Chemical Conversion of Waste for Sustainable Energy

Challenges and Opportunities For Theory and Computation

Matthew Neurock

March 1, 2016

Complexity of the Waste Feeds

Methane, light alkanes, SOx, NOx

Flared Gas

Wet Sludges

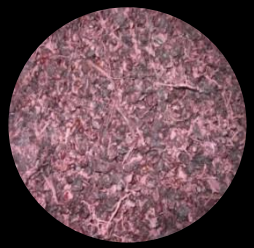
Cynthia Jenks, 2016
"Workshop on Fundamental Science Needs to Address Waste to Chemical Conversions".

Lignocellulose

Agriculture Residues

Sulfur rich lignins
Nasty!

Pulp Waste



Sugars, Oils, Cellulose

Food Processing Waste

Solid cellulose plastics

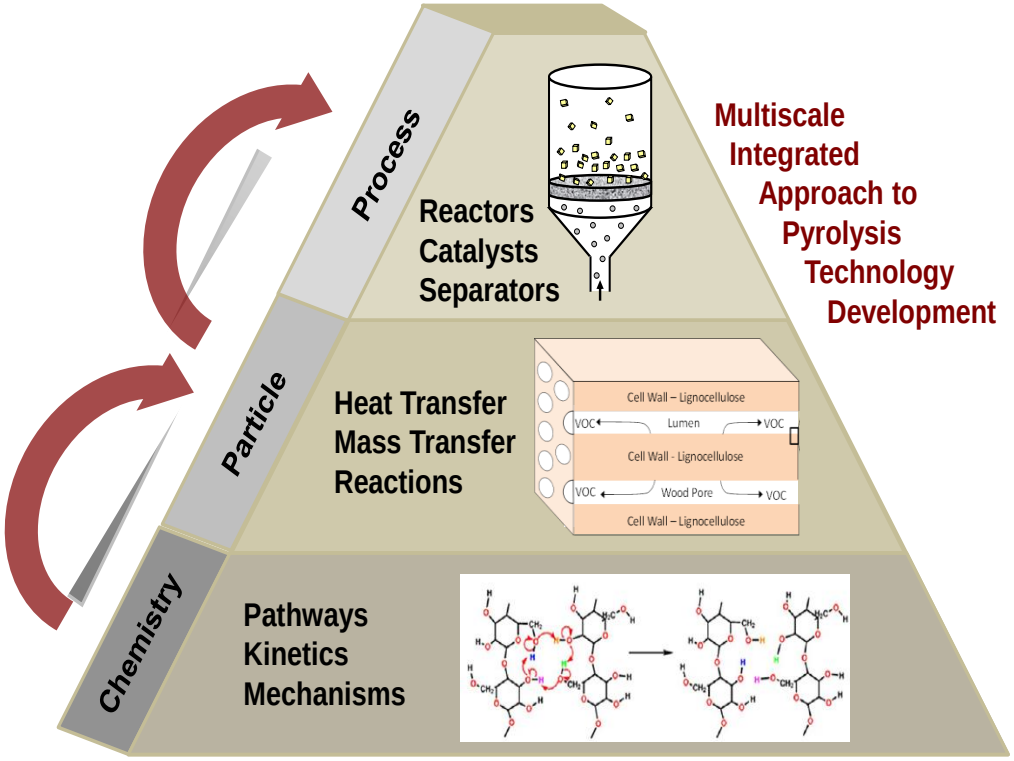
Municipal Solid Waste

Polymers of carbohydrates, proteins, and lipids

Challenges in Pyrolytic and Catalytic Conversion of Biomass

P. Dauenhauer

Challenge: Complete description of biomass pyrolysis and catalysis requires a 'ground-up' description at three length scales: molecular, particle, reactor/process.



