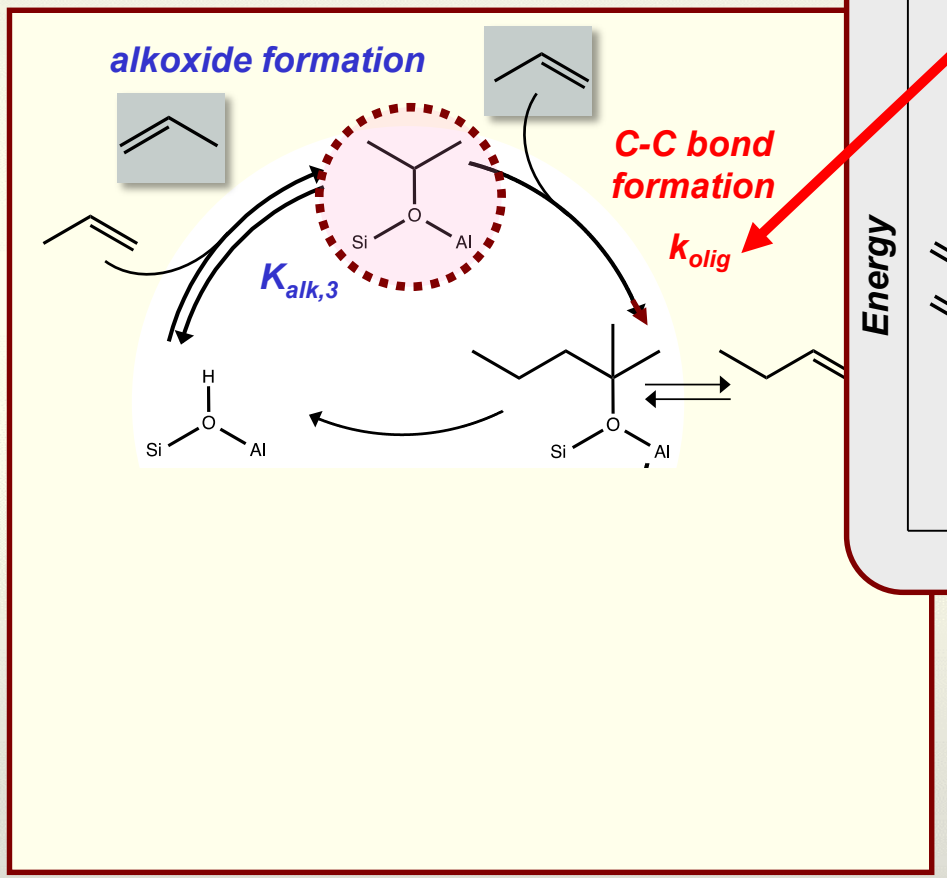
Forming new carbon-carbon bonds on solid acid catalysts …….

Michele Sarazen

polyoxometalates

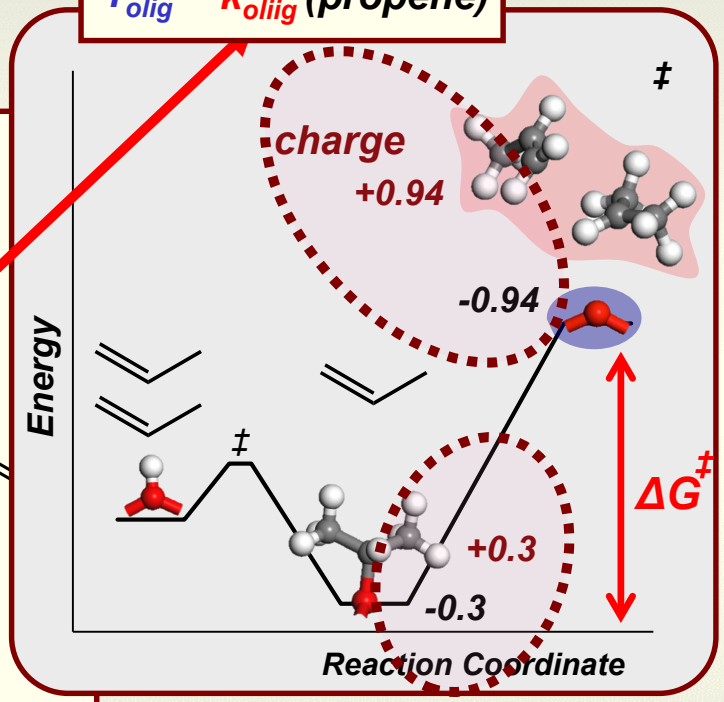


alkene dimerization on solid acids



$k_{olig} \sim exp(-\Delta G^{\ddagger}/RT)$

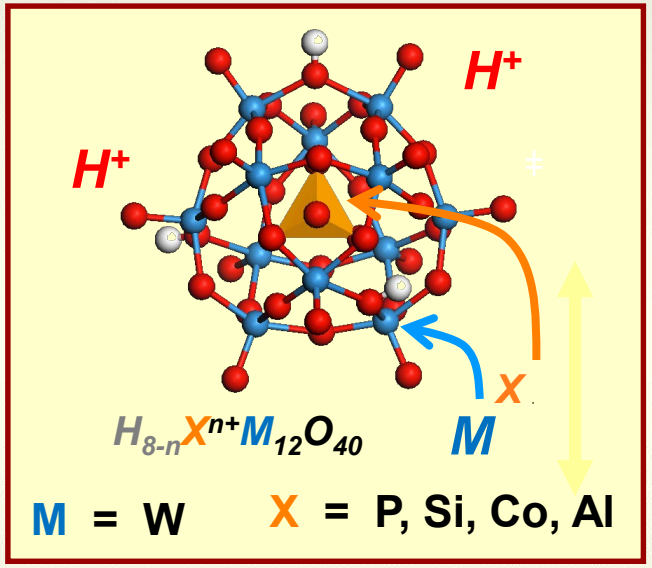
$r_{olig} = k_{oliig}$ (propene)



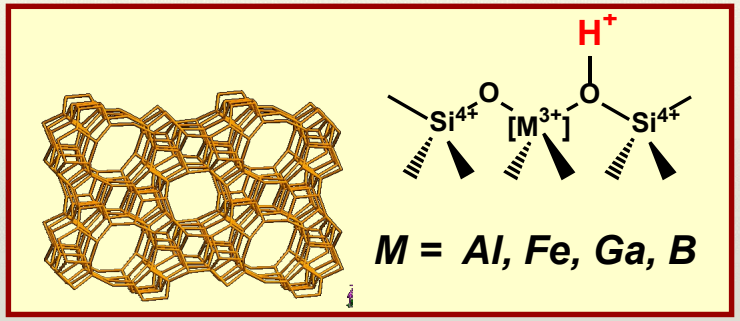
Forming new carbon-carbon bonds on solid acid catalysts …….

Michele Sarazen

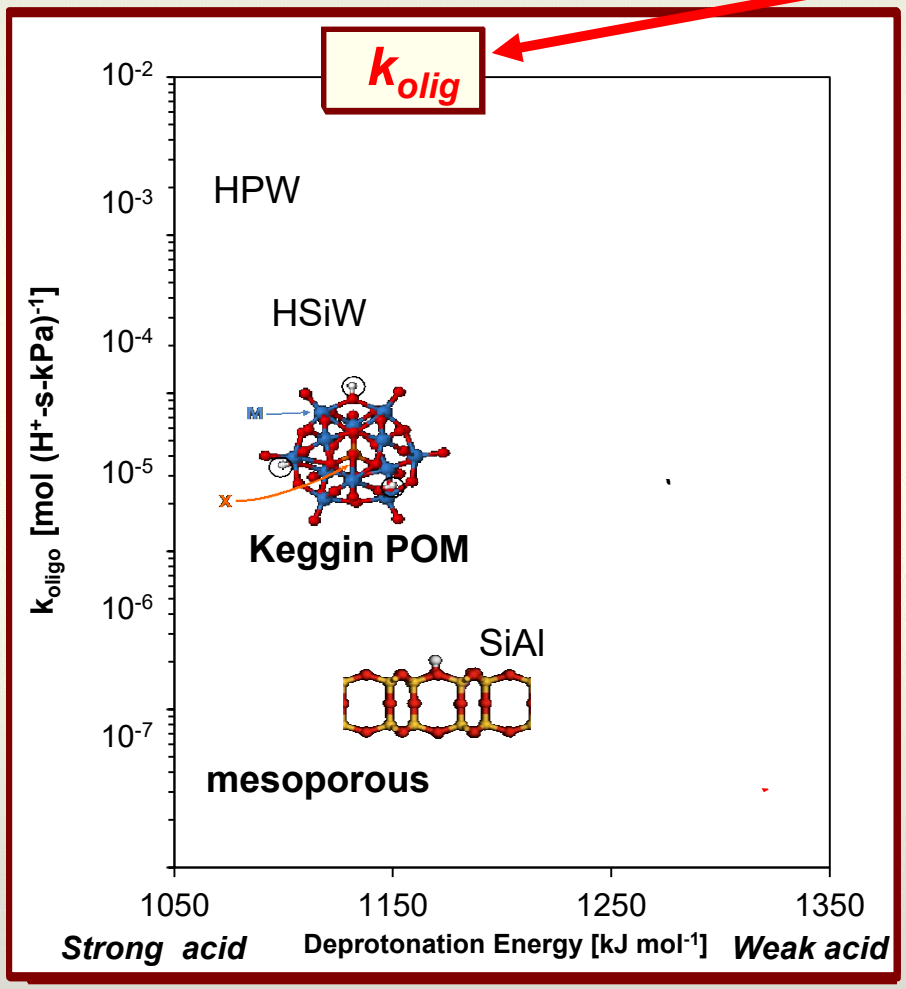
polyoxometalates



crystalline heterosilicates

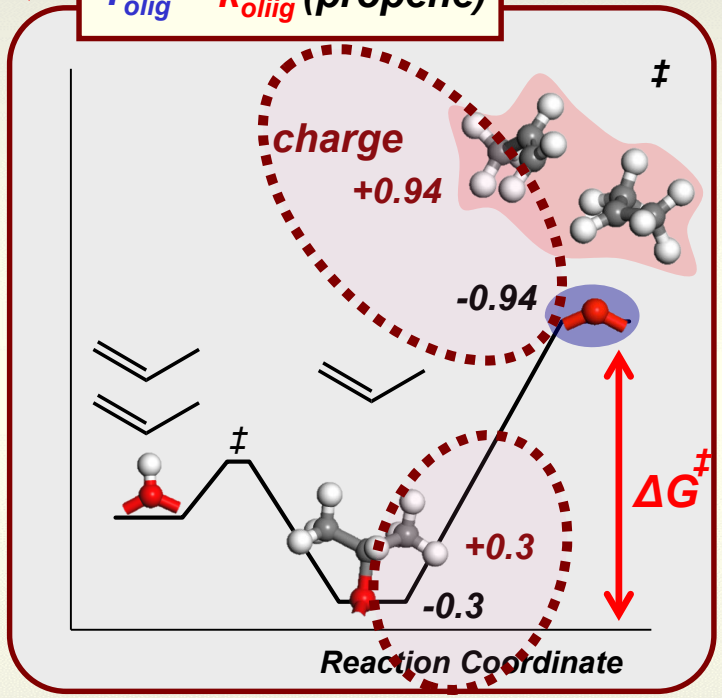


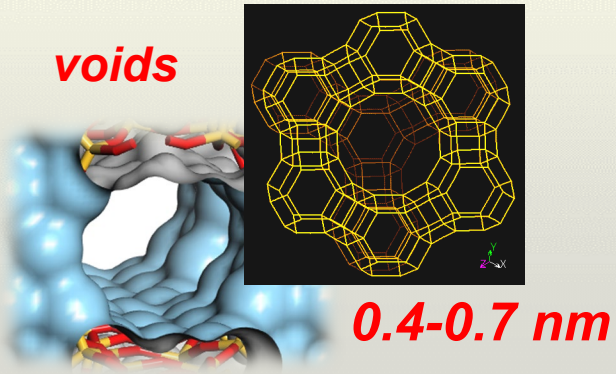
Acid strength effects on k_{olig}



$k_{olig} \sim exp(-\Delta G^{\ddagger}/RT)$

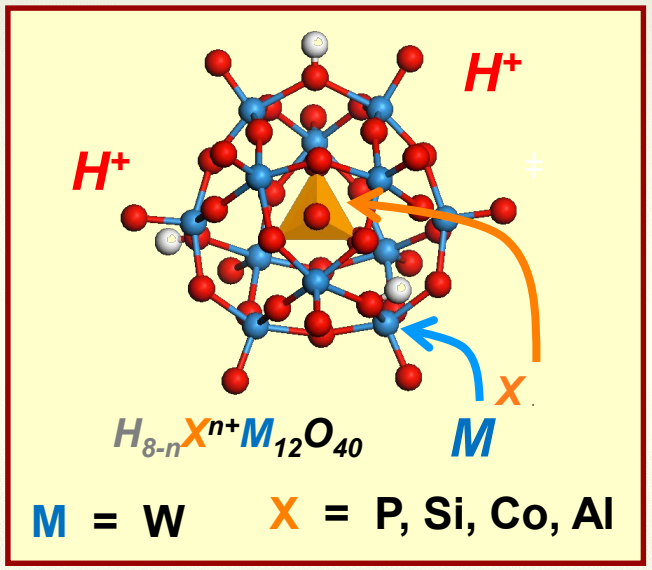
$r_{olig} = k_{oliig}$ (propene)





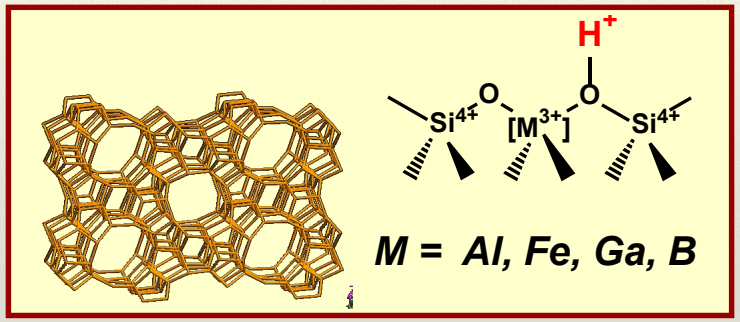
..... the combined effects of confinement and acid strength

polyoxometalates



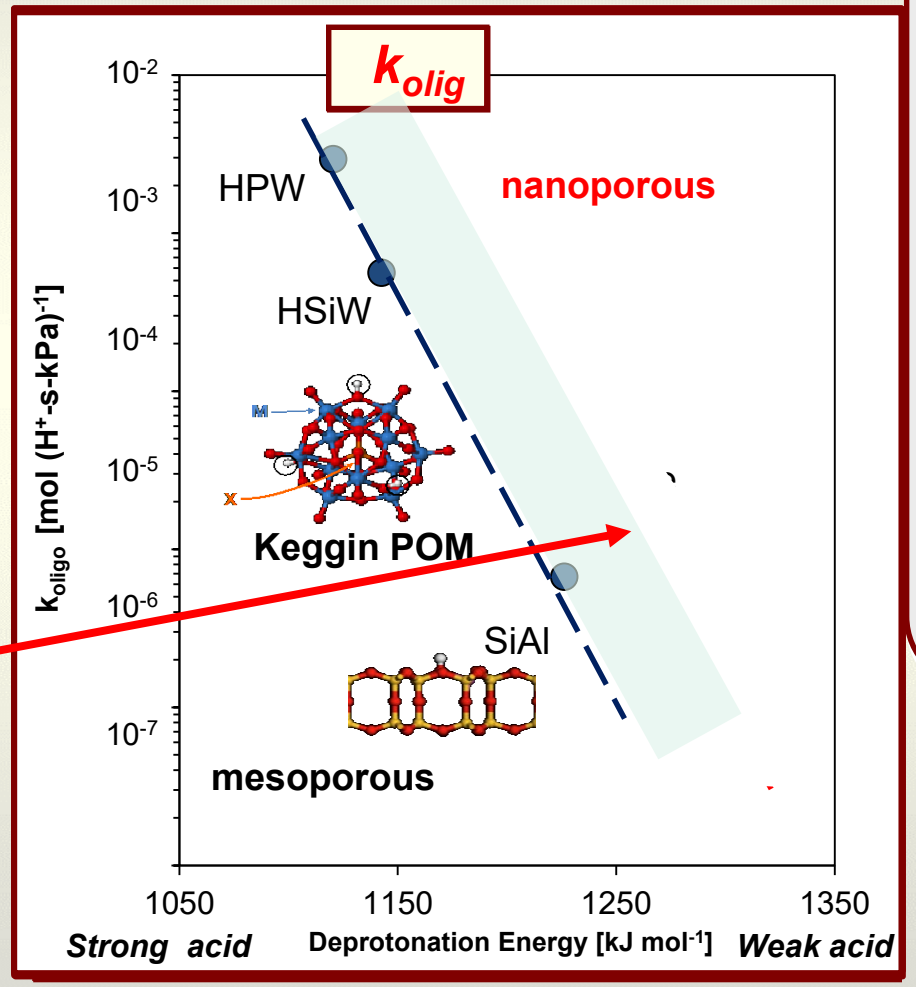
M = W X = P, Si, Co, Al

crystalline heterosilicates

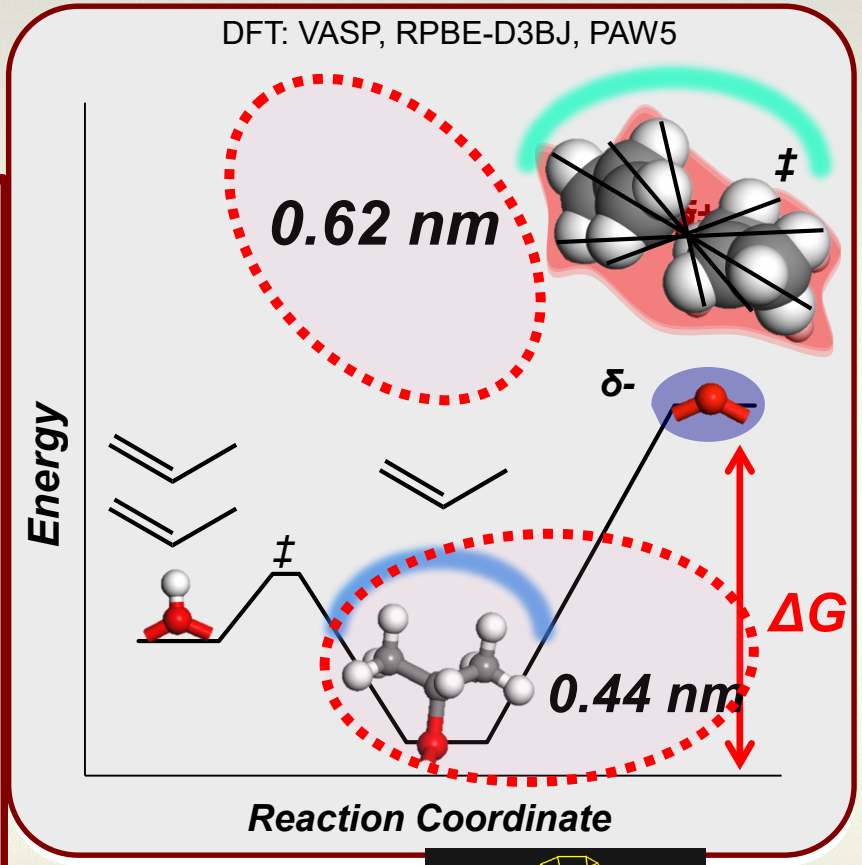


M = Al, Fe, Ga, B

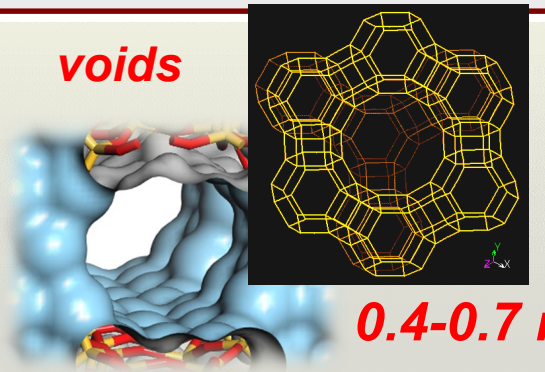
Acid strength effects on k_{olig}



DFT: VASP, RPBE-D3BJ, PAW5



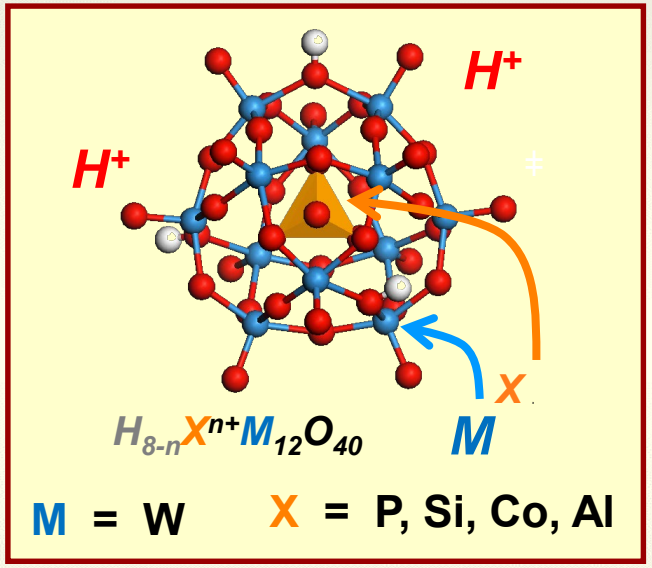
voids



0.4-0.7 nm

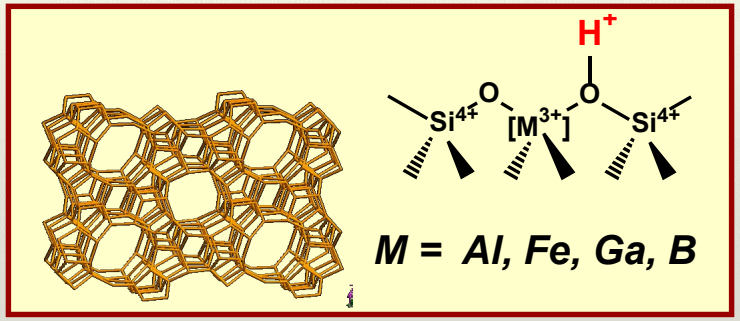
..... the combined effects of confinement and acid strength

polyoxometalates



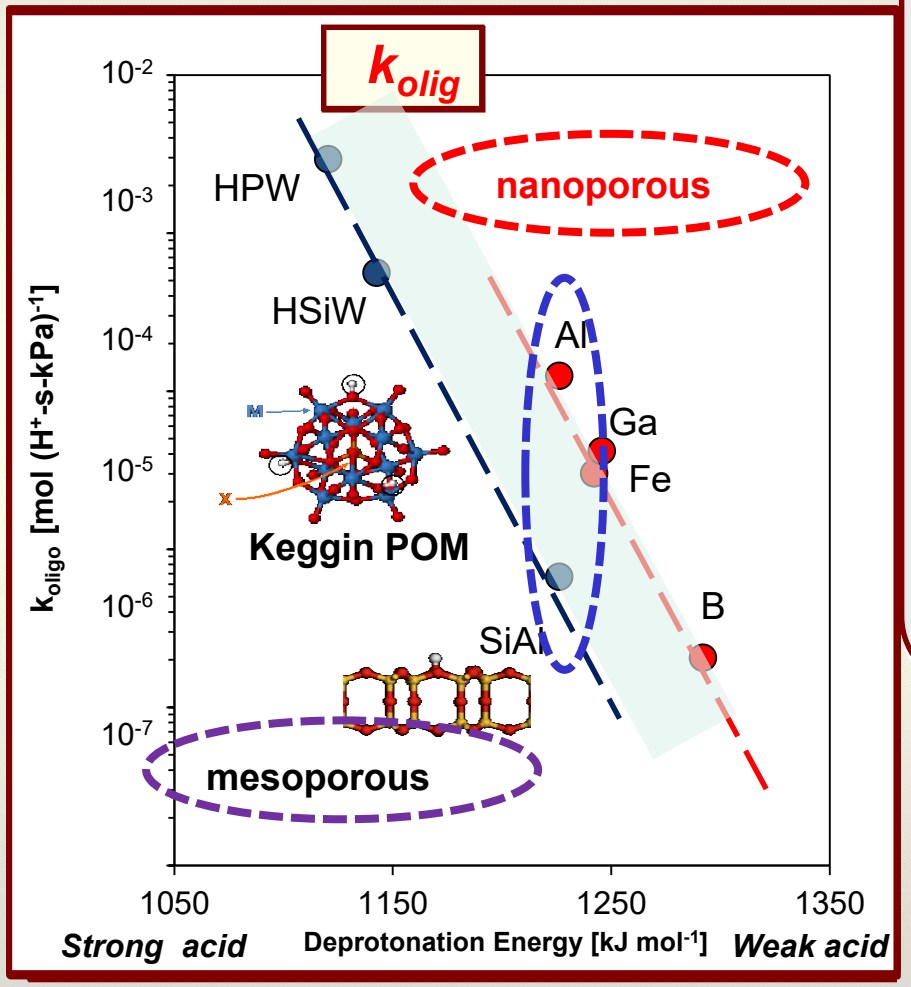
M = W X = P, Si, Co, Al

crystalline heterosilicates

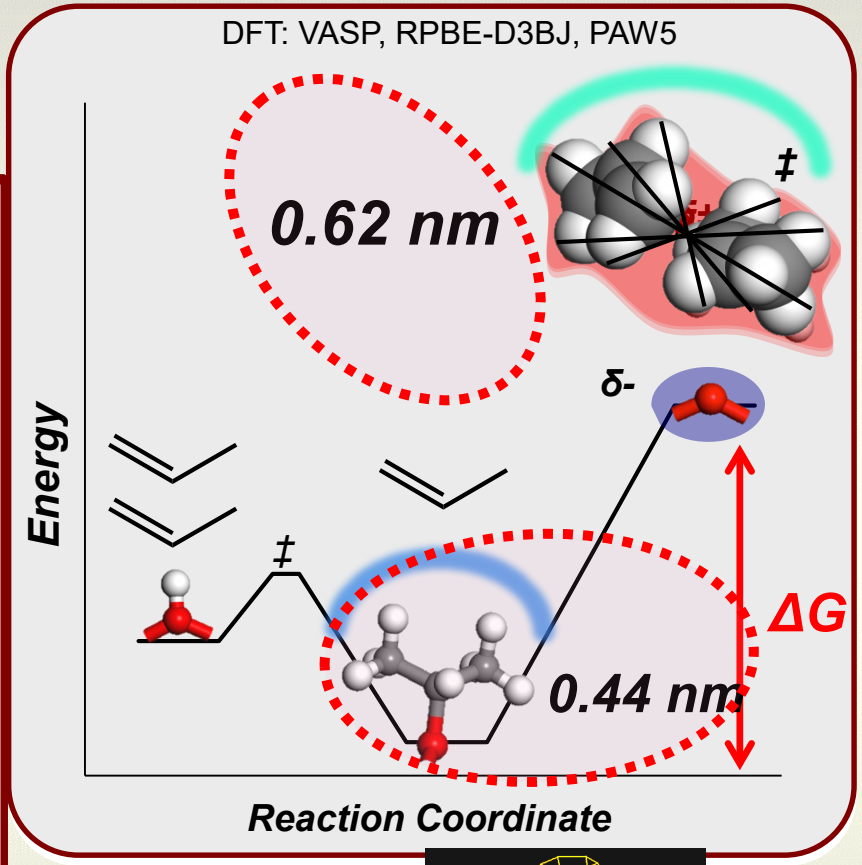


M = Al, Fe, Ga, B

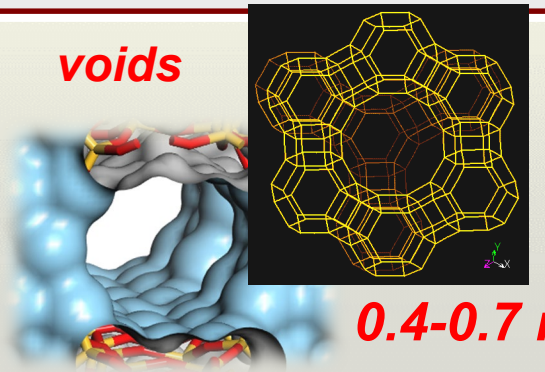
Acid strength effects on k_{olig}



DFT: VASP, RPBE-D3BJ, PAW5



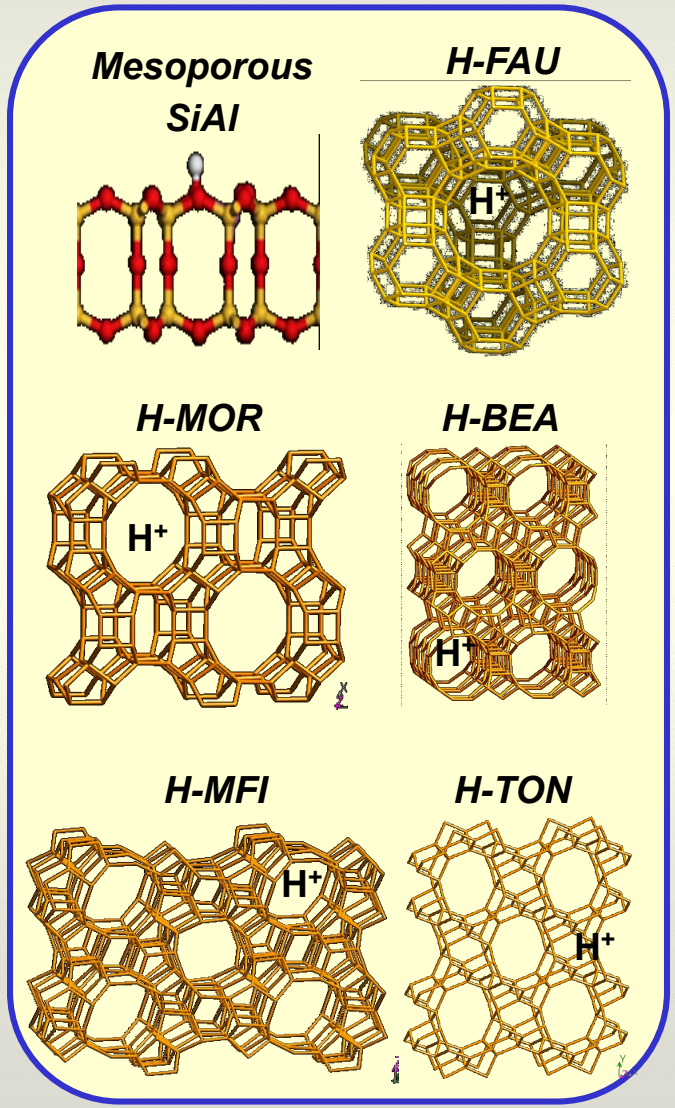
voids



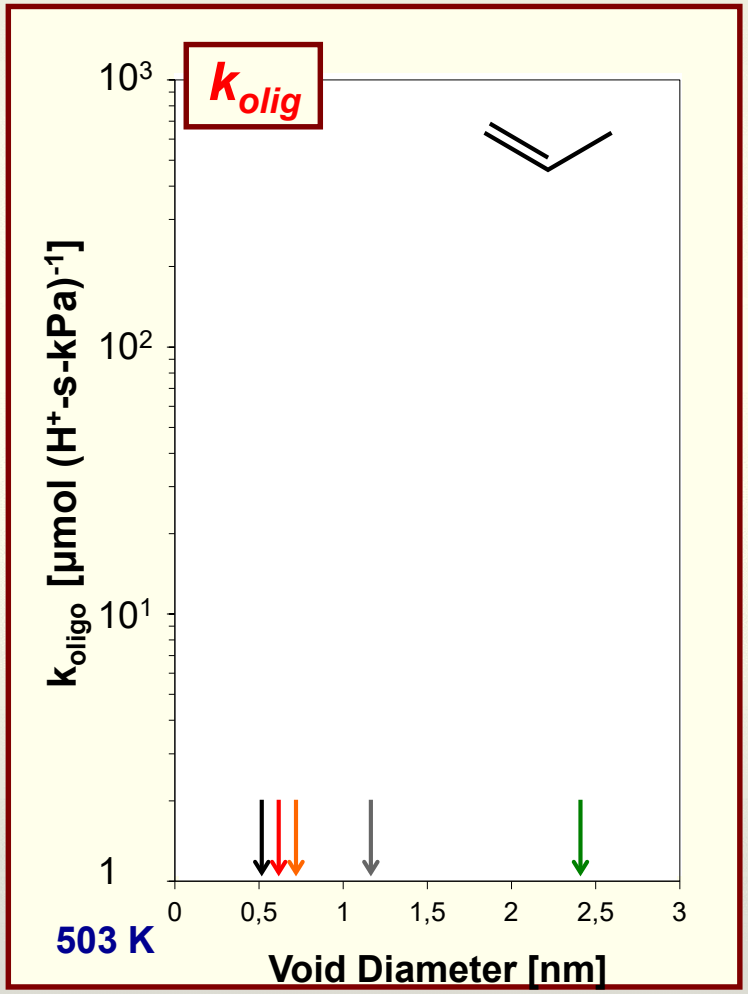
0.4-0.7 nm

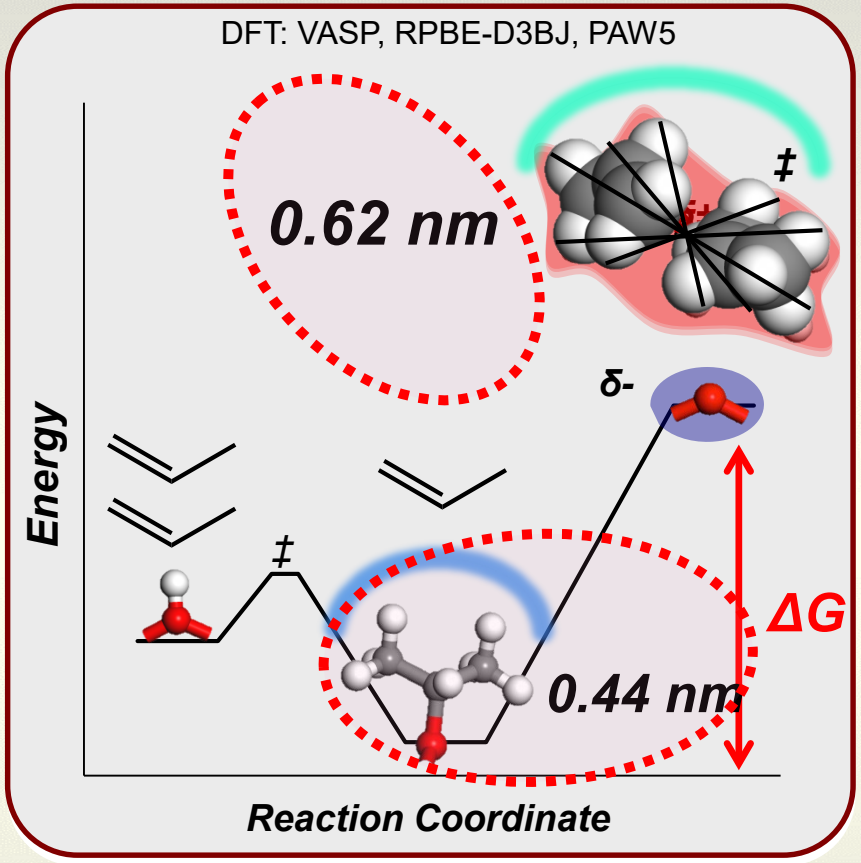
..... same binding point (acid strength) .... diverse confining voids

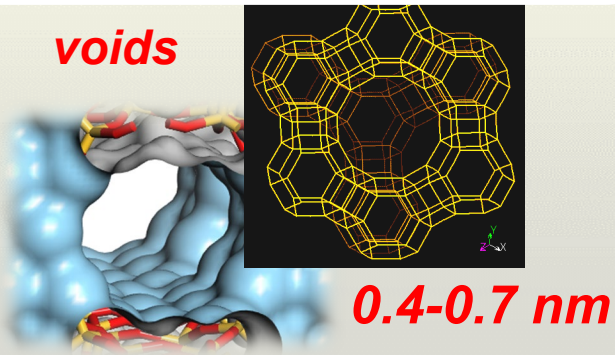
similar acid strength
different confinement environments



Void size effects on k_{olig}







C-C bond formation from alkenes: confinement effects for aluminosilicates of similar acid strength

Michele Sarazen

similar acid strength
different confinement environments

Mesoporous SiAl

H-FAU

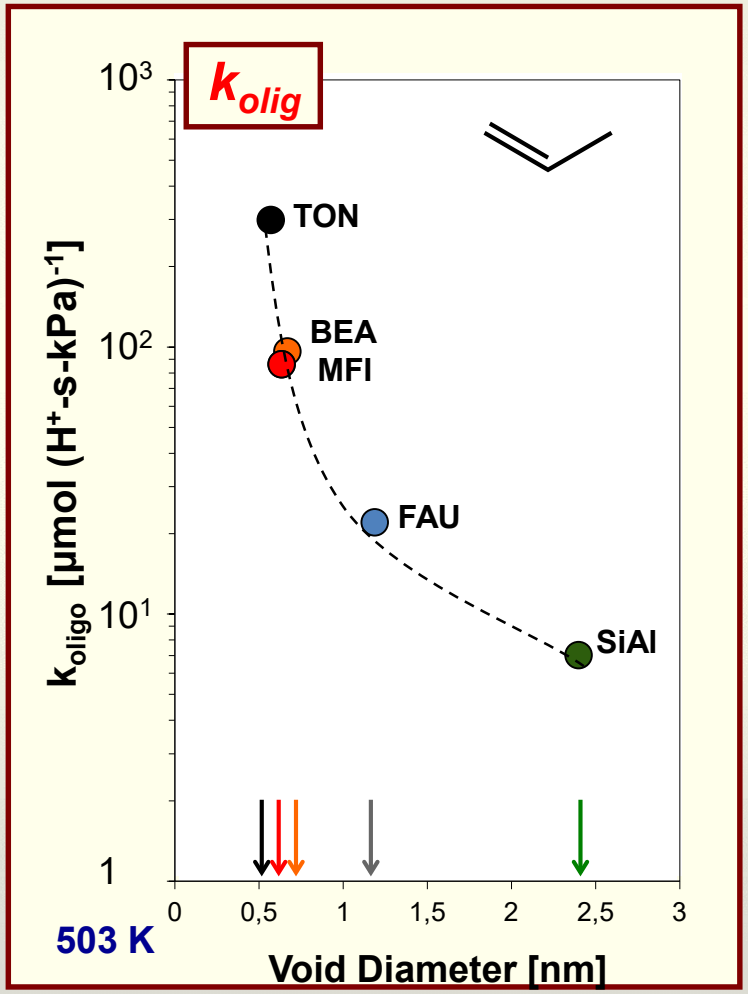
H-MOR

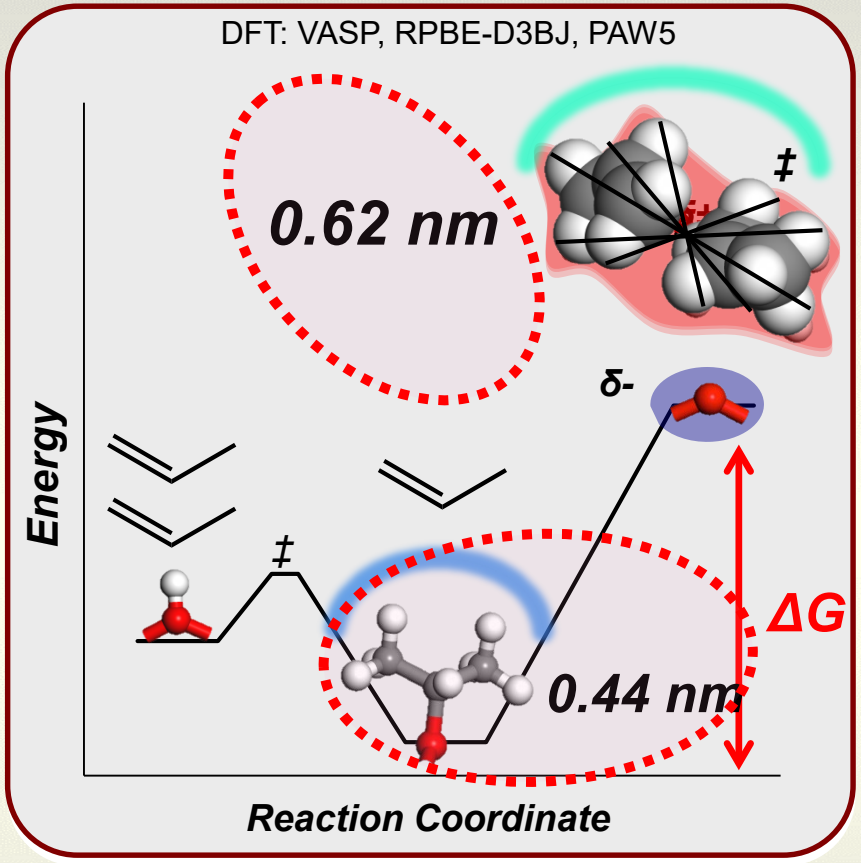
H-BEA

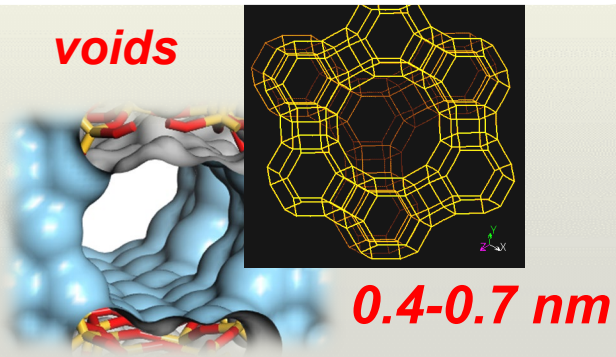
H-MFI

H-TON

Void size effects on k_{olig}

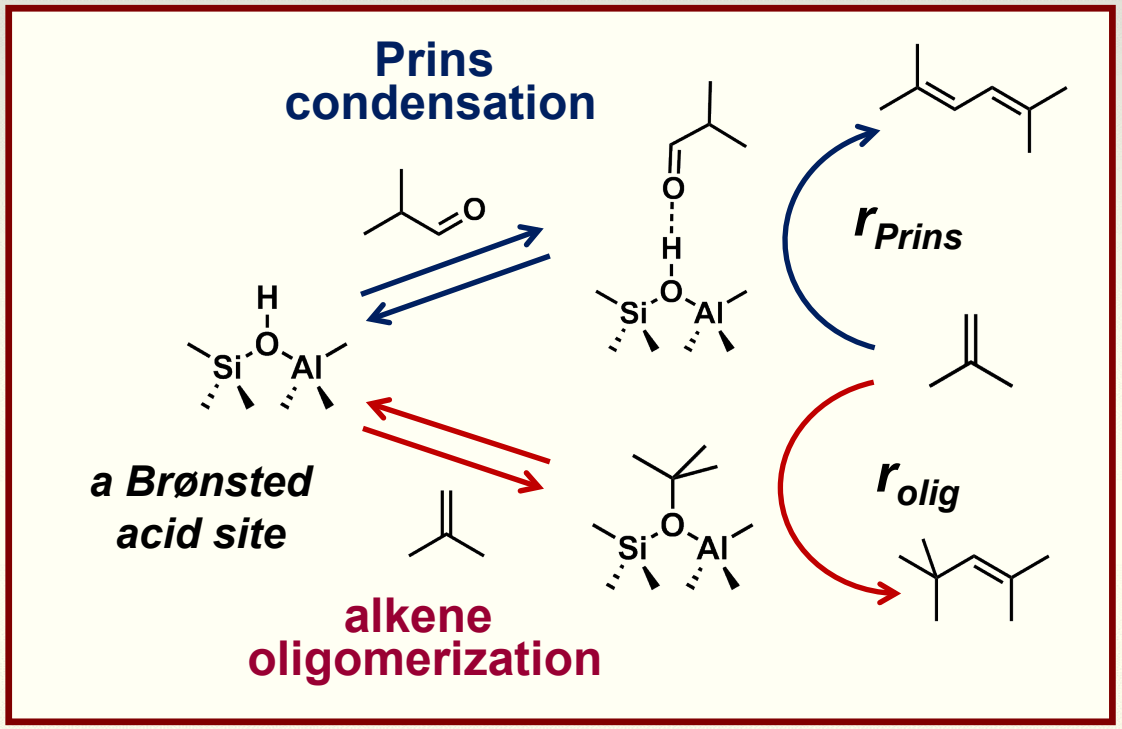






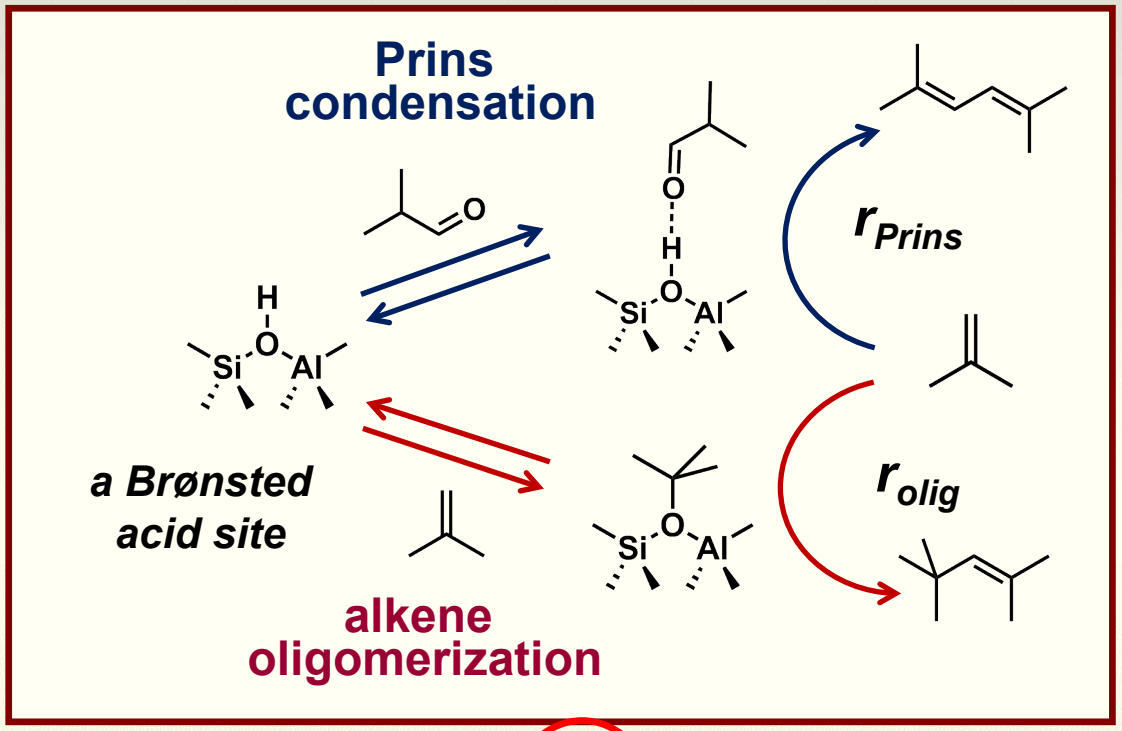
Reactivity and selectivity in alkene-alkanal reactions …..
when acid strength matters <u>for selectivity</u> ……