c. Reactors

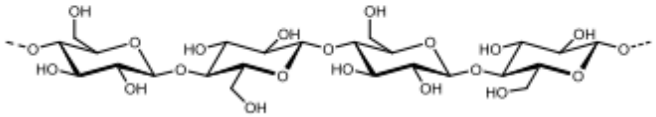
b. Particles

a. Pyrolysis and Catalytic Chemistry

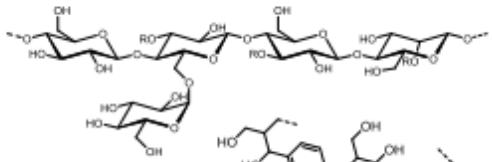
Chemistry of hydrothermal liquefaction

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

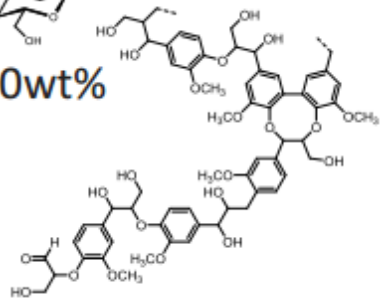
Cellulose = 0 - 45 wt%



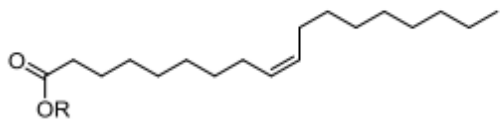
Hemicellulose = 0 - 30 wt%



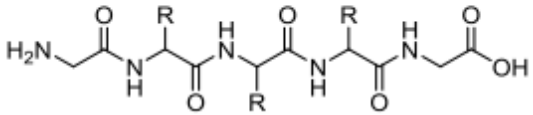
Lignin = 0 - 30wt%



Lipids/fats = 0 – 20%



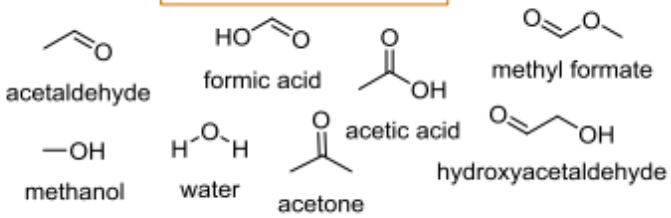
Proteins = 0 – 50 wt%



Inorganic = 0.1 - 20 wt%

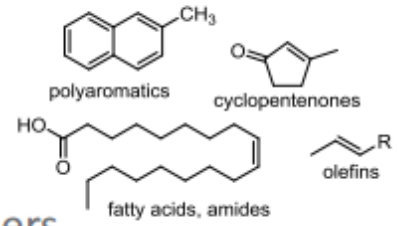
K, Na, Ca, P, Mg, Mn, Si, etc.