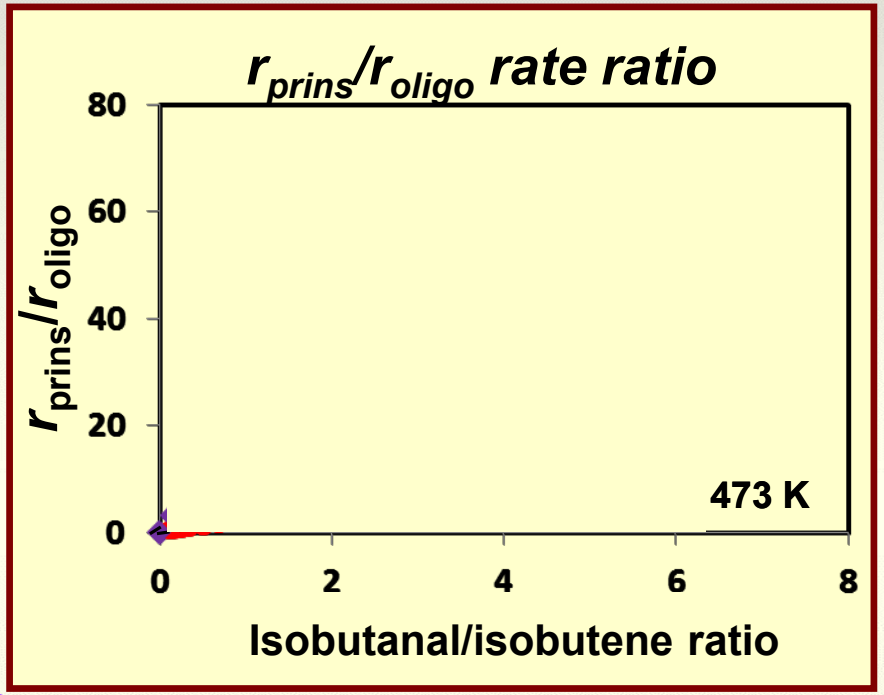
Reactivity and selectivity in alkene-alkanal reactions …..
when acid strength matters <u>for selectivity</u> ……

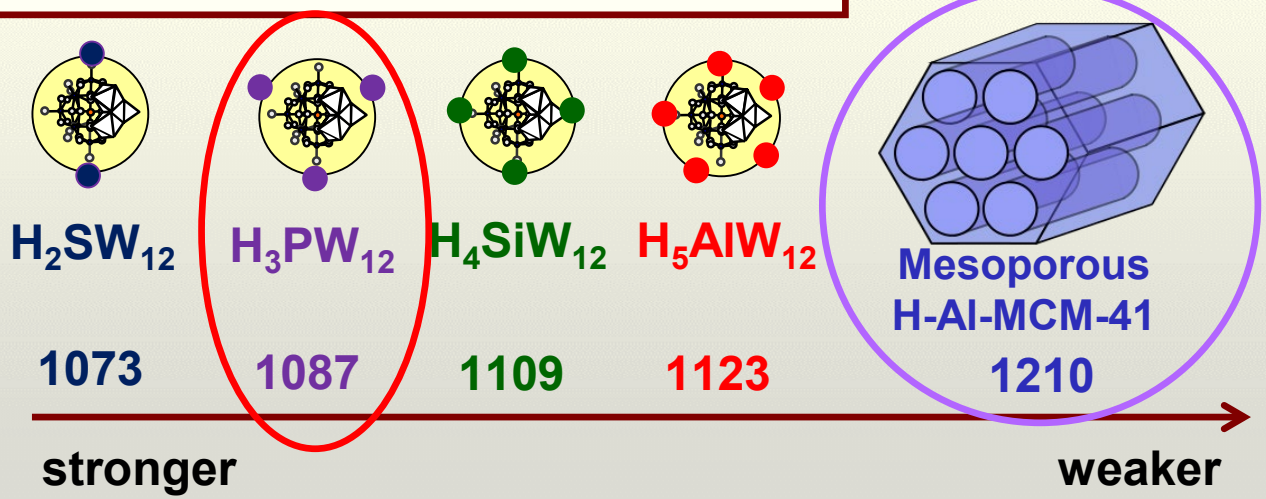


Shuai Wang

Reactivity and selectivity in alkene-alkanal reactions ….. when acid strength matters <u>for selectivity</u> ……



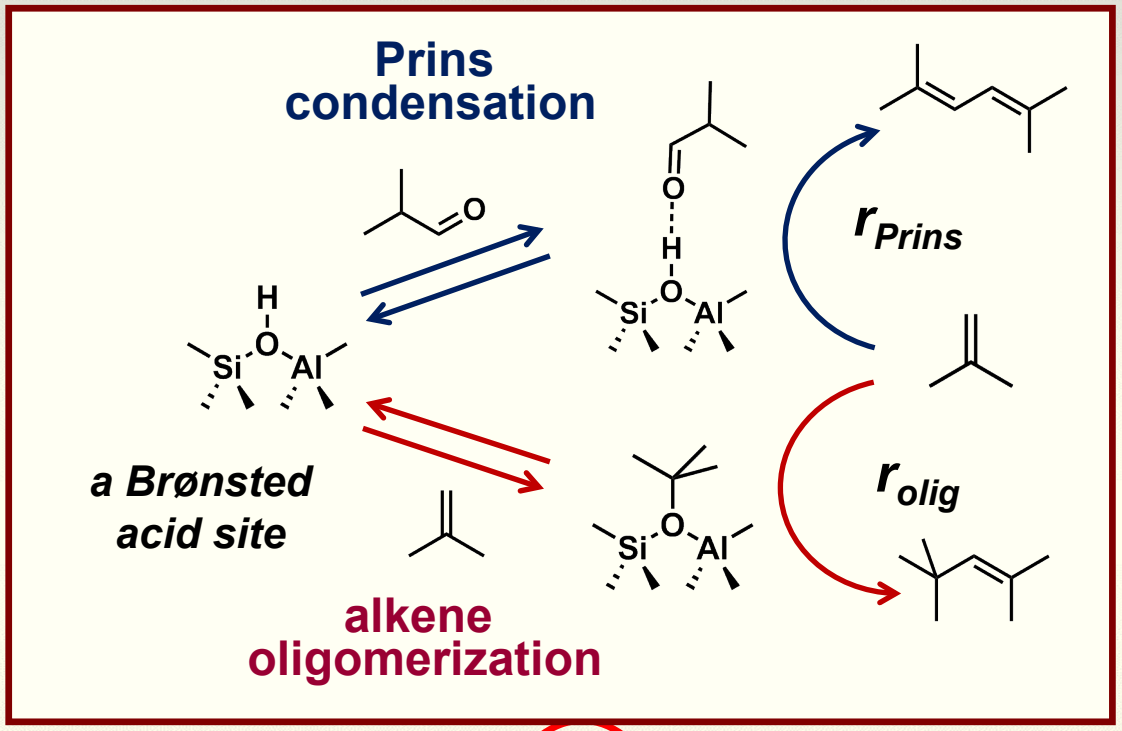


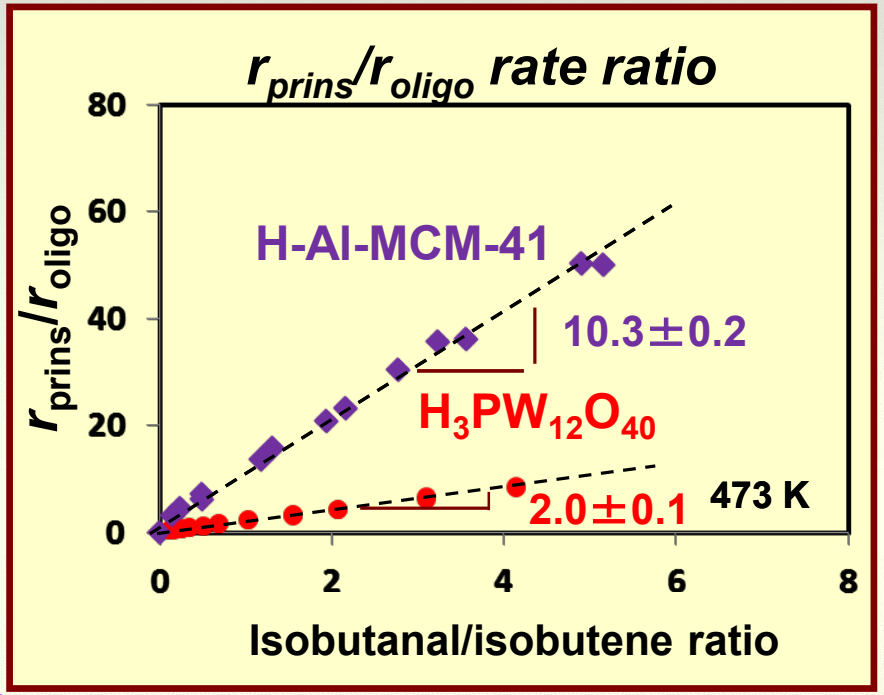


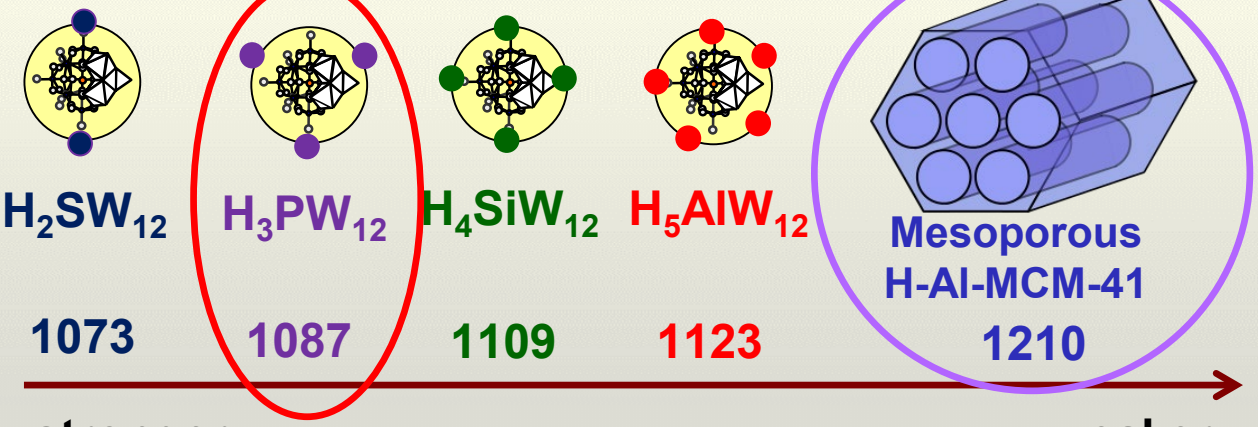
Shuai Wang

VASP, PBE, PAW5

Reactivity and selectivity in alkene-alkanal reactions ….. when acid strength matters <u>for selectivity</u> ……





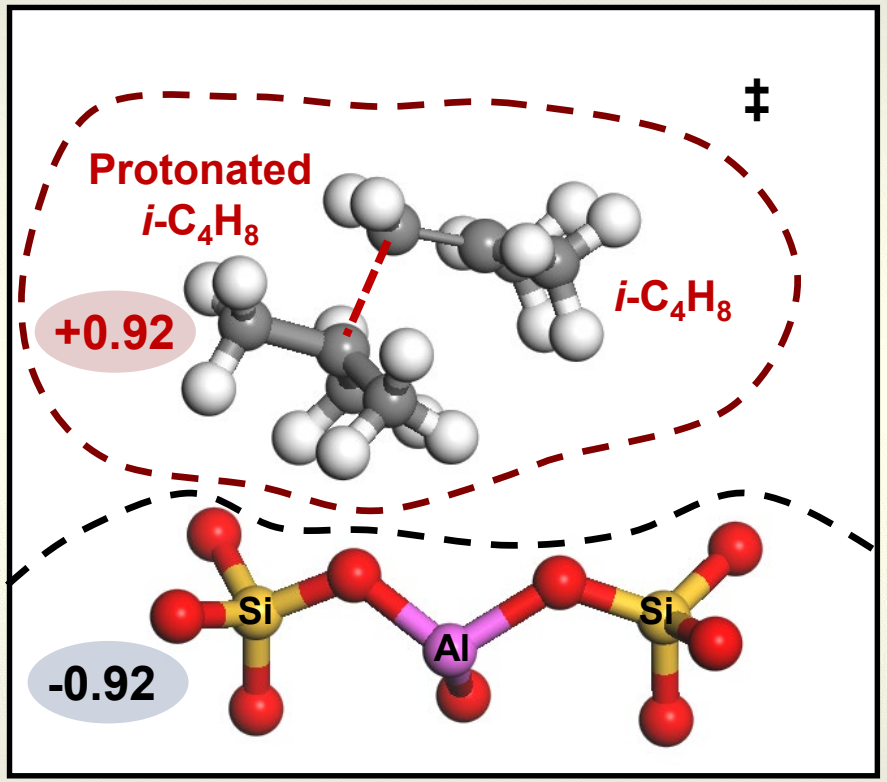


Shuai Wang

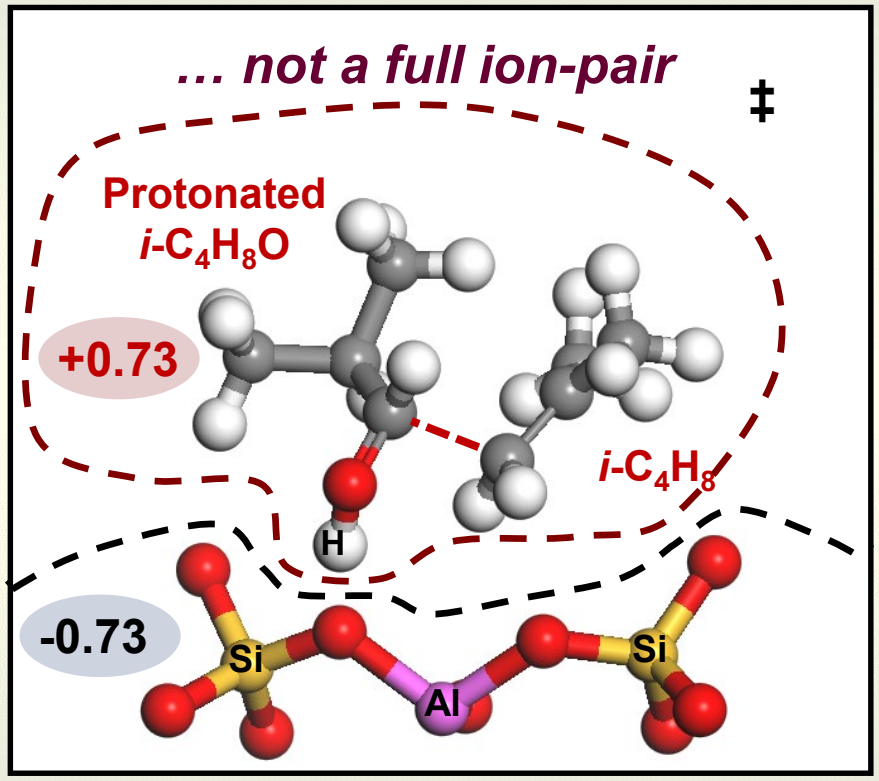
VASP, PBE, PAW5

Reactivity and selectivity in alkene-alkanal reactions ….. when acid strength matters <u>for selectivity</u> ……

Oligomerization transition state



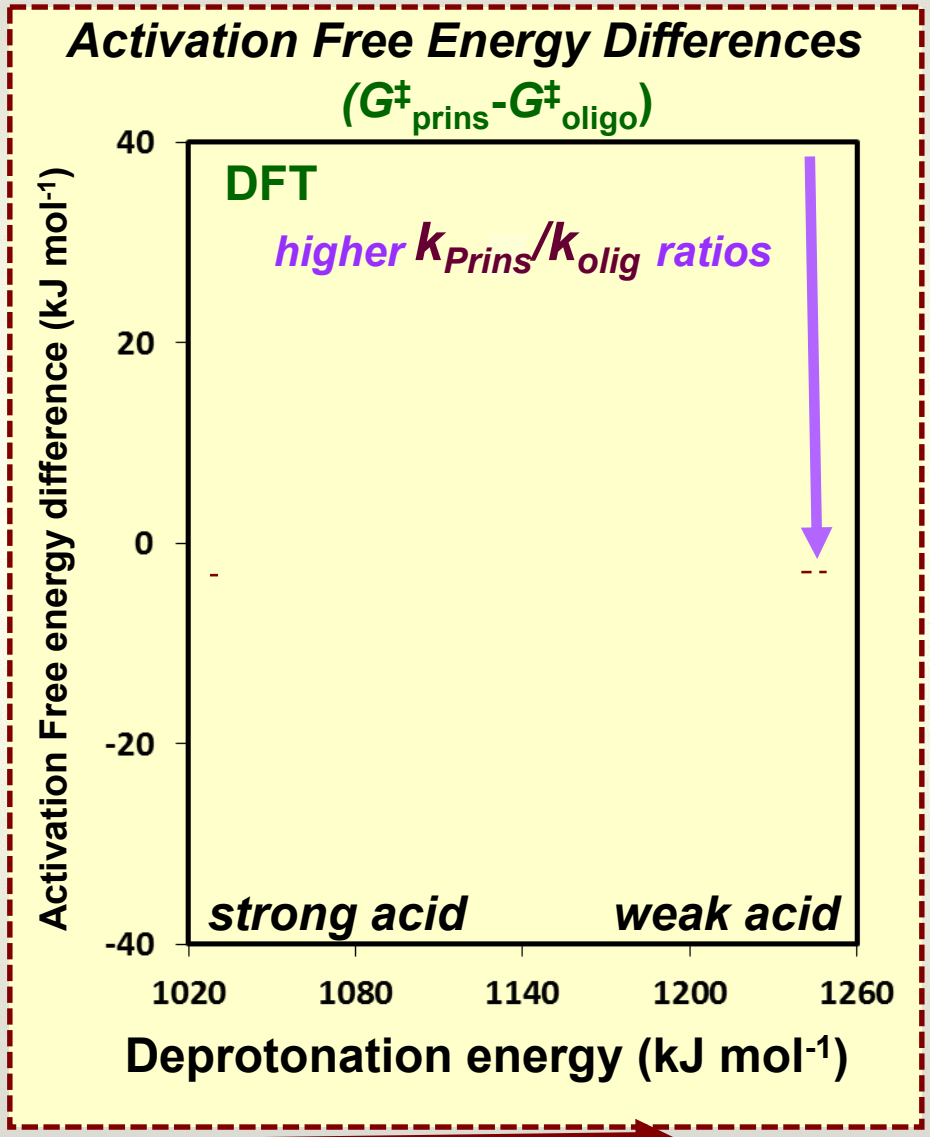
Prins condensation transition state



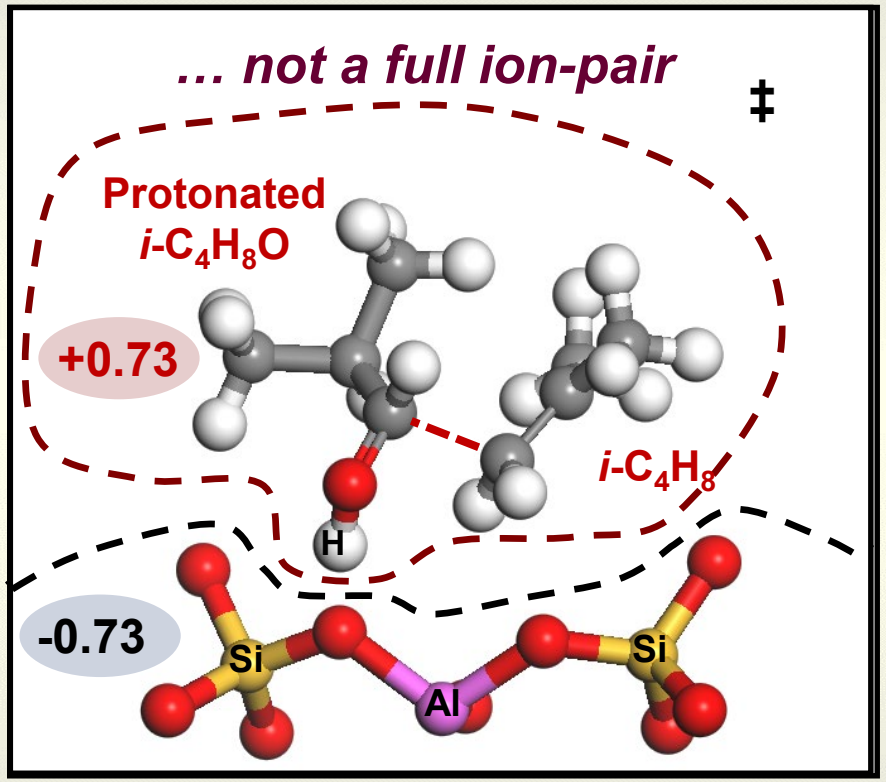
Weaker acids favor channels mediated by less "charged" transition states

VASP, PBE, PAW5

Reactivity and selectivity in alkene-alkanal reactions …..
when acid strength matters <u>for selectivity</u> ……



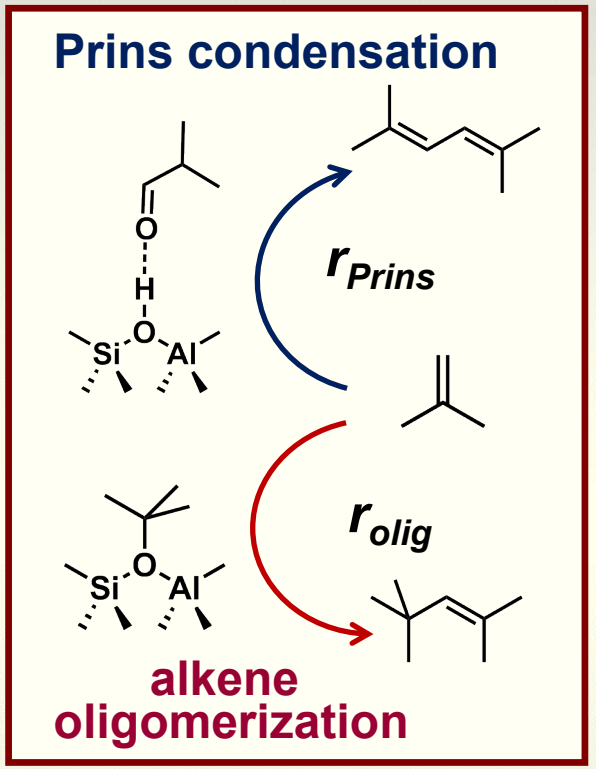
Prins condensation transition state



PBE+D3BJ, PAW5, 473 K, 1 bar,
with respect to a bare proton site
and gaseous reactants

VASP, PBE, PAW5

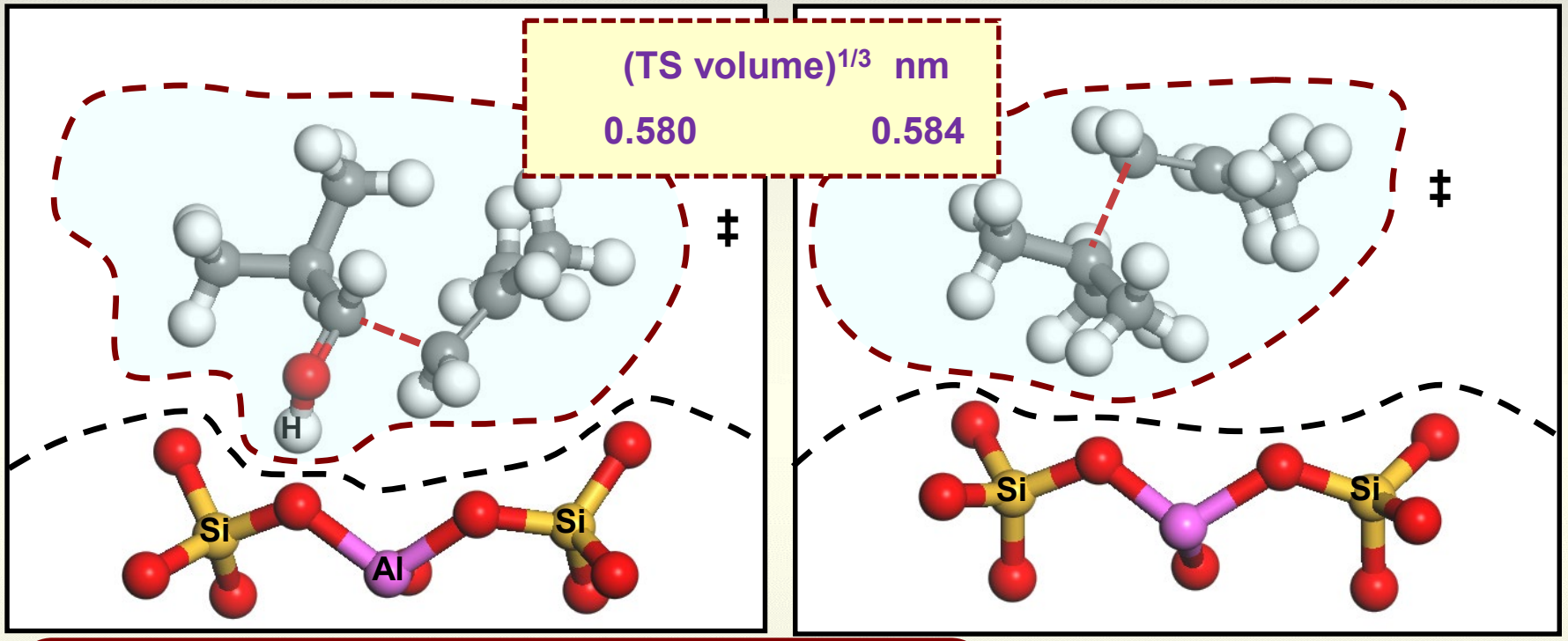
Reactivity and selectivity in alkene-alkanal reactions …..
when confinement effects do NOT matter for selectivity_……



Reactivity and selectivity in alkene-alkanal reactions ….. when confinement effects do NOT matter for selectivity_……

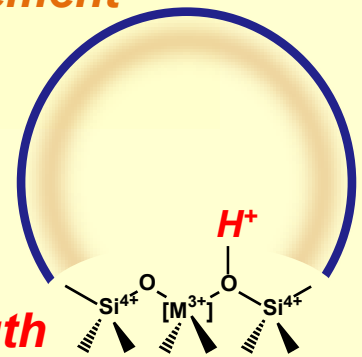
Prins condensation

Oligomerization



Confinement

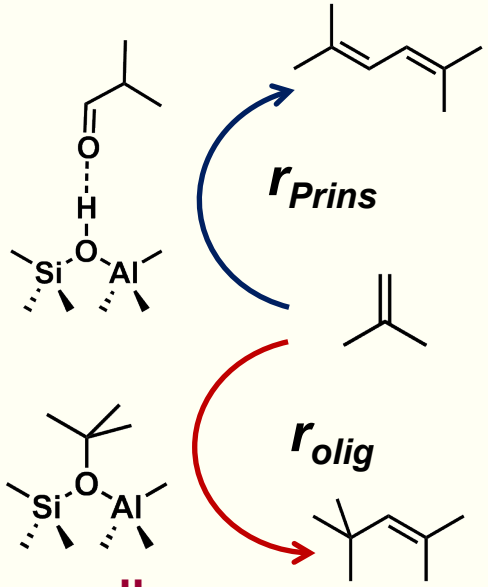
- *Void size around the proton*
- *Stability of the conjugate anion*



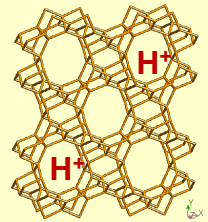
Acid Strength

Aluminosilicates …. similar acid strength, diverse confinement

Prins condensation



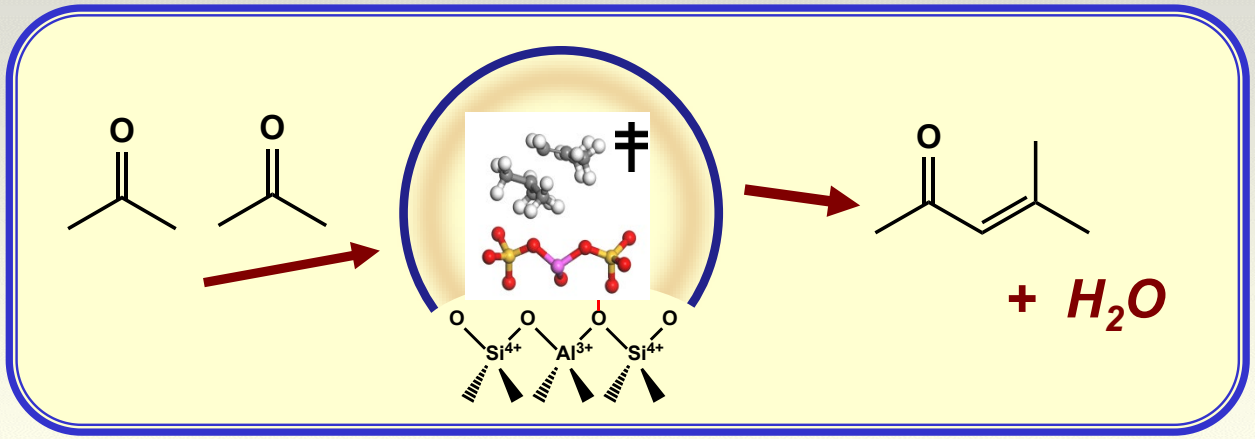
alkene oligomerization



k_{prins}/k_{oligo} = 10-15

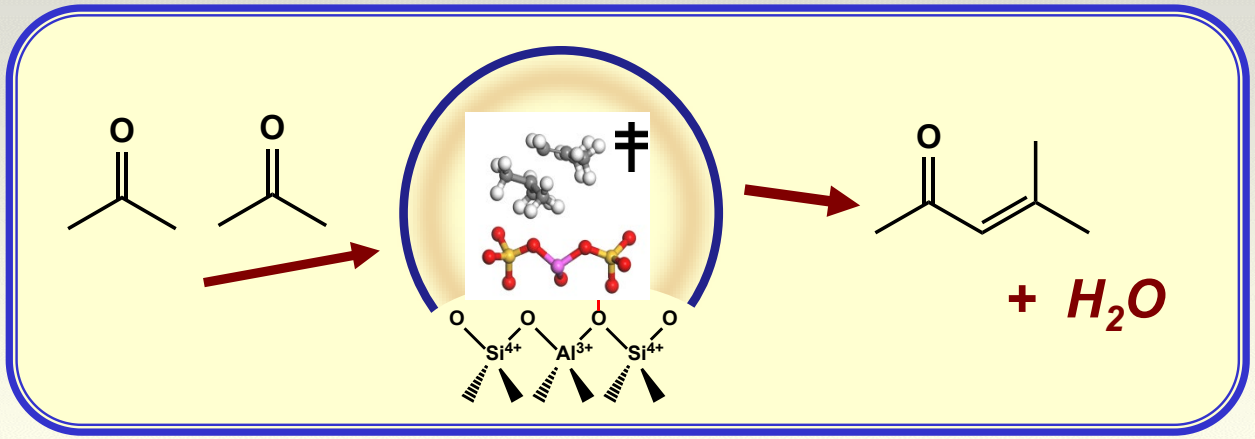
(473 K)

Reactivity and selectivity in aldol condensation reactions …..
when size is NOT all that matters for selectivity_……

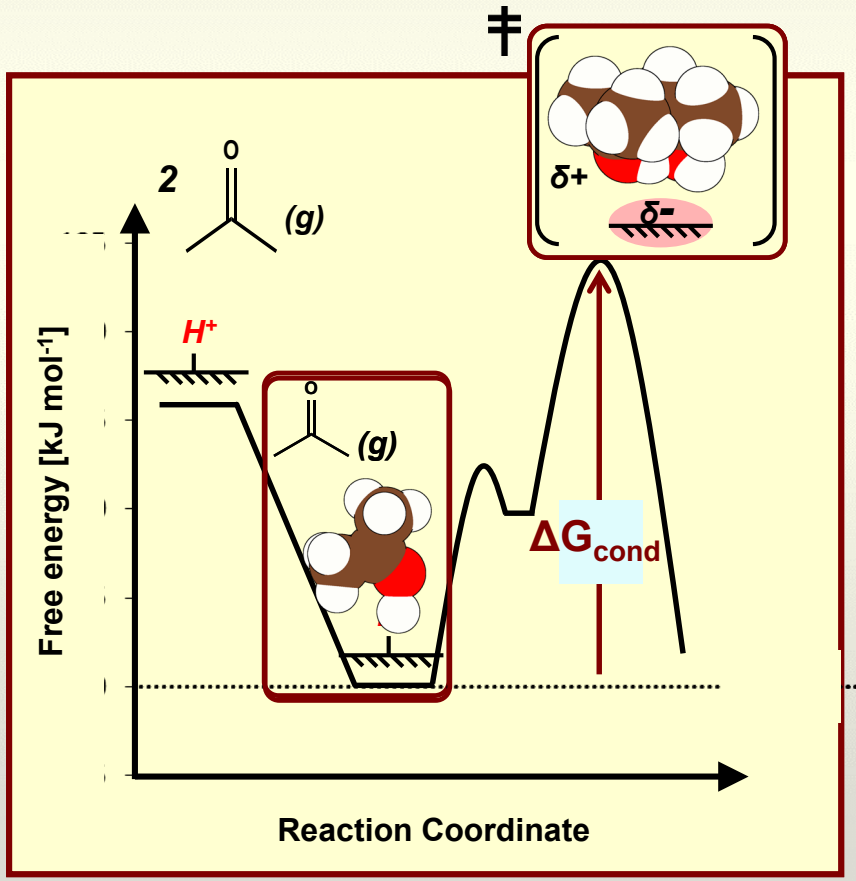


Confinement of relevant precursors and transition states: aldol condensation on aluminosilicate solid acids

Stanley Herrmann

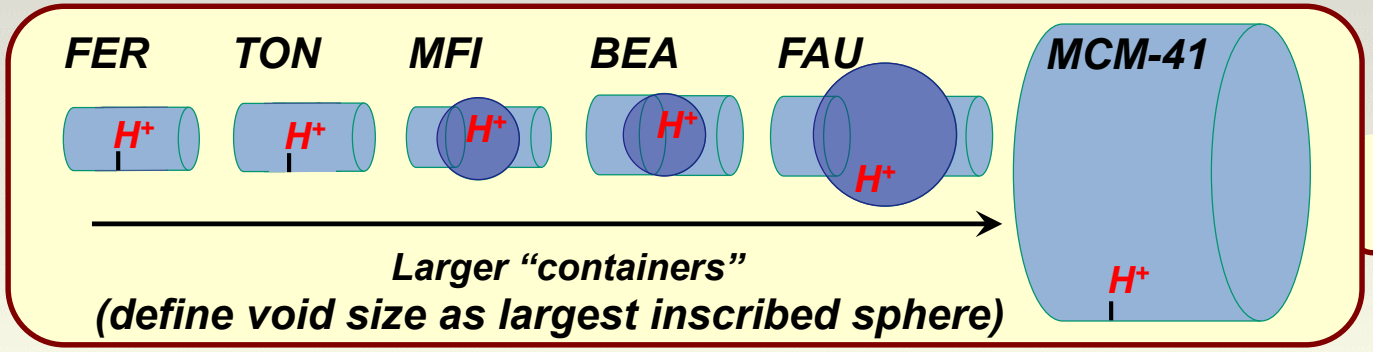


$$r = k_{cond}(\text{Acetone})$$



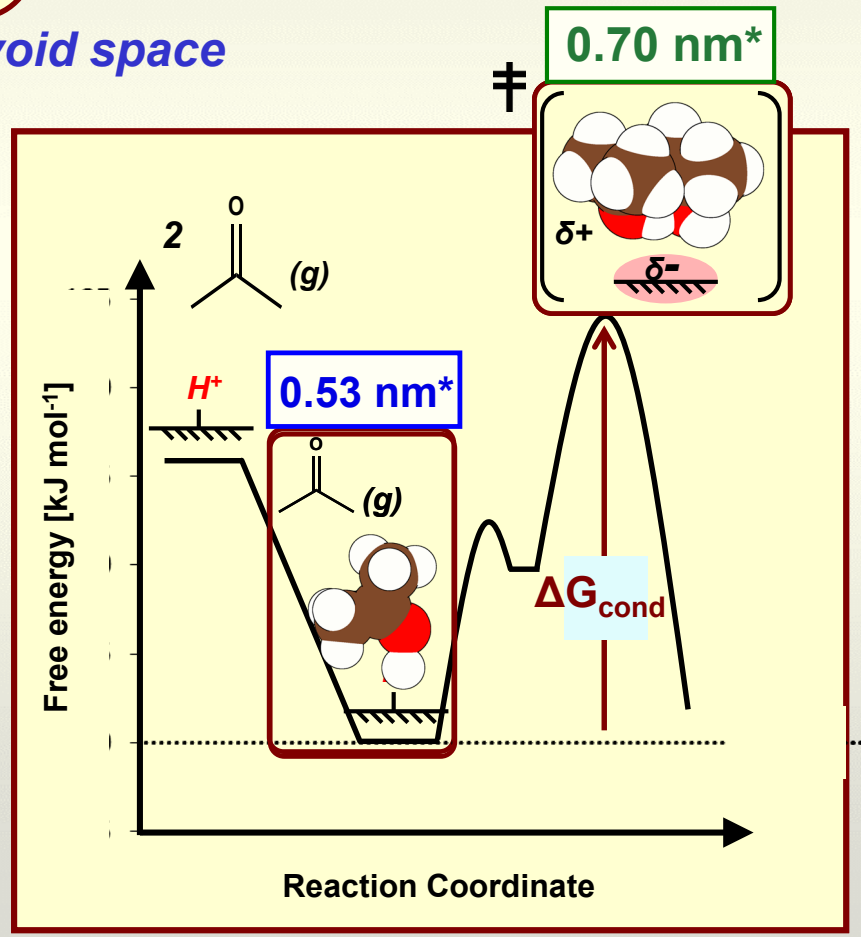
Confinement of relevant precursors and transition states: aldol condensation on aluminosilicate solid acids

Stanley Herrmann



$$r = k_{cond}(\text{Acetone})$$

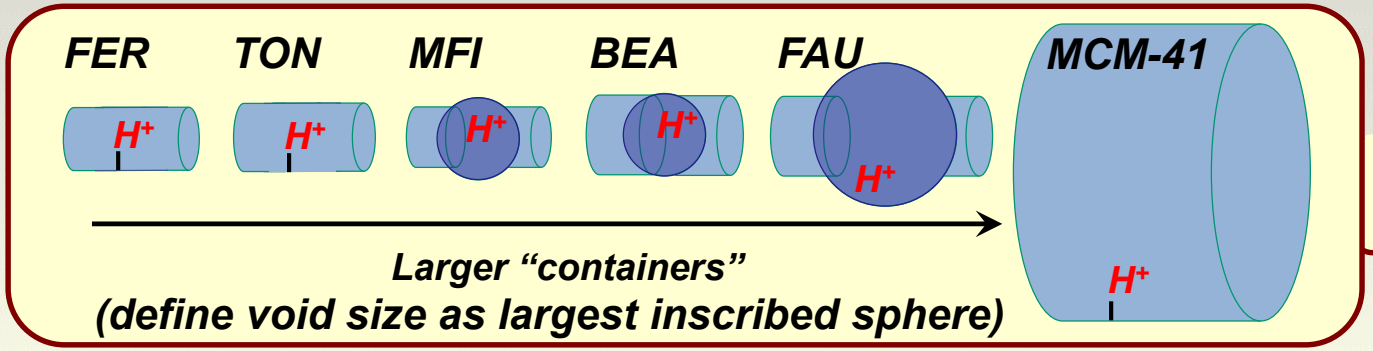
….. similar acid strength but different void space



*DFT: VASP, RPBE+D3, PAW5

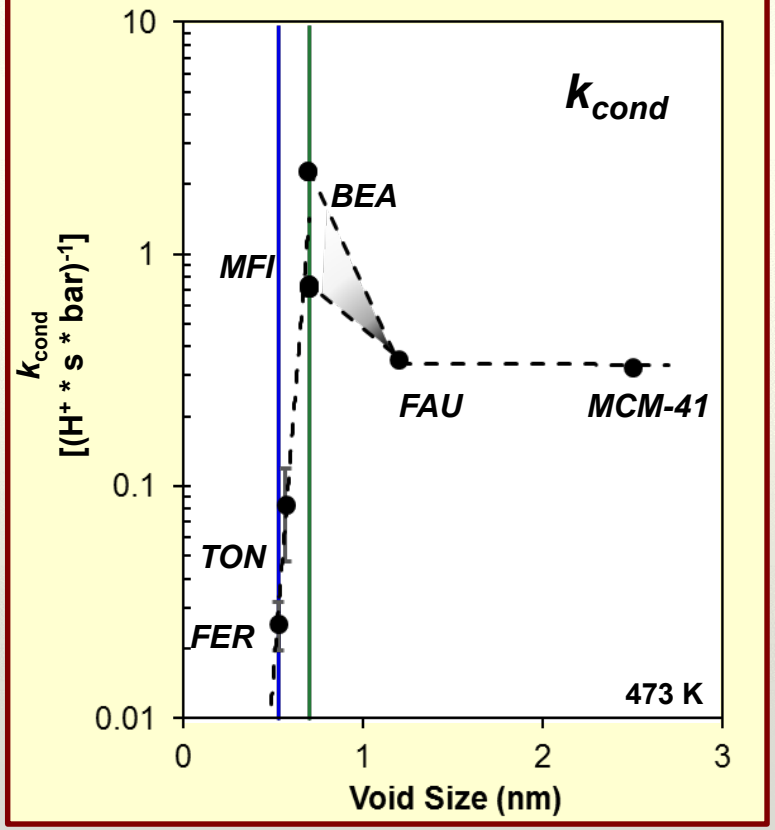
Confinement of relevant precursors and transition states: aldol condensation on aluminosilicate solid acids

Stanley Herrmann



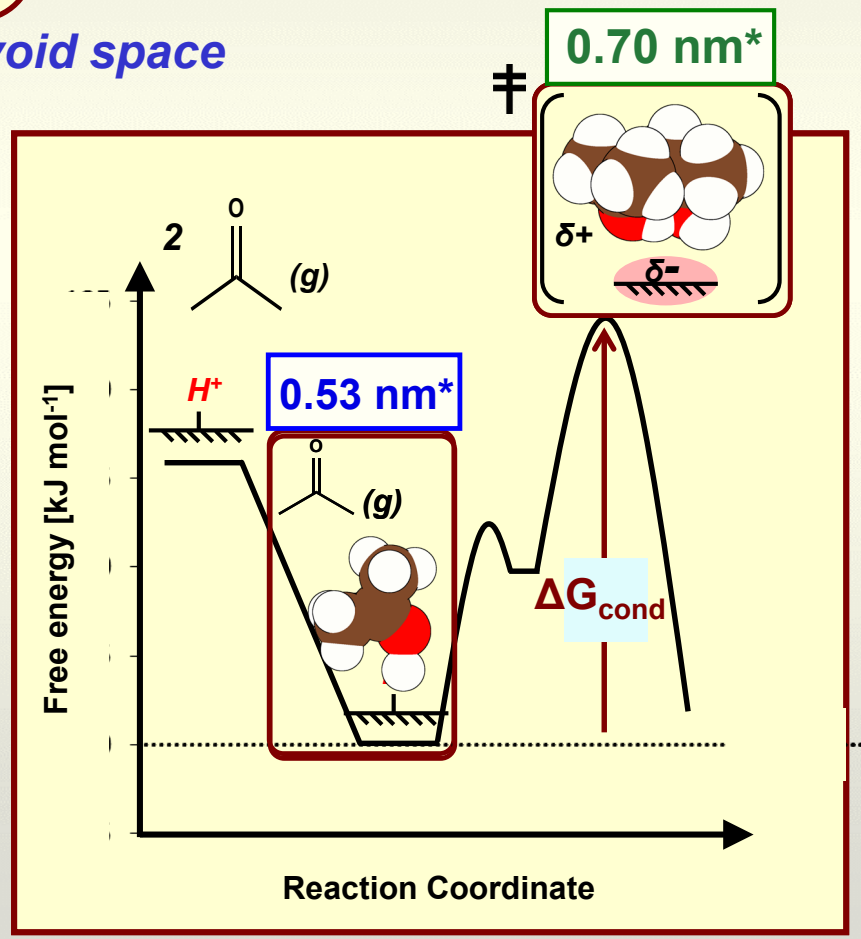
$$r = k_{cond}(\text{Acetone})$$

Measured aldol condensation rate constant (per H^+)



…. similar acid strength but different void space

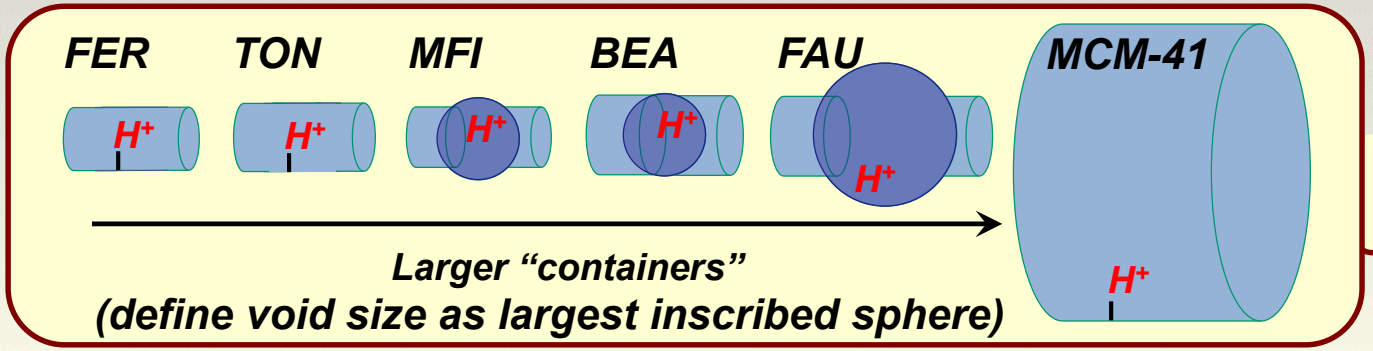
…. the size of the container obviously matters