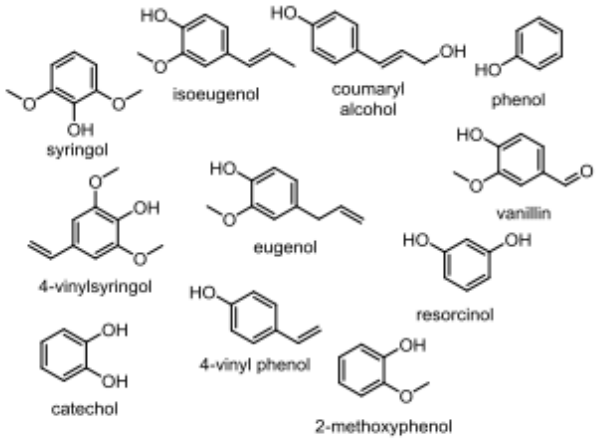
Water phase



Biocrude oil phase

No sugars
Few ketones,
Few aldehydes
Low alcohols
Few aliphatic ethers

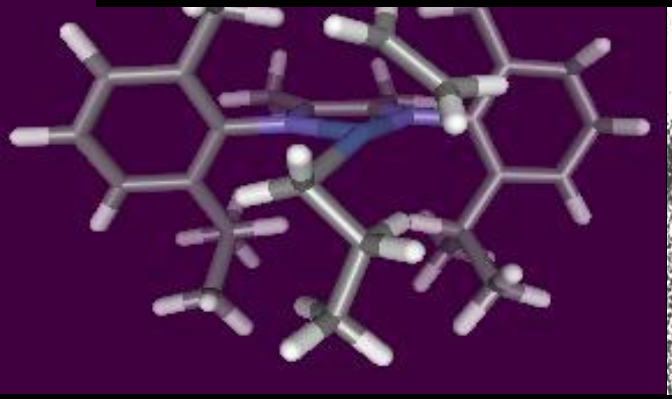




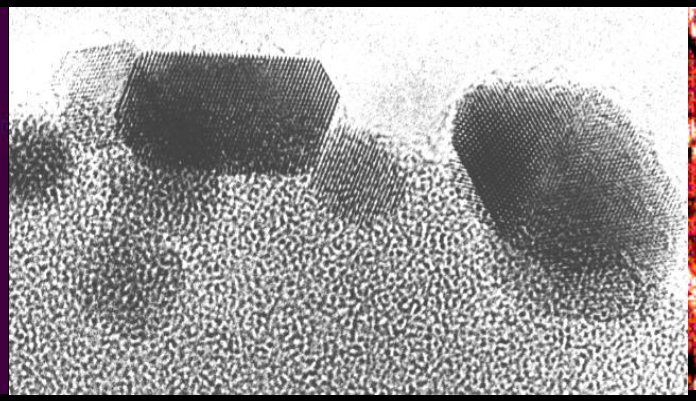
7

J. Holladay PNNL

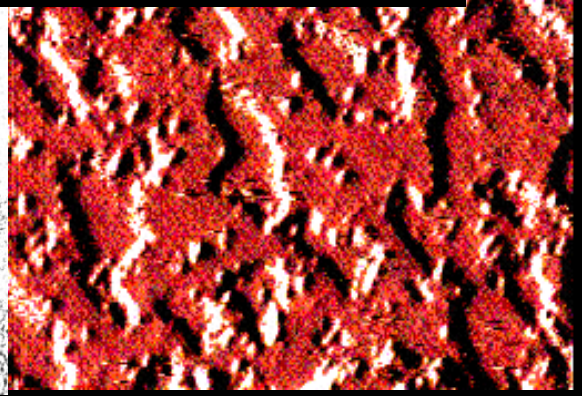
Challenges of Current Material Architectures