*DFT: VASP, RPBE+D3, PAW5

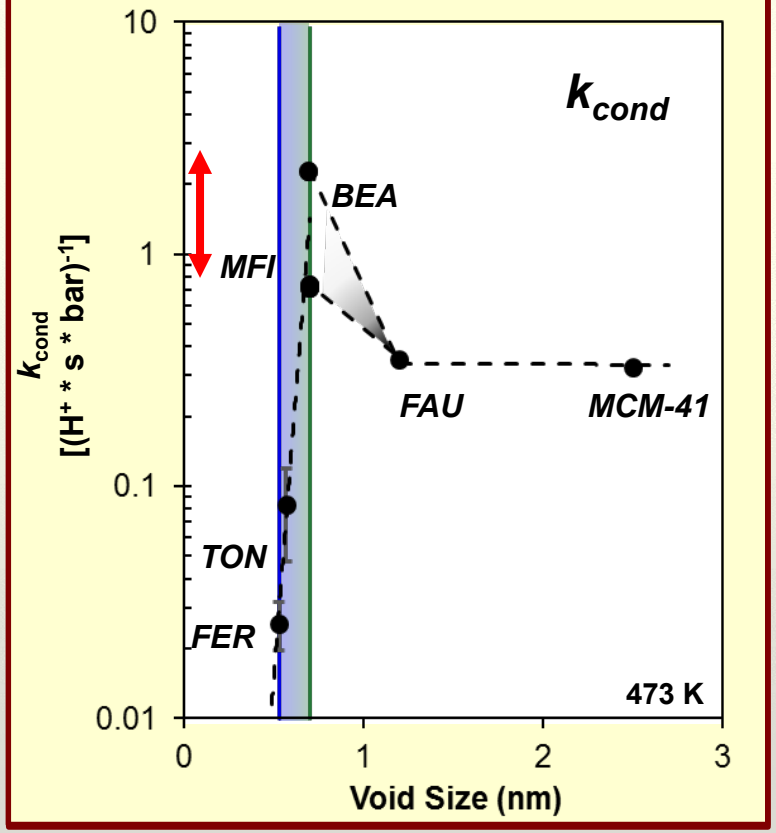
Confinement of relevant precursors and transition states: aldol condensation on aluminosilicate solid acids

Stanley Herrmann



$$r = k_{cond}(\text{Acetone})$$

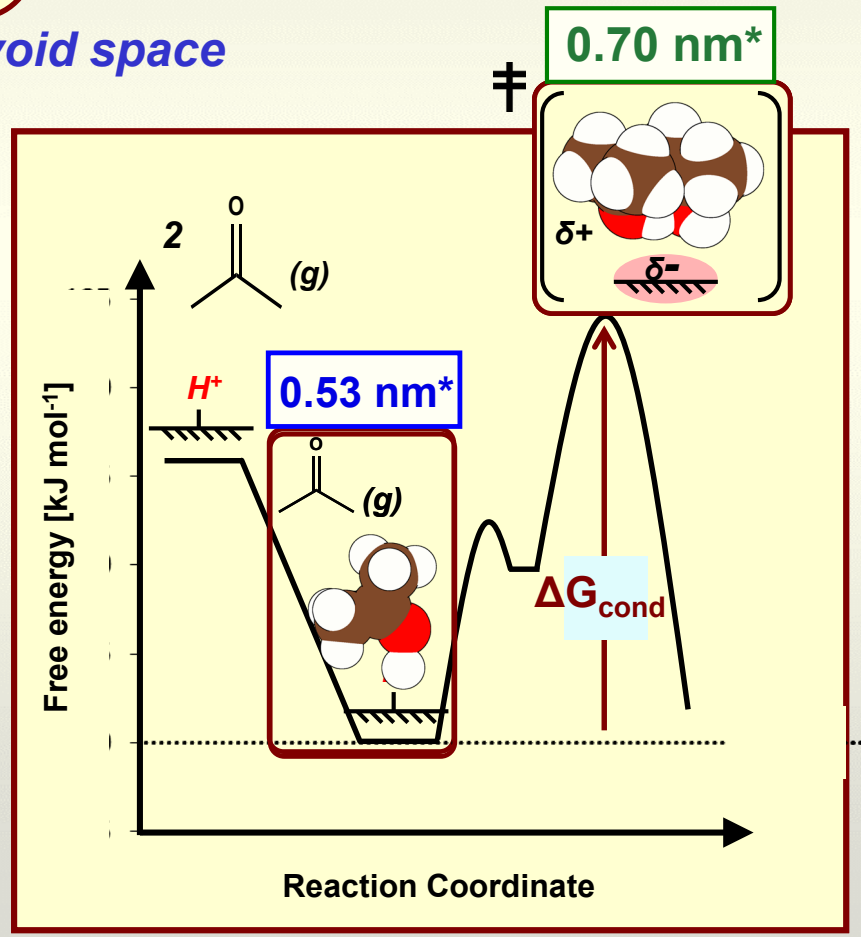
Measured aldol condensation rate constant (per H^+)



…. similar acid strength but different void space

…. the size of the container obviously matters

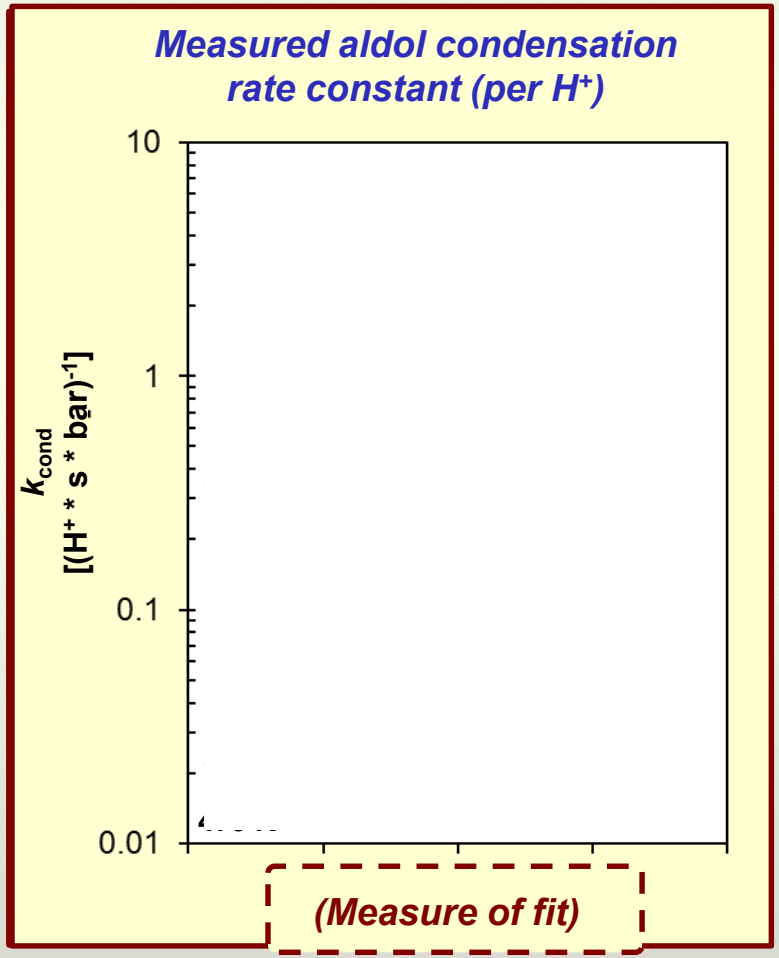
…. when such sizes approach those of intermediates and transition states

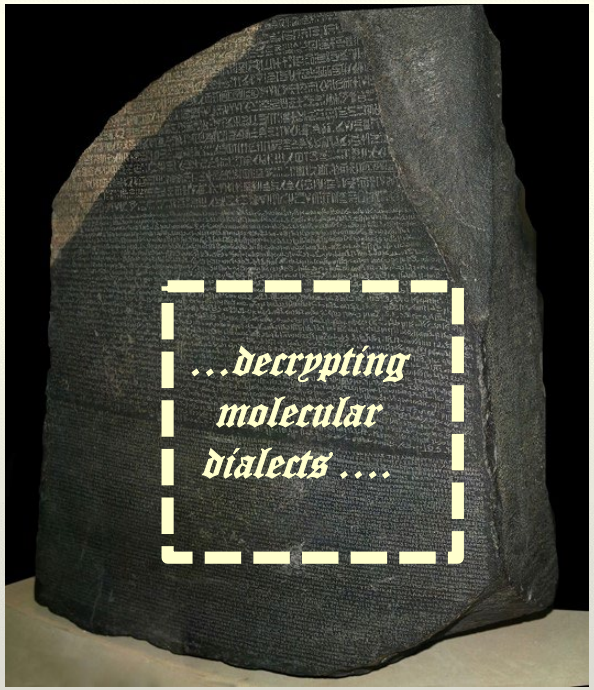


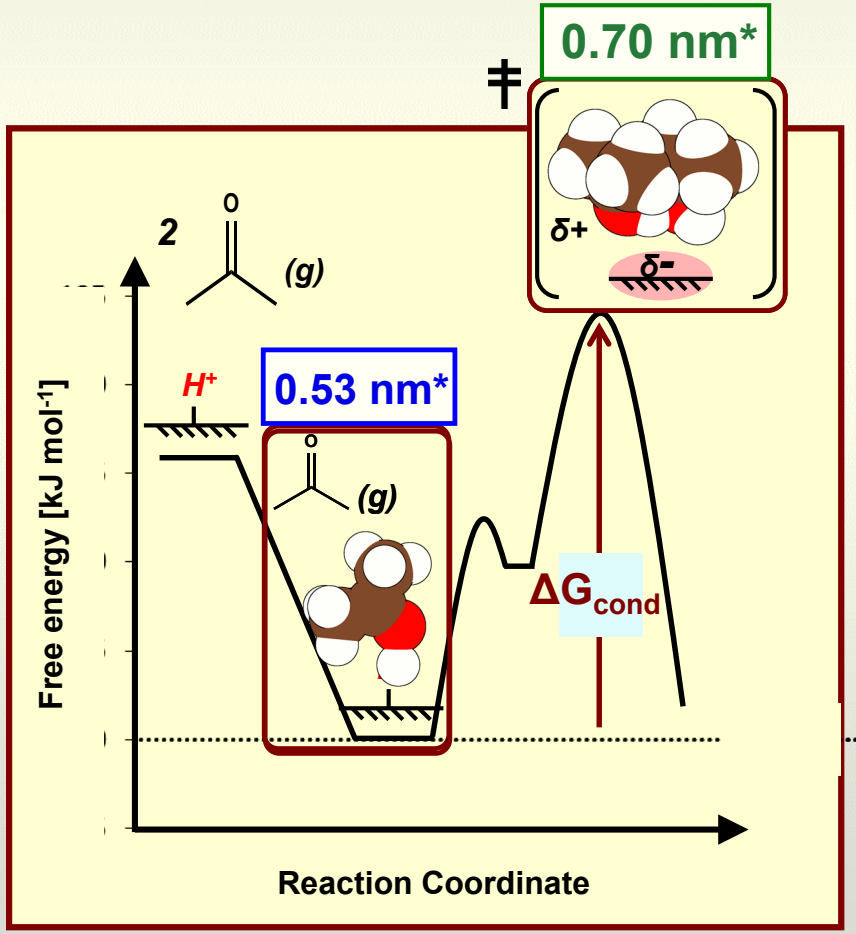
*DFT: VASP, RPBE+D3, PAW5

Descriptors of reactivity in terms of energies ….. not just composition or structure: aldol condensation

…. accounting for host-guest fit through (van der Waals) energy descriptors …. not just metrics of size and shape



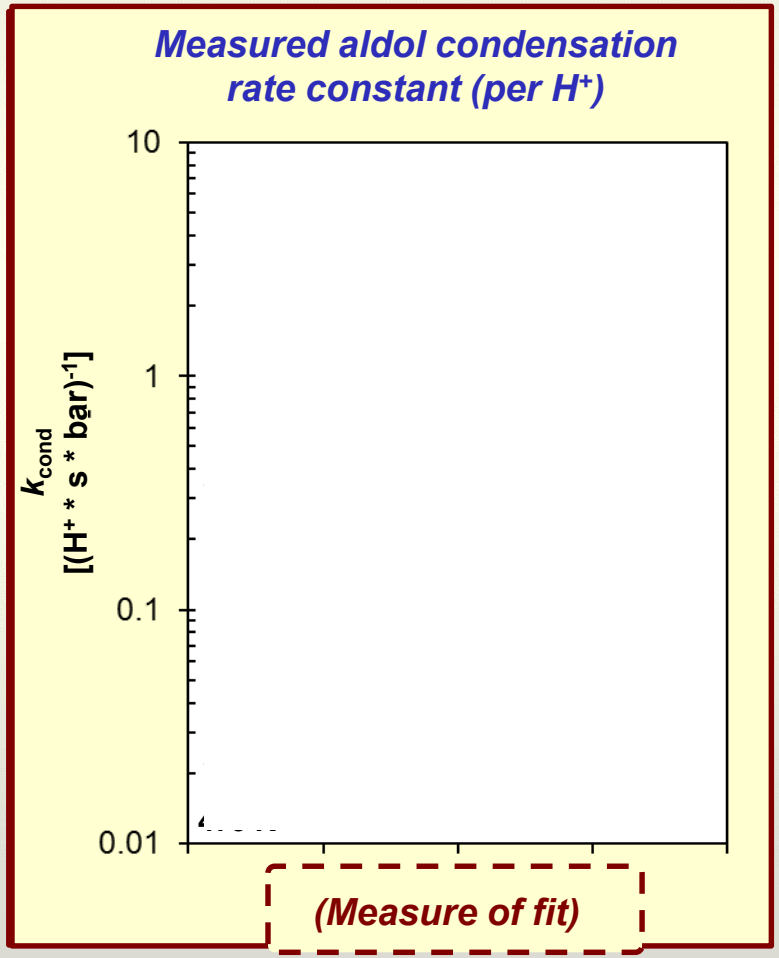


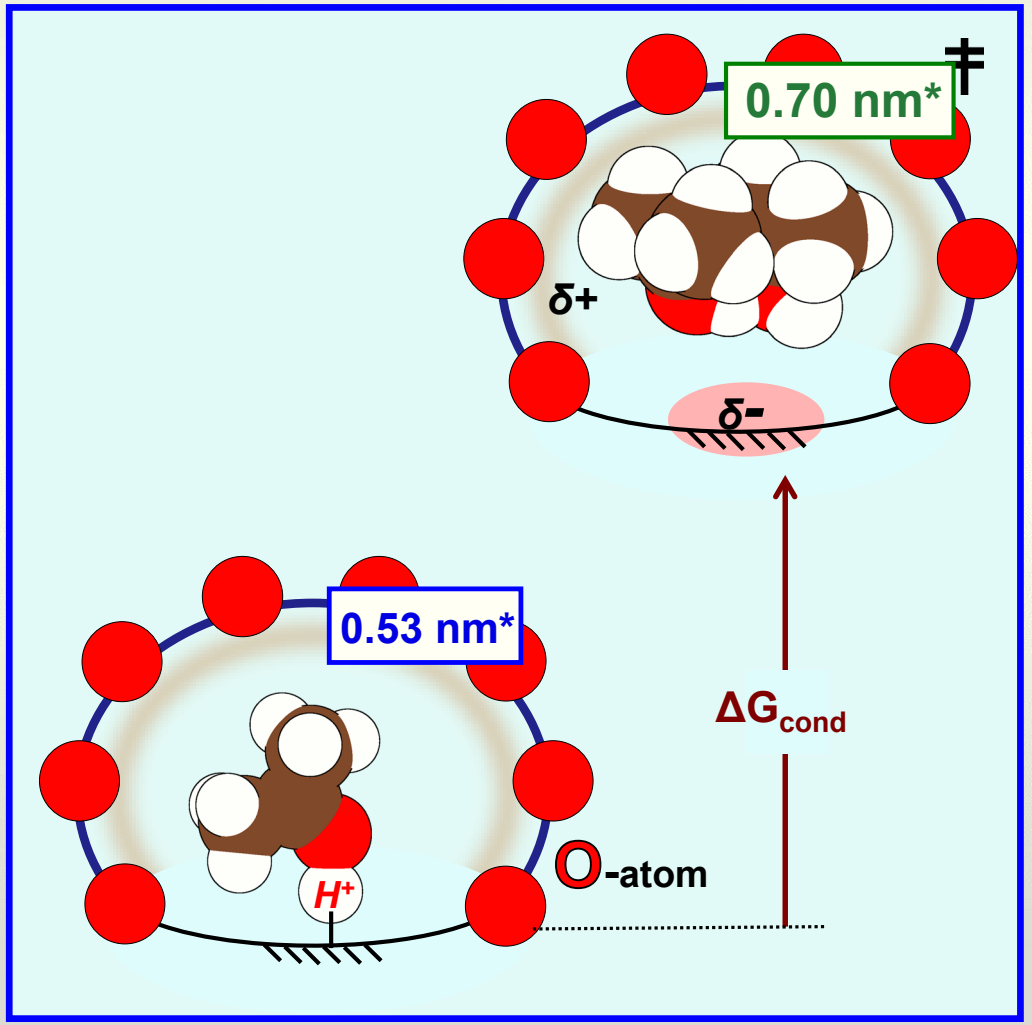


*DFT: VASP, RPBE+D3, PAW5

Descriptors of reactivity in terms of energies ….. not just composition or structure: aldol condensation

…. accounting for host-guest fit through (van der Waals) energy descriptors …. not just metrics of size and shape

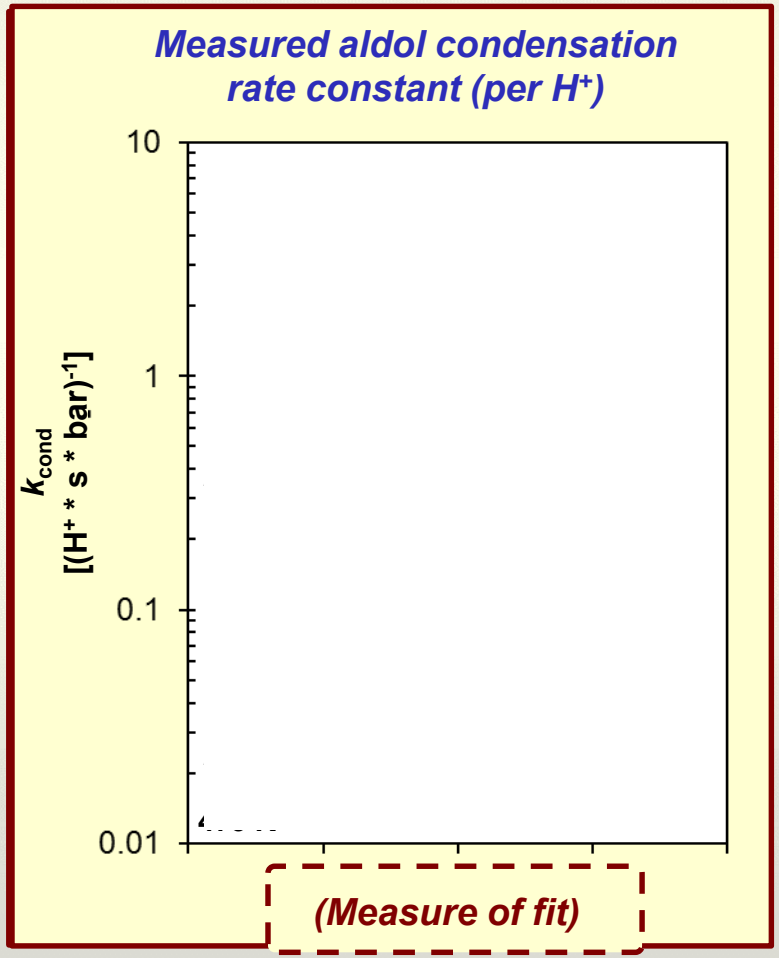


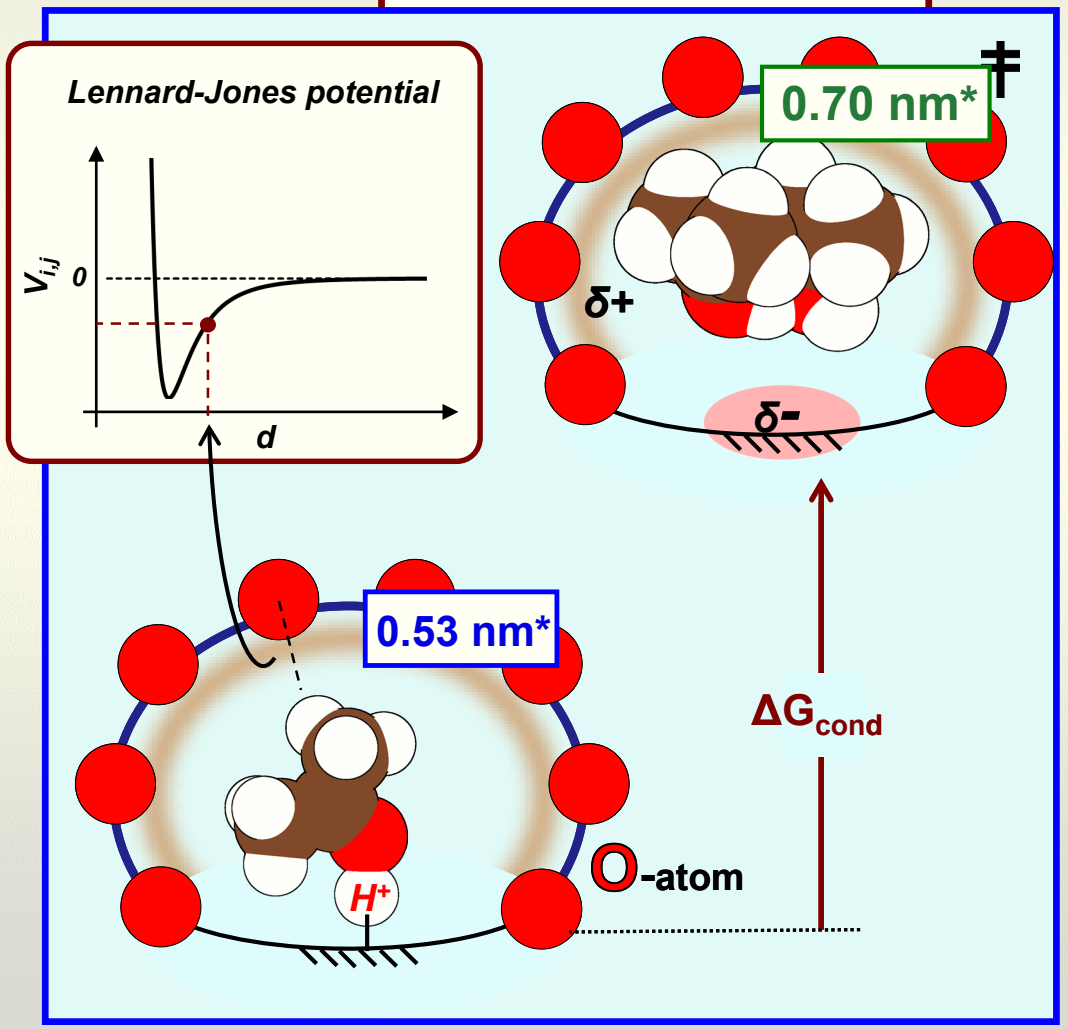


Descriptors of reactivity in terms of energies …..
not just composition or structure: aldol condensation

…. accounting for host-guest fit through
(van der Waals) energy descriptors
…. not just metrics of size and shape

$$\chi = \sum_{j}^{O_{zeo}} \sum_{i}^{X_{ads}} V_{i,j}$$

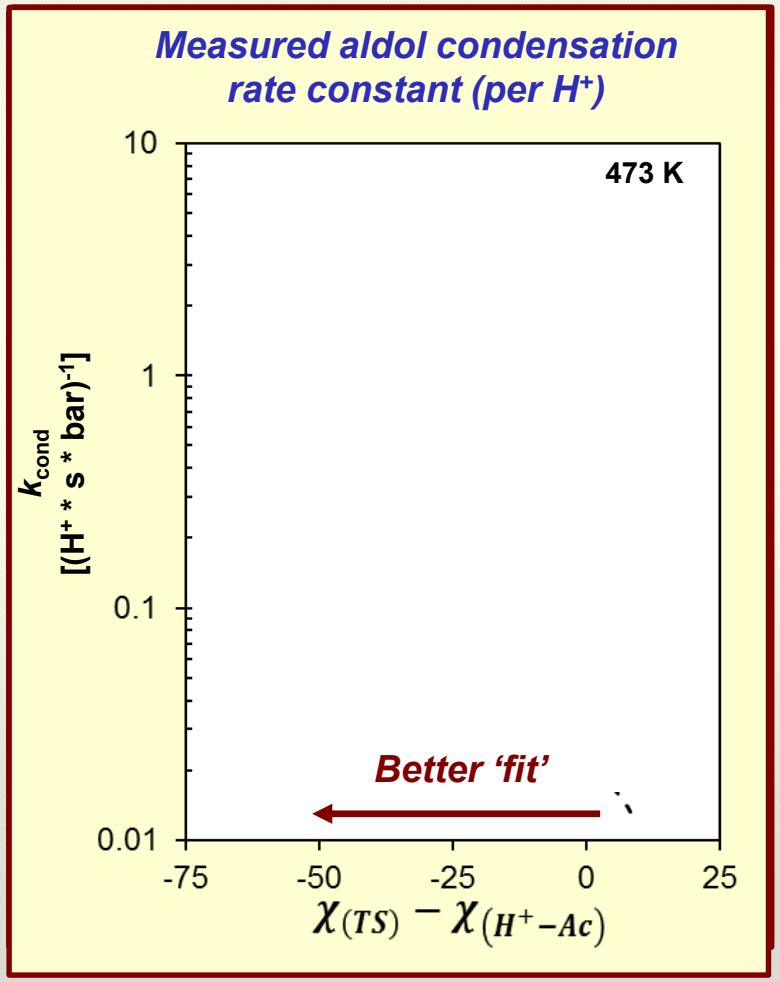


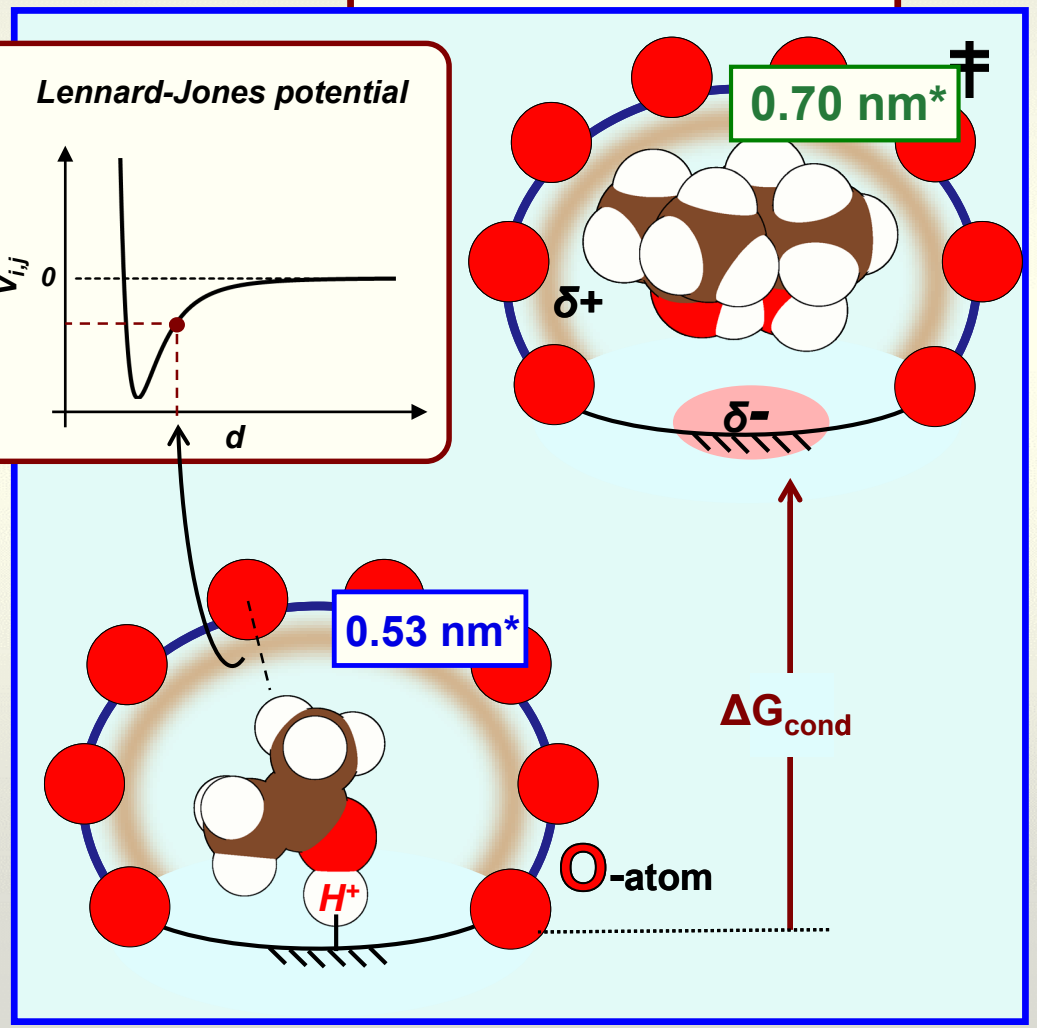


Descriptors of reactivity in terms of energies ….. not just composition or structure: aldol condensation

…. accounting for host-guest fit through (van der Waals) energy descriptors …. not just metrics of size and shape

$$\chi = \sum_{j}^{O_{zeo}} \sum_{i}^{X_{ads}} V_{i,j}$$



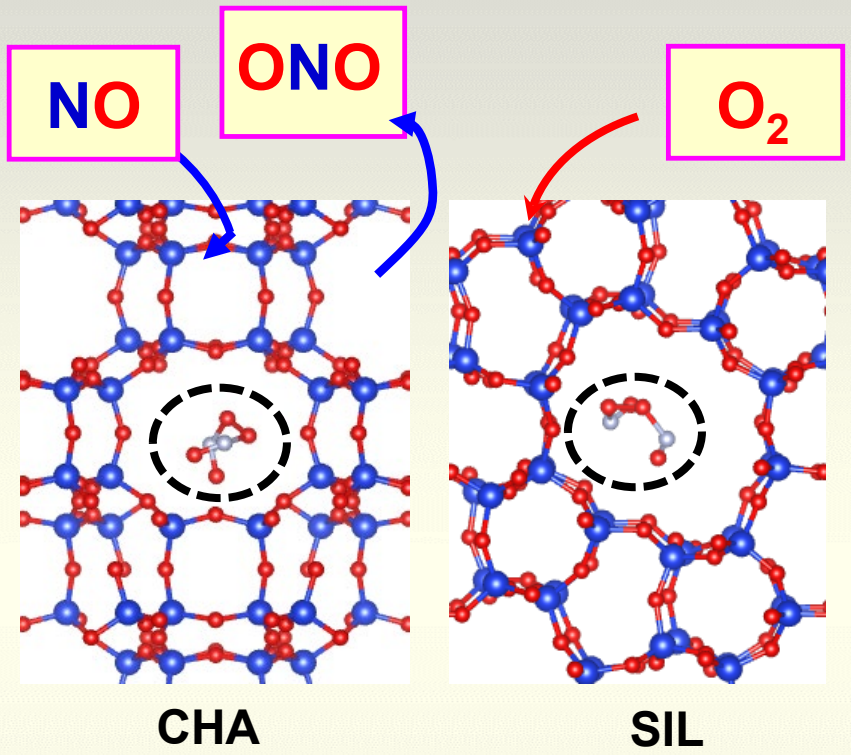


… confinement matters <u>even</u> without a binding point

Silicates without defects or grafting points catalyze NO-O_2 reactions at ambient temperature

… with same kinetic trends as homogeneous routes

$$r = k\,(NO)^2\,(O_2)$$



Nancy Artioli
Matteo Maestri

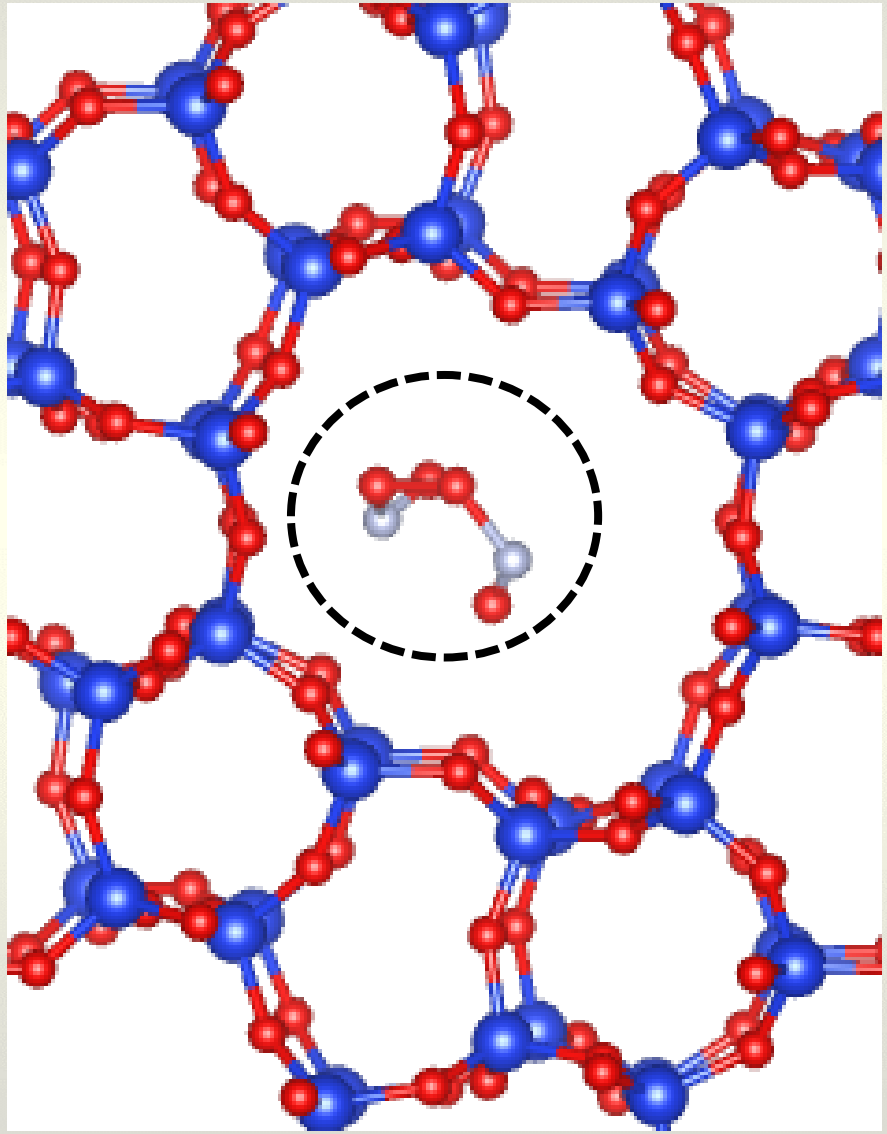
… confinement matters <u>even</u> without a binding point

Silicates without defects or grafting points catalyze NO-O_2 reactions at ambient temperature

… with same kinetic trends as homogeneous routes

$$r = k\,(NO)^2\,(O_2)$$

Nancy Artioli
Matteo Maestri

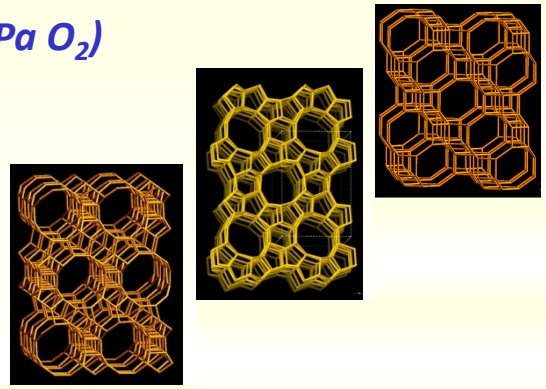


… confinement matters <u>even</u> without a binding point

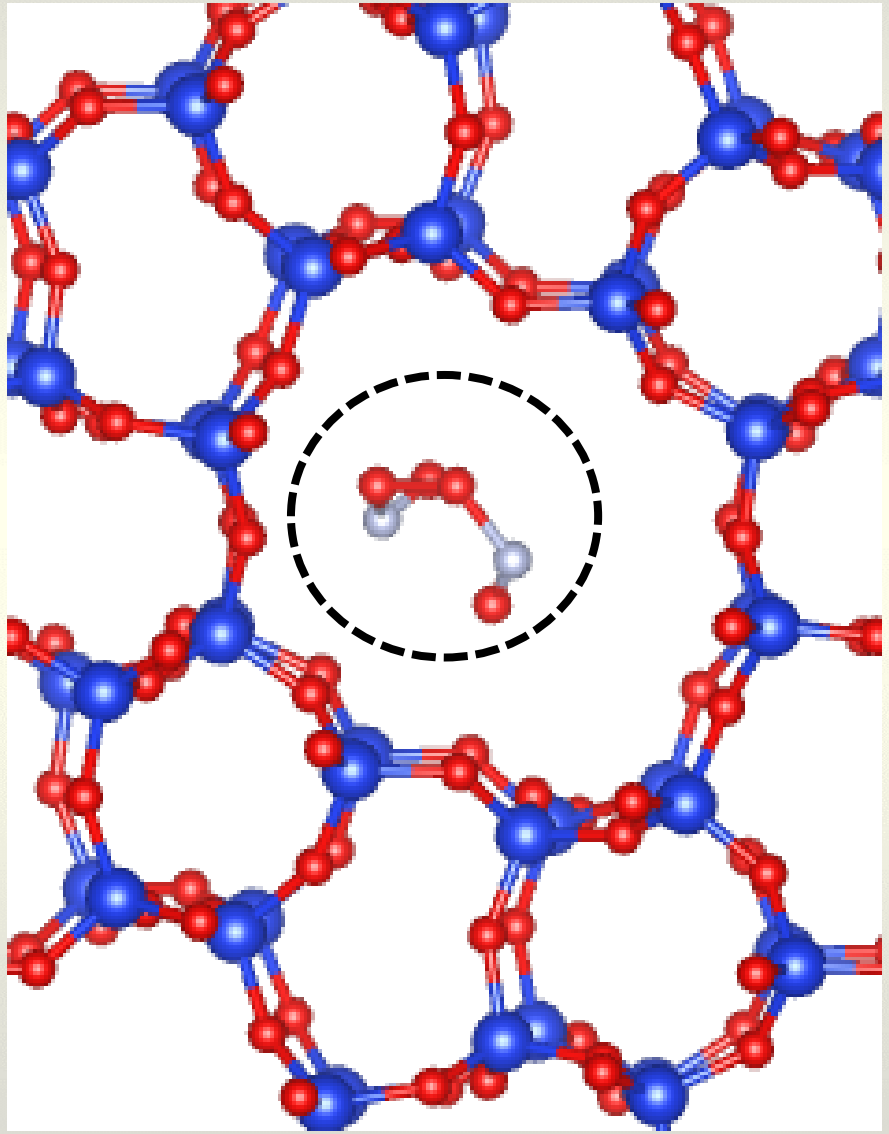
… defect-free siliceous zeolites

300 K

(100 Pa NO, 5 kPa O_2)



	silica	BEA	SIL	CHA
Largest cavity diameter (nm)		0.69	0.70	0.80

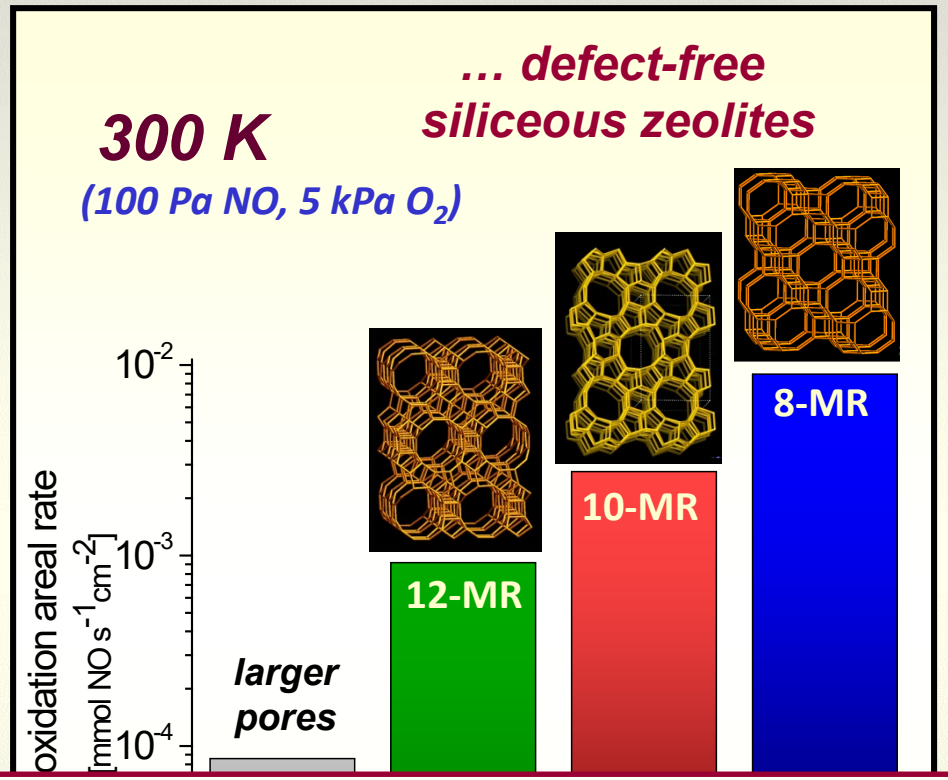


… confinement matters even without a binding point

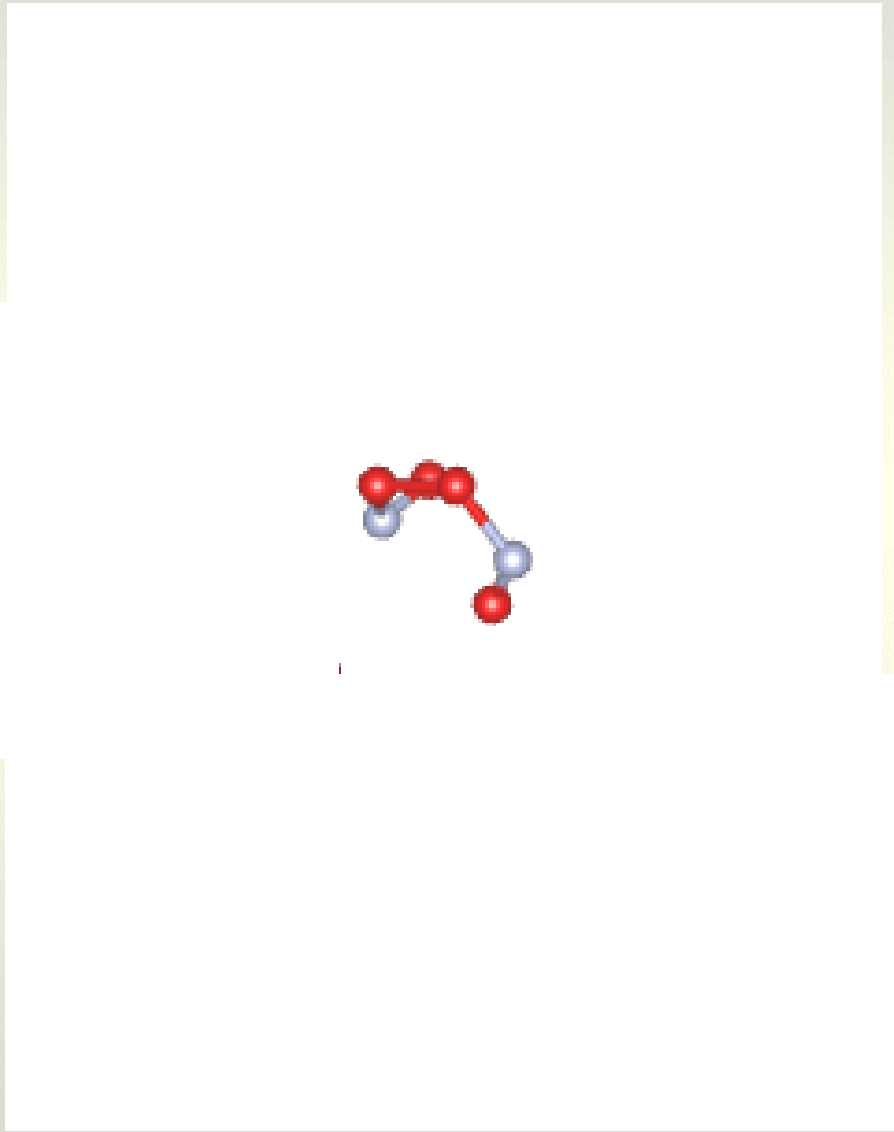
… defect-free siliceous zeolites

300 K

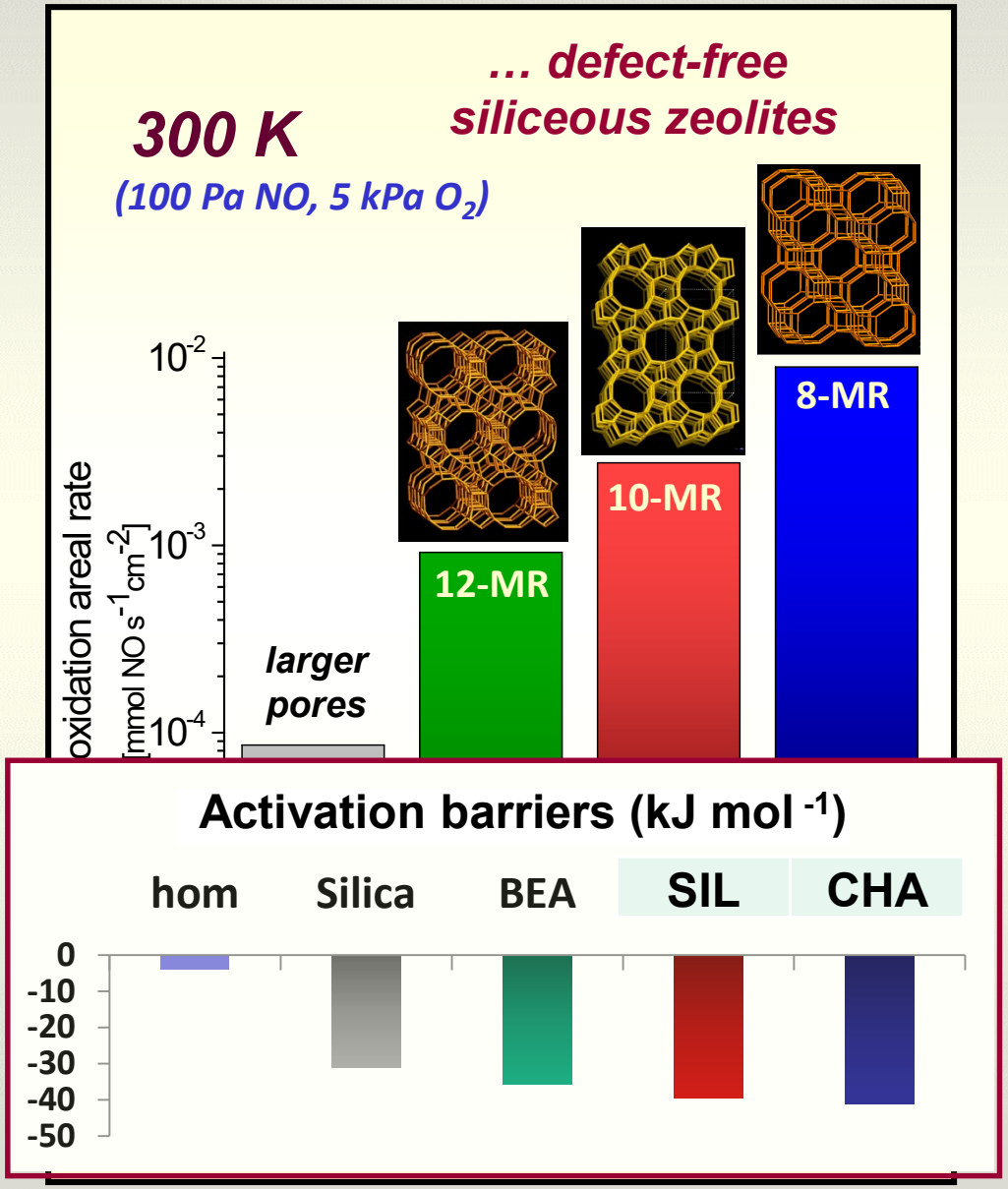
(100 Pa NO, 5 kPa O_2)