Homogeneous



Supported Metals

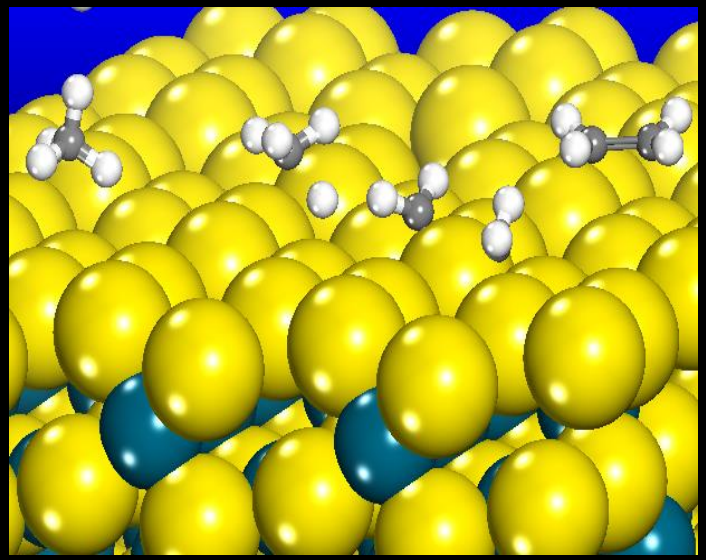


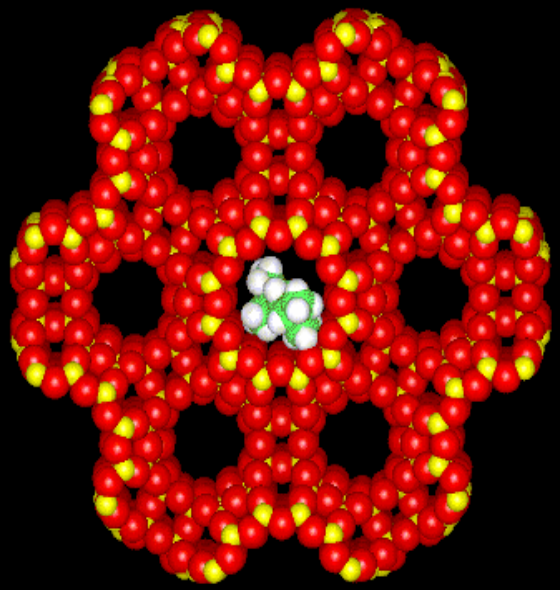
Metals Surface

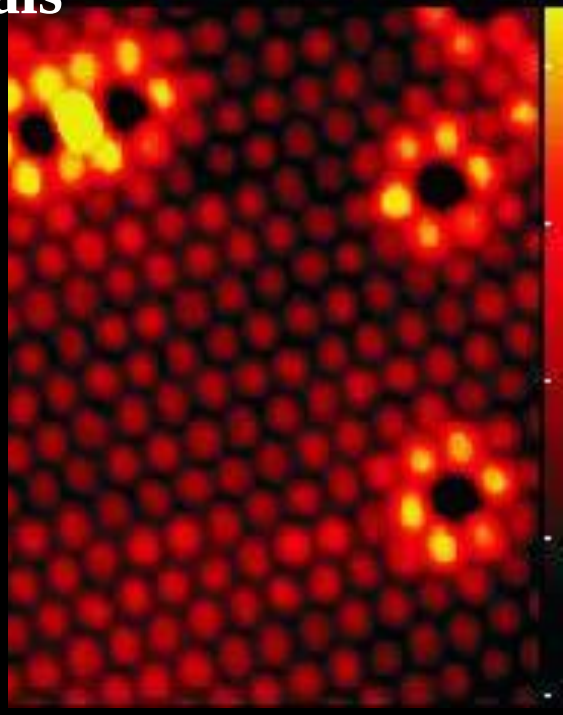
Bimetallics

Sulfides, Carbides, Nitrides

Microporous Materials







Catalysis for Nanostructured Materials, NSF WTEC study, 2010.