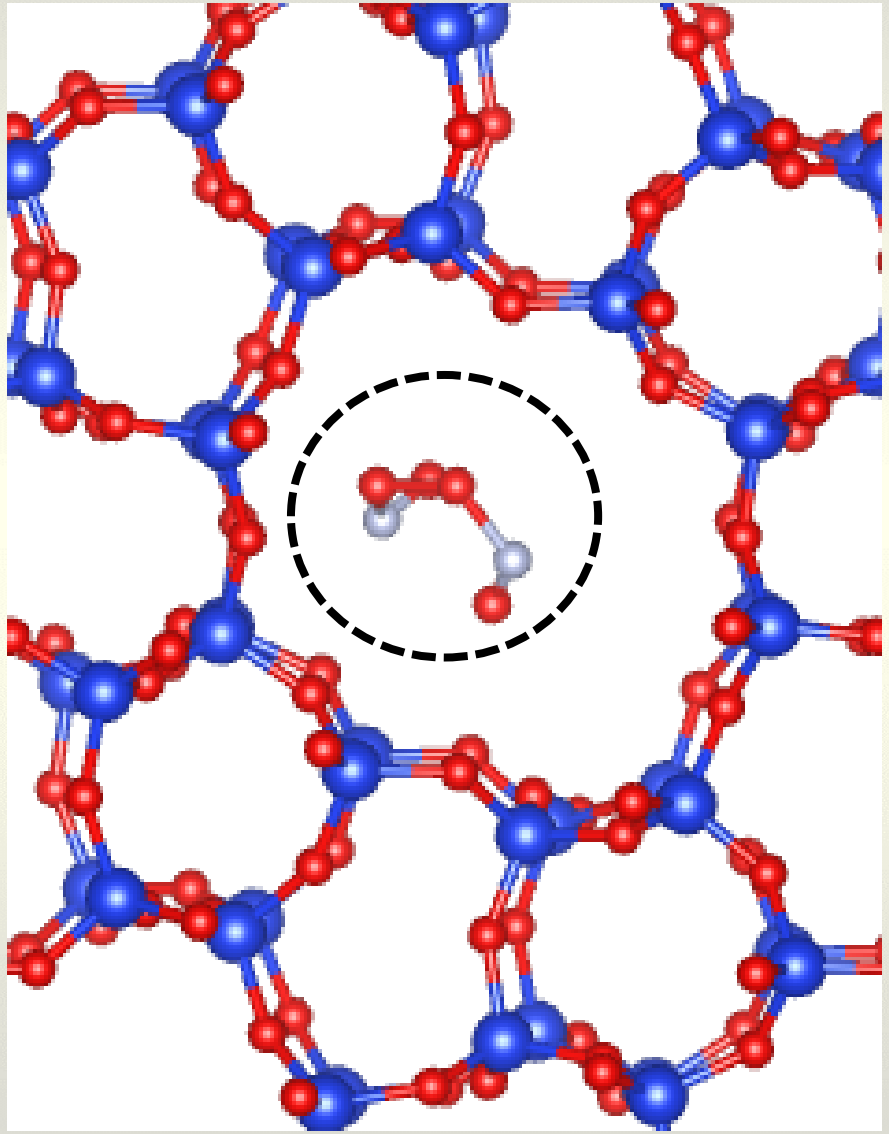


12-MR 10-MR 8-MR



… confinement matters even without a binding point



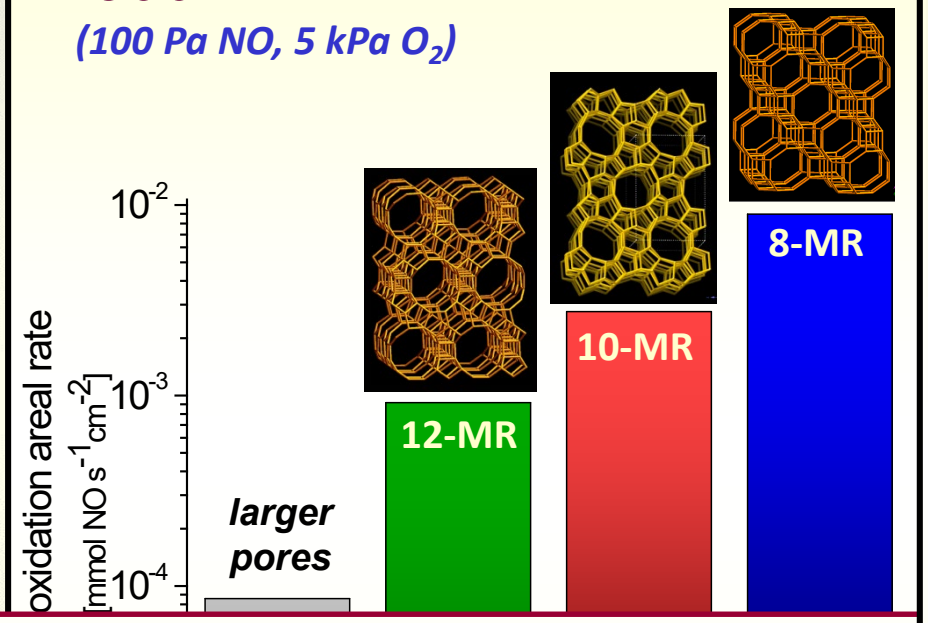


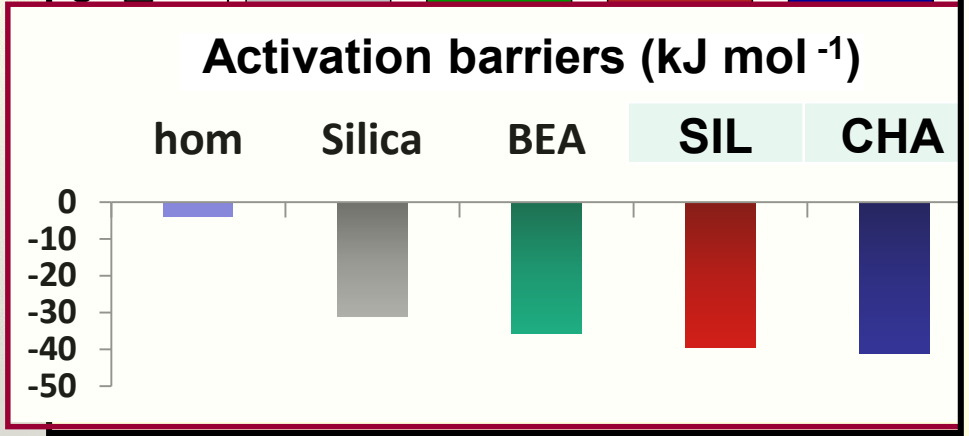
… confinement matters even without a binding point

… defect-free siliceous zeolites

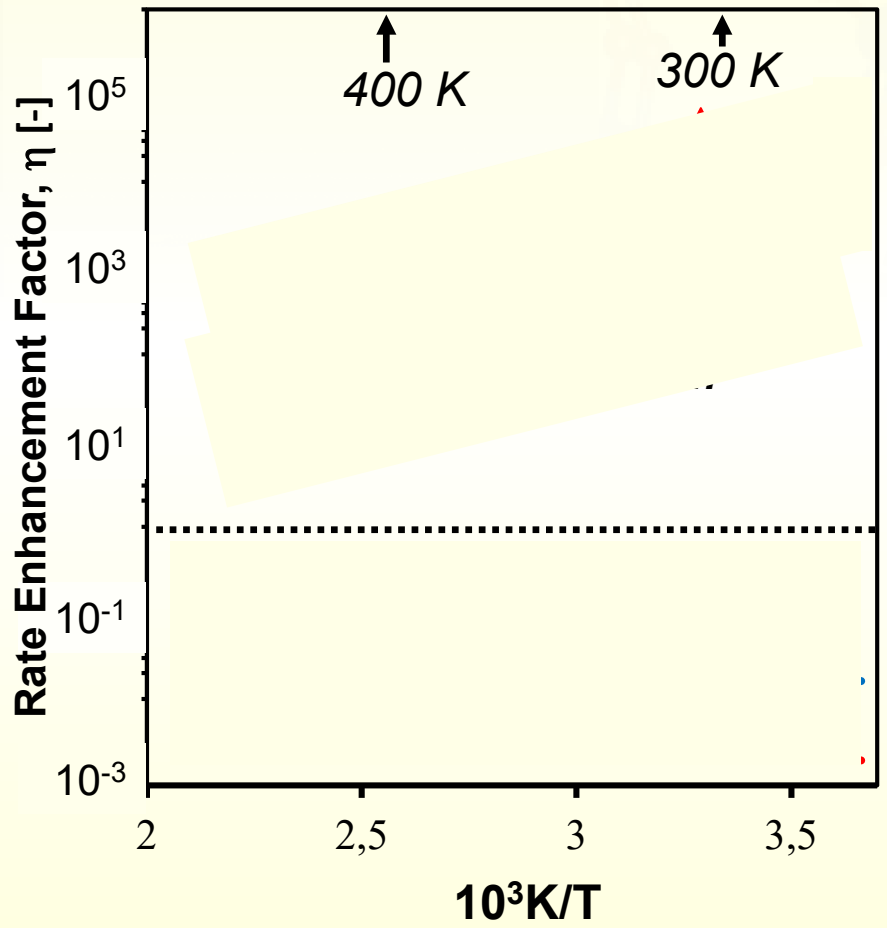
300 K

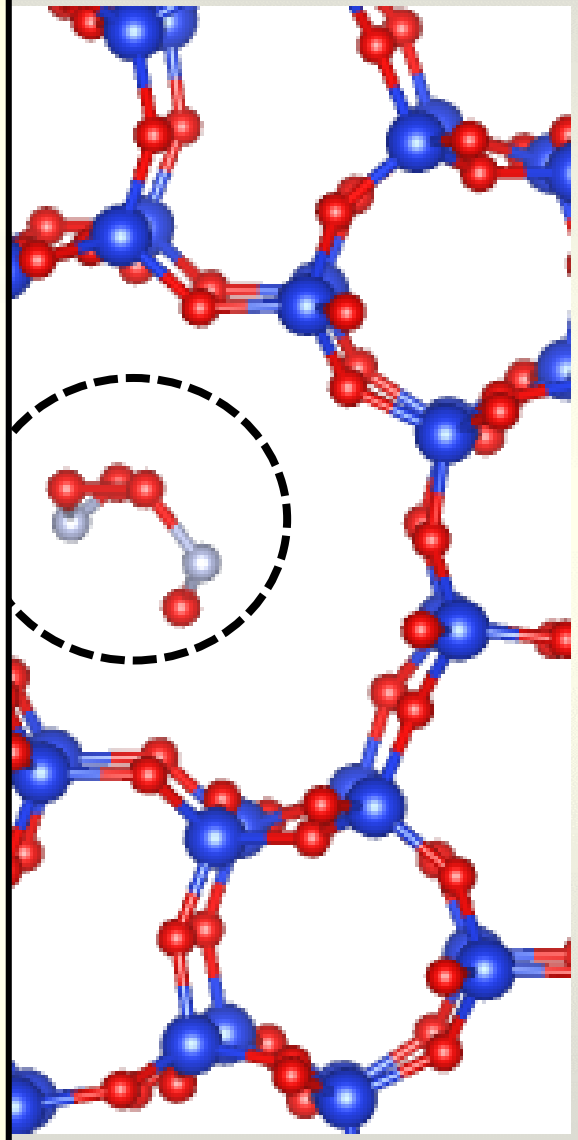
(100 Pa NO, 5 kPa O_2)





$$\eta = \frac{r_{conf}}{r_{homg}} = \exp\left(-\frac{G^{\ddagger}_{conf} - G^{\ddagger}_{homg}}{RT}\right)$$





12-MR 10-MR 8-MR

Quantum Espresso - Periodic DFT-PBE-vdW scheme: Grimme-D2

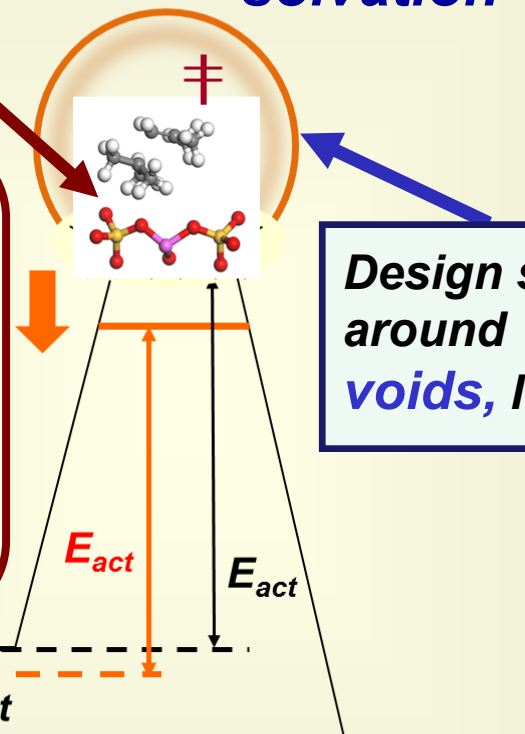
Guiding molecules across energy landscapes

Construct and probe specific "binding points"

….. acid strength impacts reactivity and selectivity

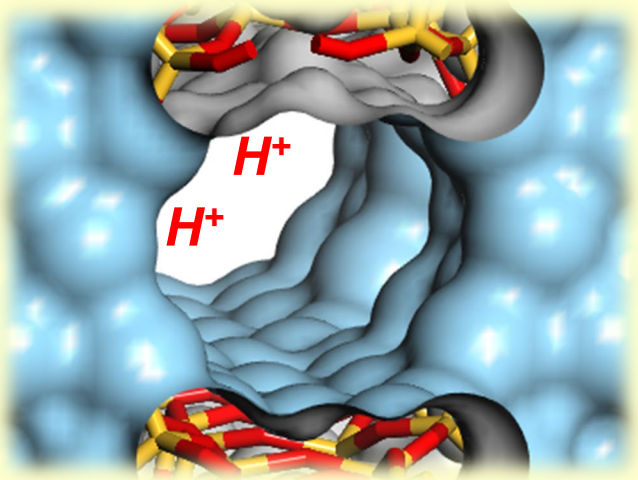
…. charge (and charge distribution) in bound precursors and transition states

"solvation"



Design solvating environments around "binding points": voids, liquids, dense adlayers

voids



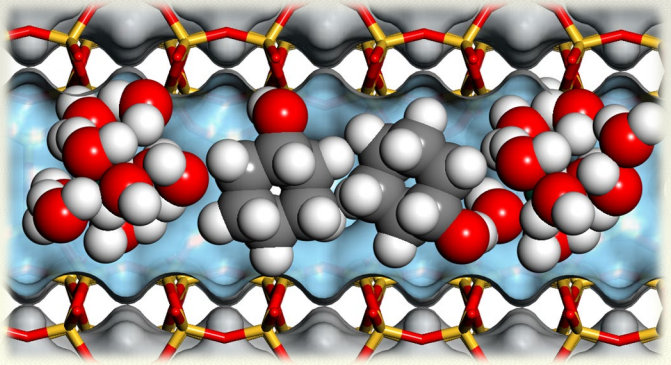
inorganic hosts

….. confinement impacts reactivity and selectivity

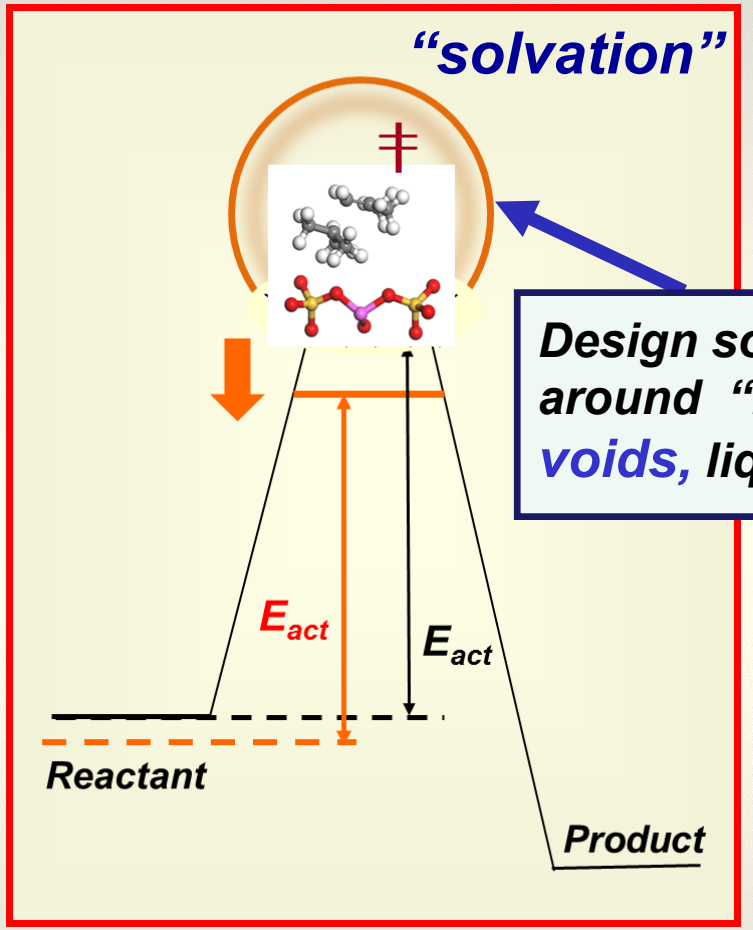
…. size (and shape) of "containers", bound precursors, and transition states

"Environmental" effects in catalysis … the outer sphere effects

liquids

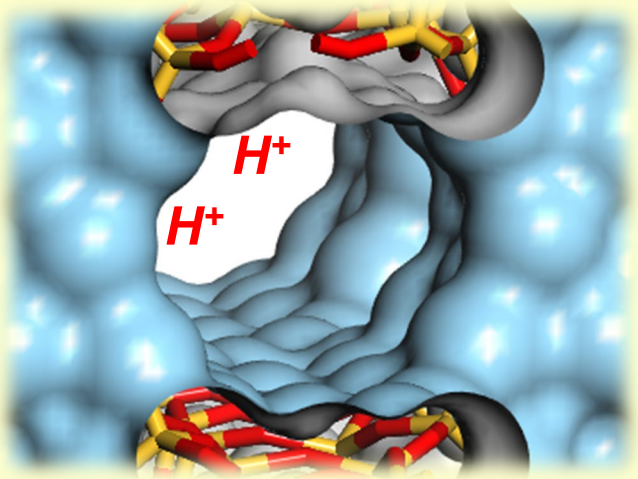


…. more flexible and diverse in composition



Design solvating environments around "binding points": voids, liquids, dense adlayers

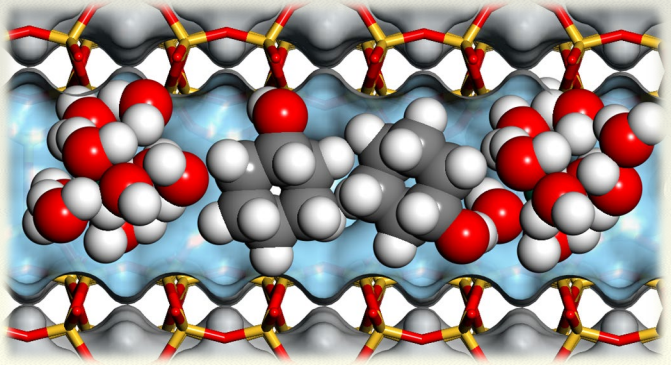
voids



inorganic hosts

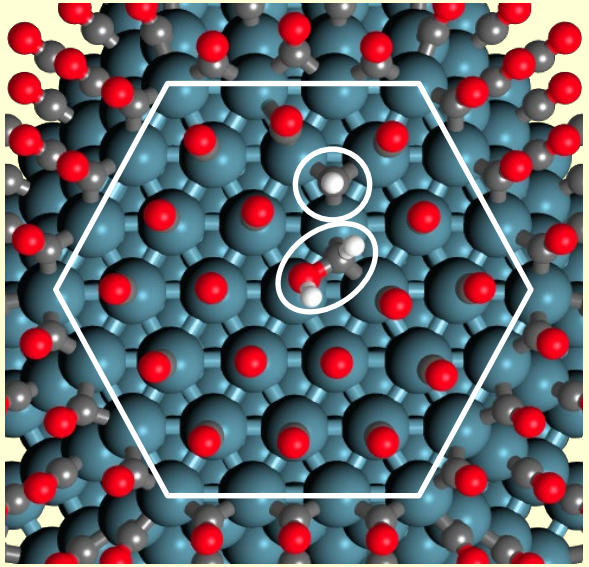
"Environmental" effects in catalysis … the outer sphere effects

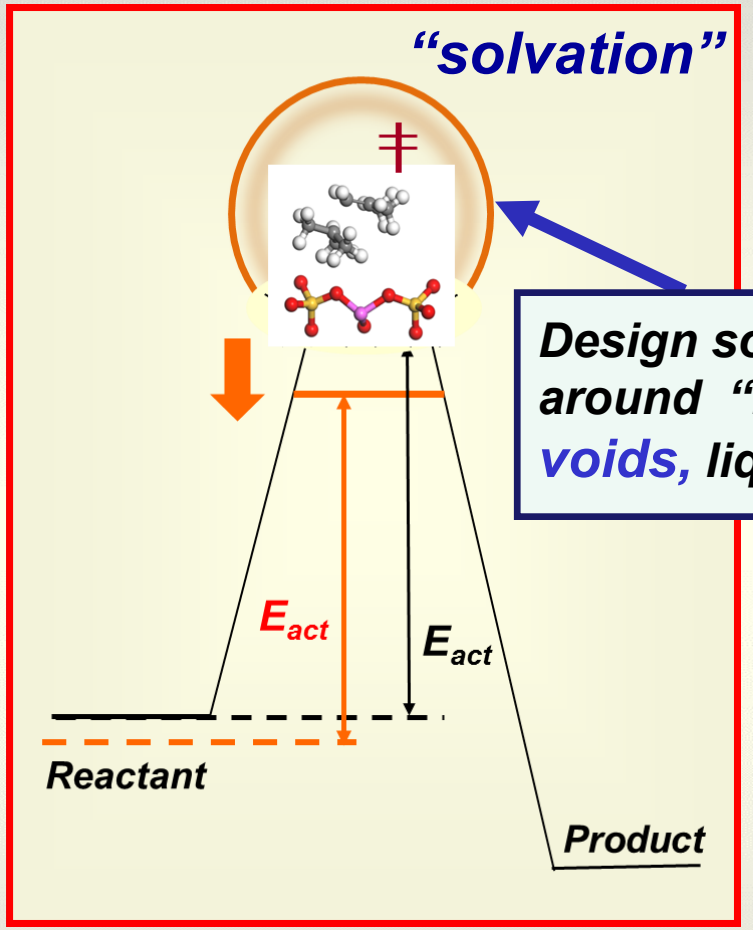
liquids



…. more flexible and diverse in composition

dense adlayers

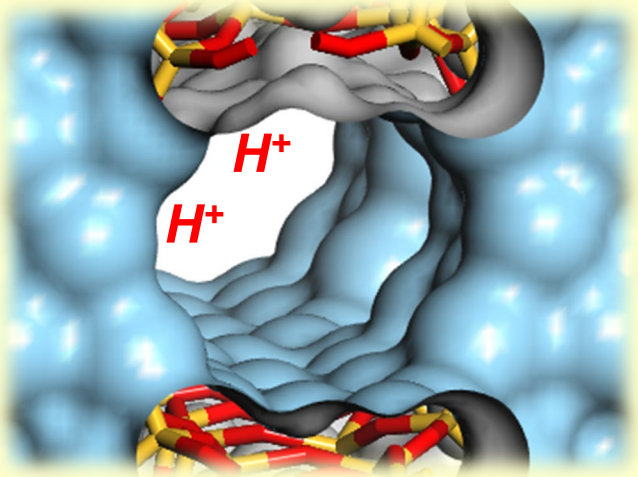




Design solvating environments around "binding points": voids, liquids, dense adlayers

…. bound species as solvents and "anti-solvents"

voids

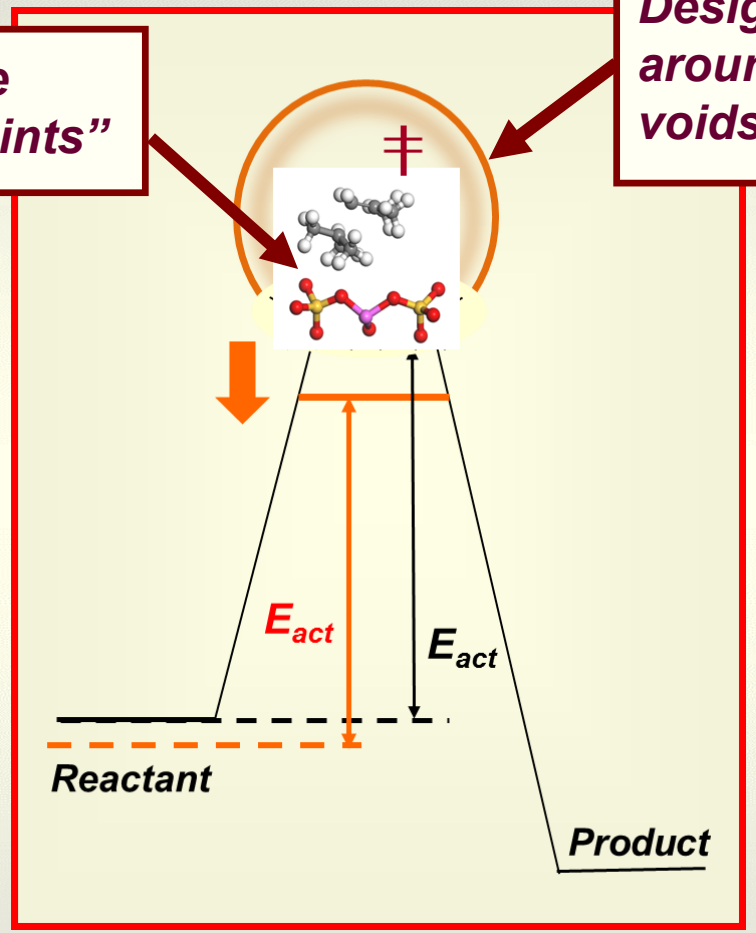


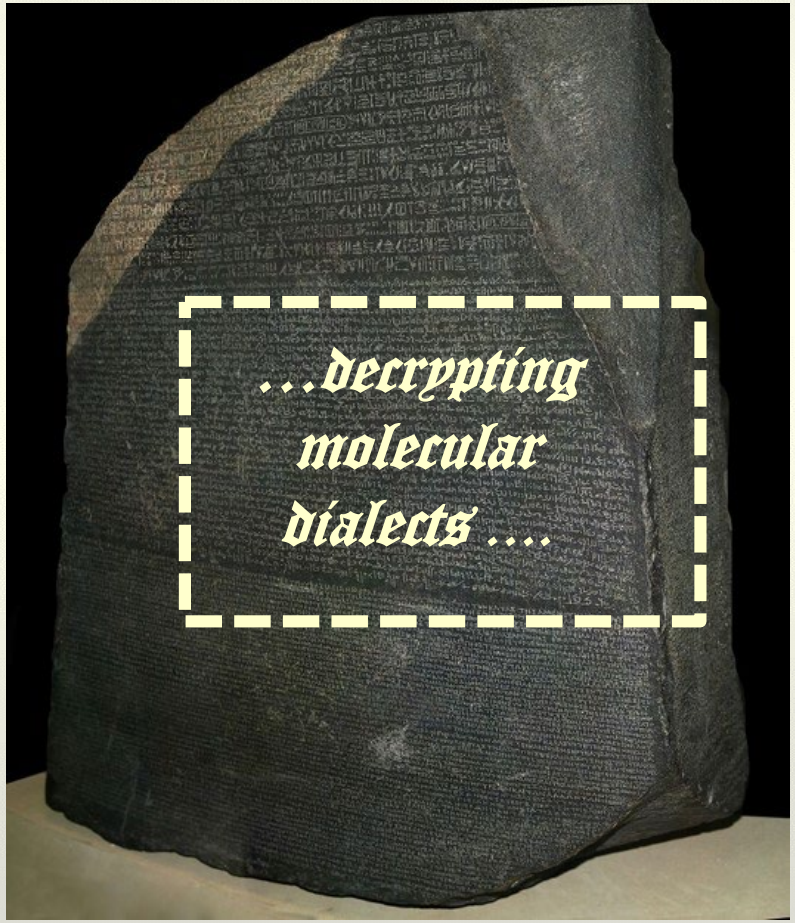
inorganic hosts

Catalysis: Guiding molecules across energy landscapes ….. and the tools that shape such landscapes

Construct and probe specific "binding points"

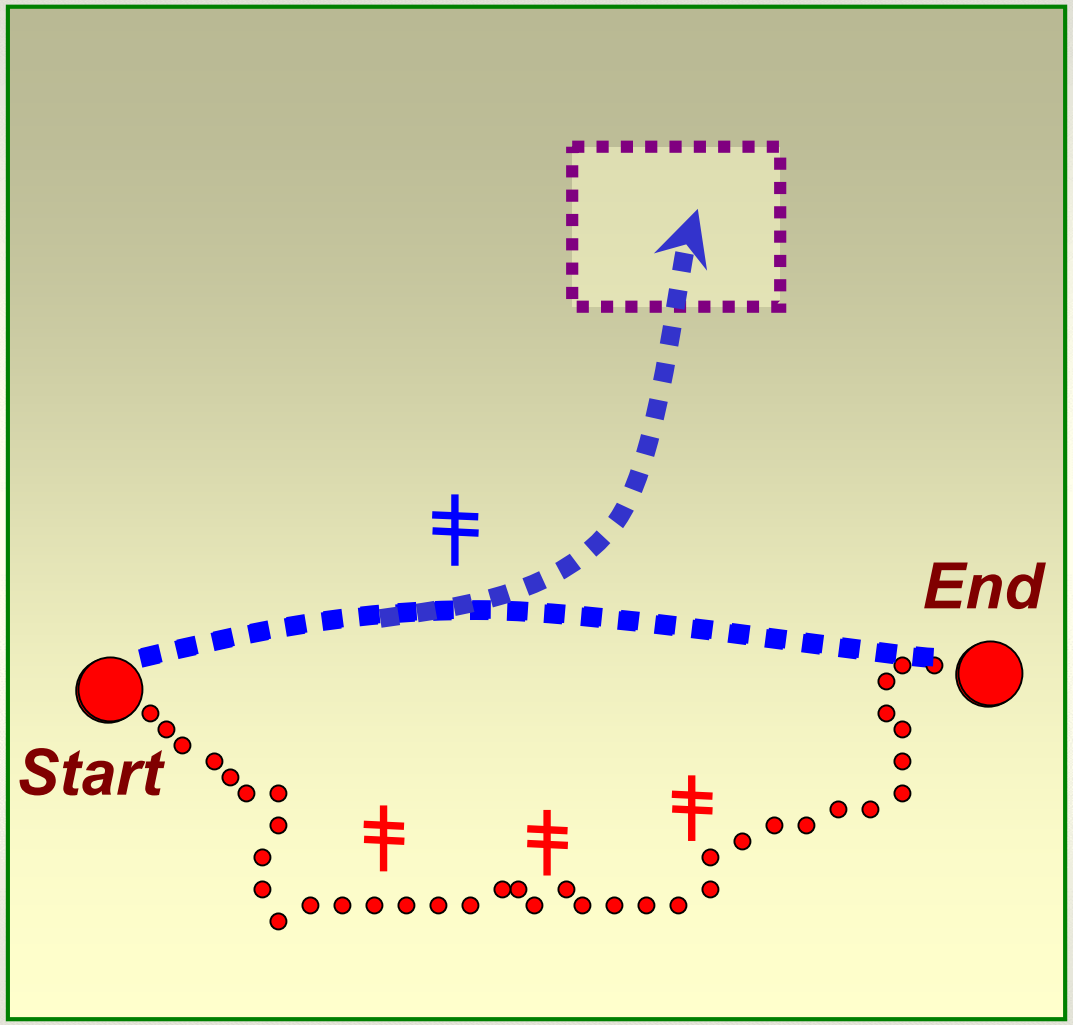
Design solvating environments around "binding points": voids, liquids, dense adlayers



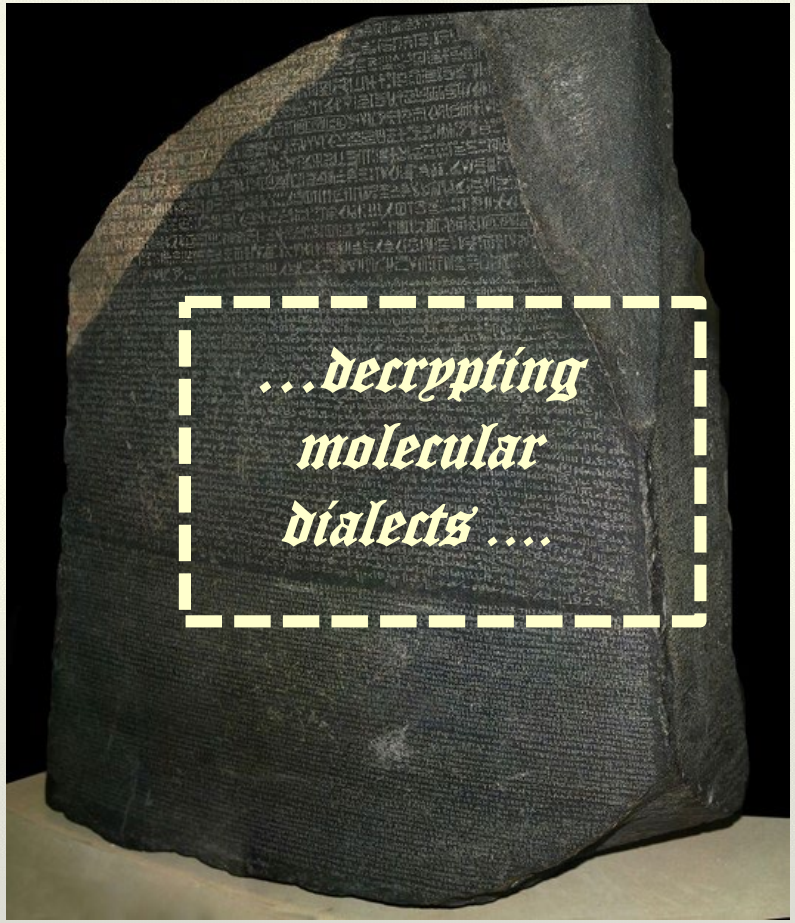


… connect reactivity/selectivity with energies (not just compositions or structures)

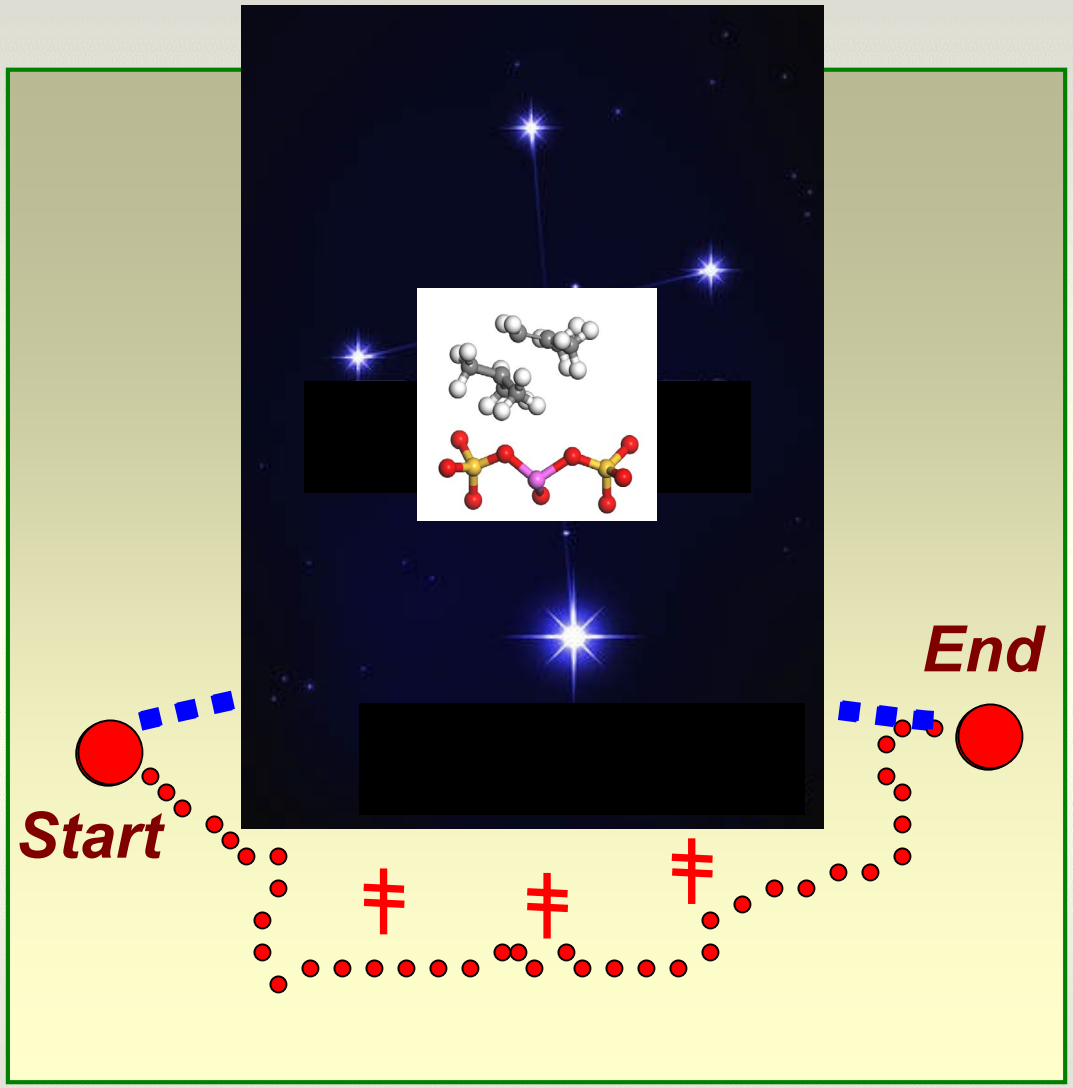
“Staring at transition states …”



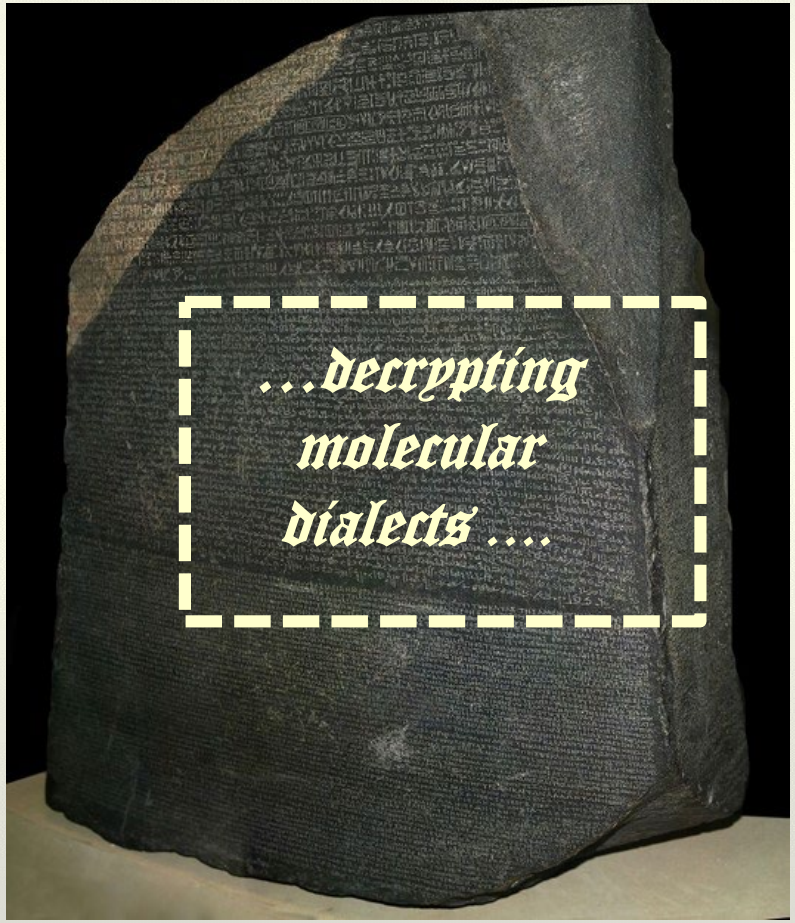
… connect reactivity/selectivity with energies (not just compositions or structures)



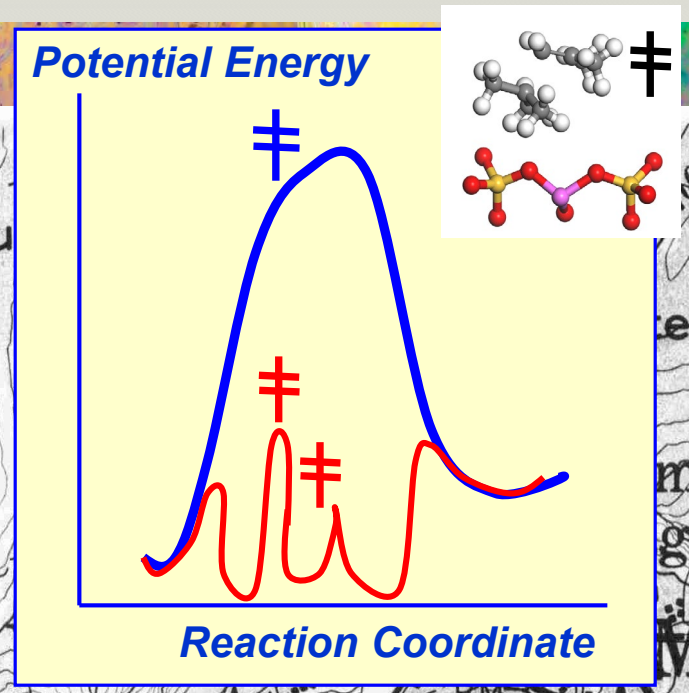
“Staring at transition states …”



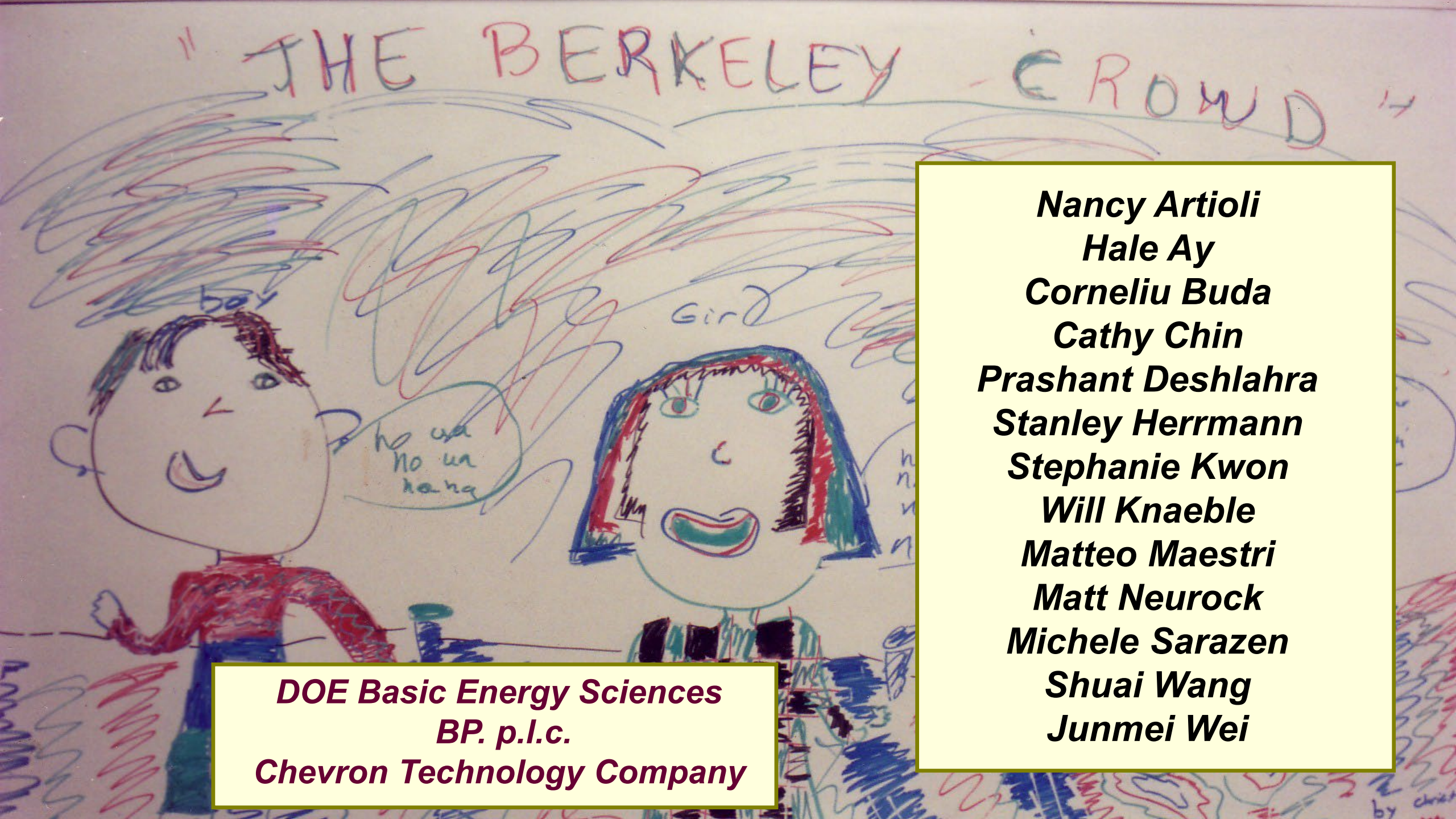
… connect reactivity/selectivity with energies (not just compositions or structures)



Surface catalysis …. channeling molecules through energy landscapes



…… staring at transition states



DOE Basic Energy Sciences
BP. p.l.c.
Chevron Technology Company

Nancy Artioli
Hale Ay
Corneliu Buda
Cathy Chin
Prashant Deshlahra
Stanley Herrmann
Stephanie Kwon
Will Knaeble
Matteo Maestri
Matt Neurock
Michele Sarazen
Shuai Wang
Junmei Wei

may your mountain passes never be steep .....