Selective Molecular Transformations

Model Compound Studies

Catalyst Needs and Opportunities

Fundamental Model Catalytic Studies

Selective activation of C-O, C-H & C-C bonds of oxygenates

Polyols, Cyclic Ethers, Acids, Aldehydes and Ketones

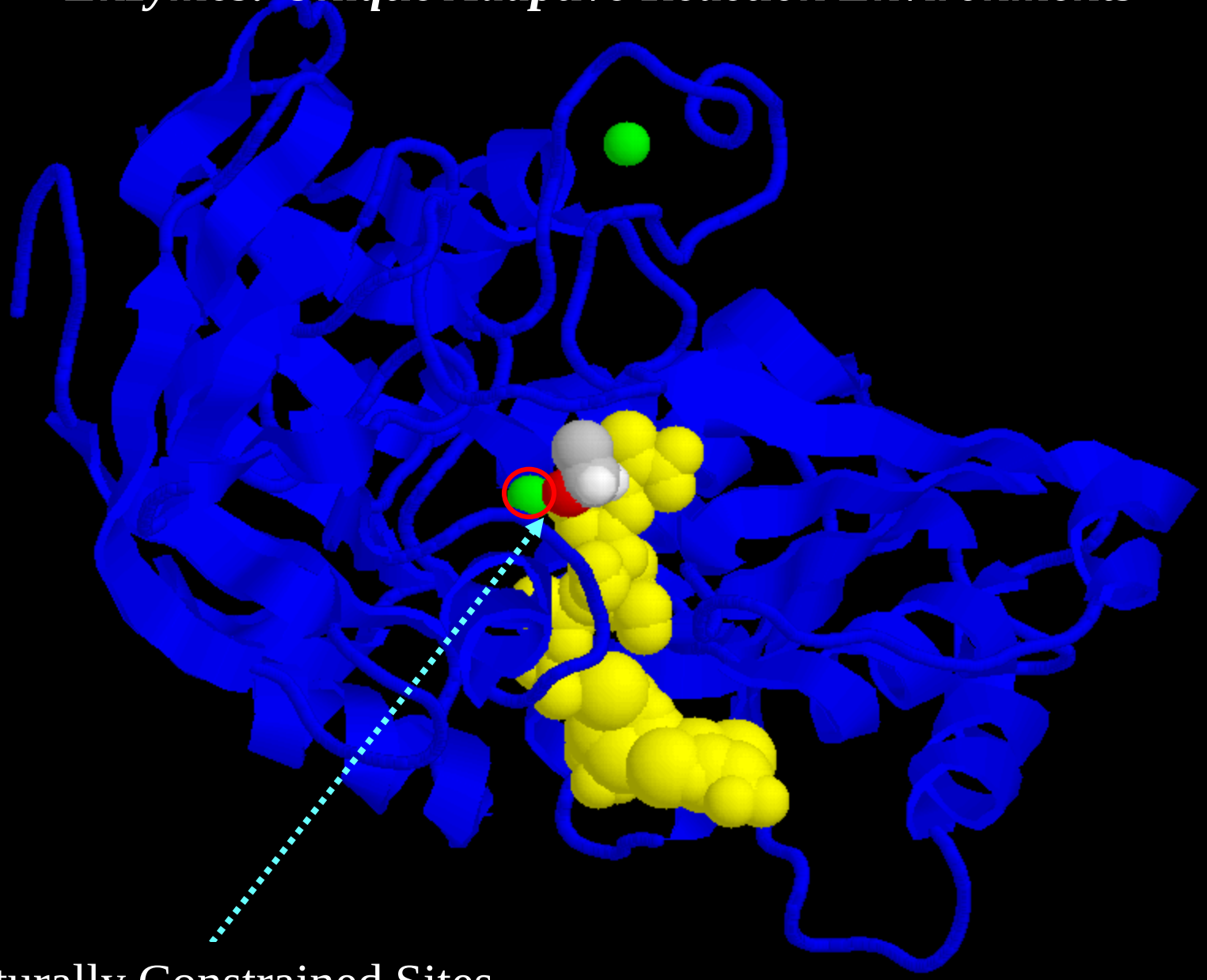
Activation and conversion of phenolics

Activation and conversion of methane and light alkanes

Gas to liquids - Fischer Tropsch Synthesis

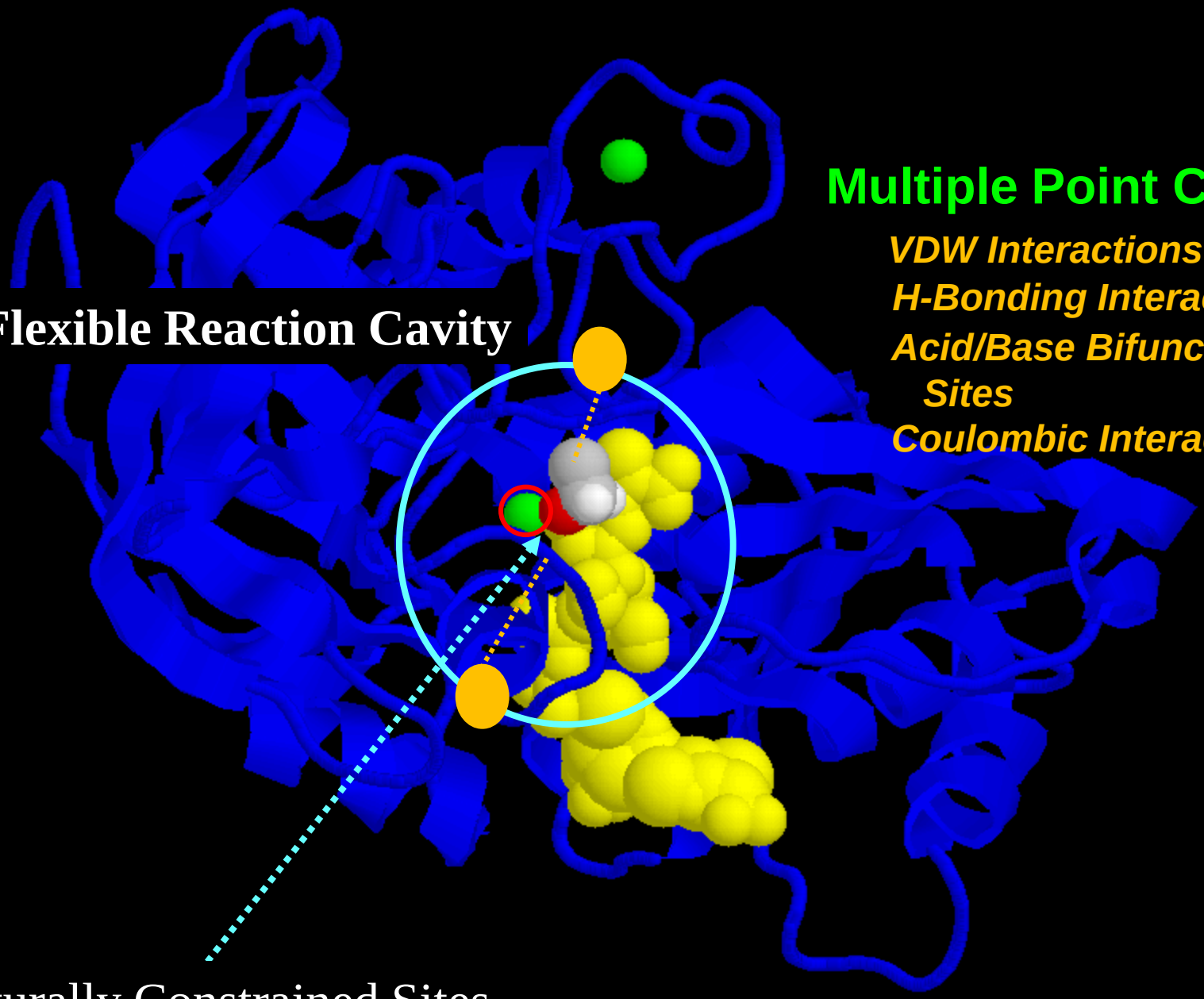
Manipulating and Controlling Molecular Transformations

Enzymes: Unique Adaptive Reaction Environments



Structurally Constrained Sites

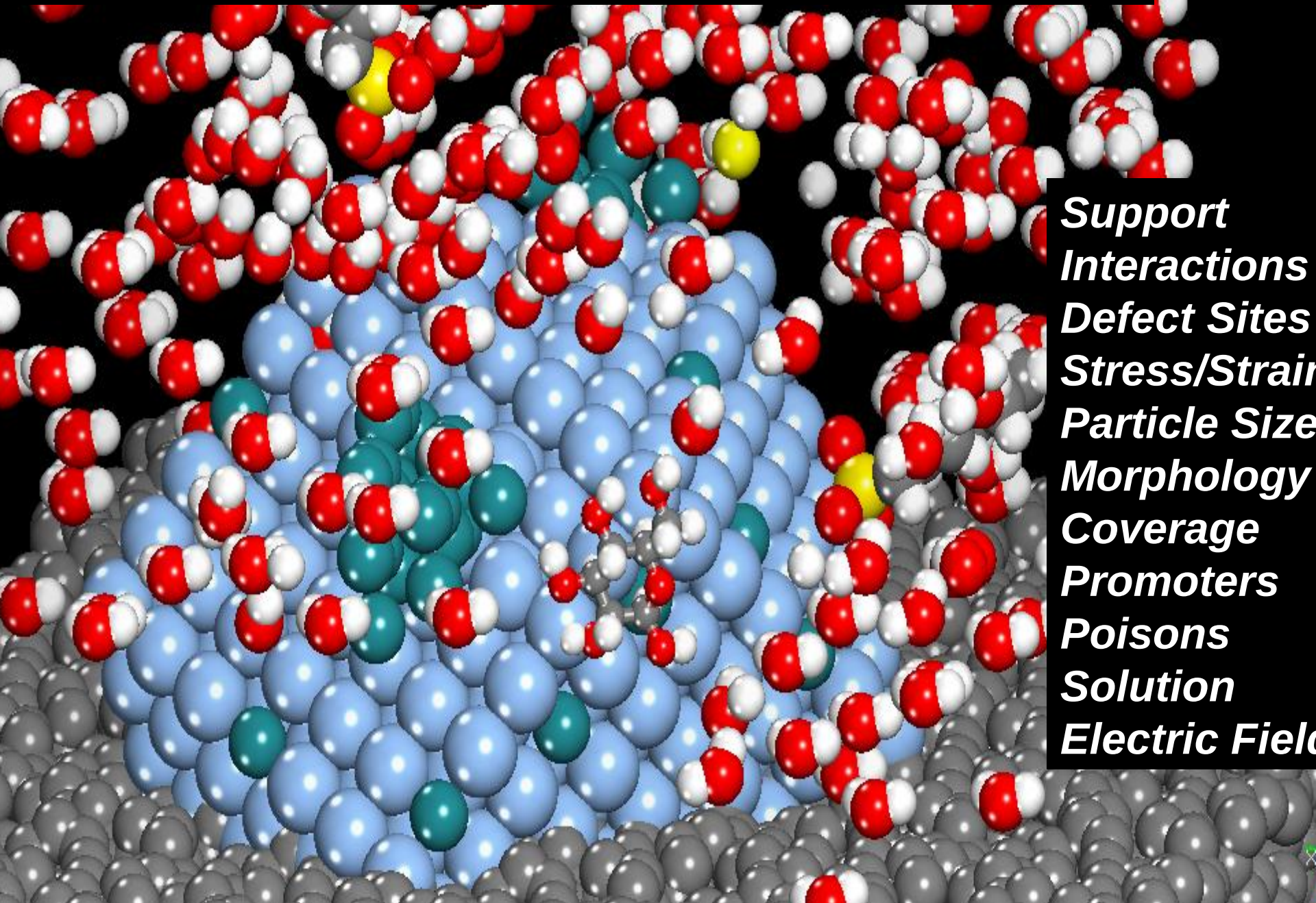
Manipulating and Controlling Molecular Transformations



Multiple Point Contact

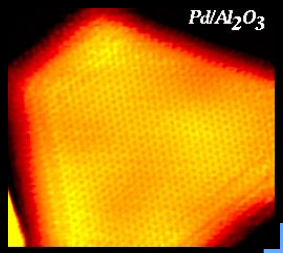
VDW Interactions
H-Bonding Interactions
Acid/Base Bifunctional Sites
Coulombic Interactions

Catalytic Sites & Their Environment



Support
Interactions
Defect Sites
Stress/Strain
Particle Size
Morphology
Coverage
Promoters
Poisons
Solution
Electric Field

Multiscale Modeling Development



Time

Reactor Modeling

Haldor Topsoe

Nanoscale Properties

MC Methods
Deterministic Methods
CFD

Atomic Structure

Brownian Dynamics
Finite Element Methods

Electronic Structure

Molecular Dynamics
Monte Carlo Simulation

$$V_r = 1/2 k_{IJ} \left(r - r_{ij}\right)^2$$

10^4-10^5 Atoms

Ab Initio Quantum Mechanics
Ab Initio Molecular Dynamics

100's of Atoms

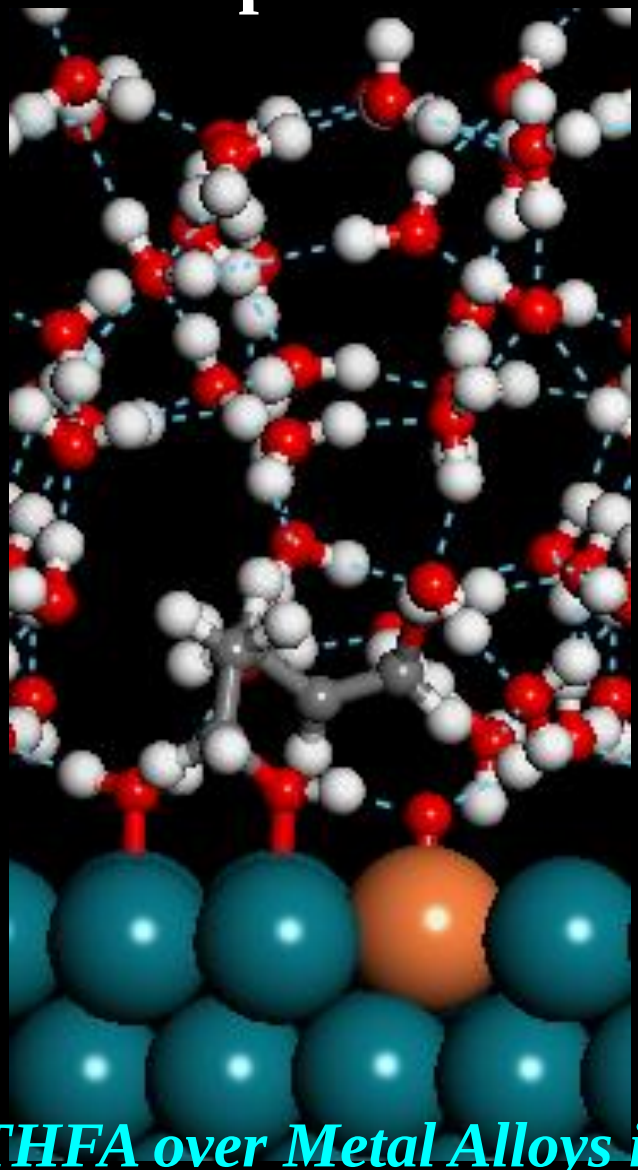
$$H\Psi = E\Psi$$

Length

M. Neurock

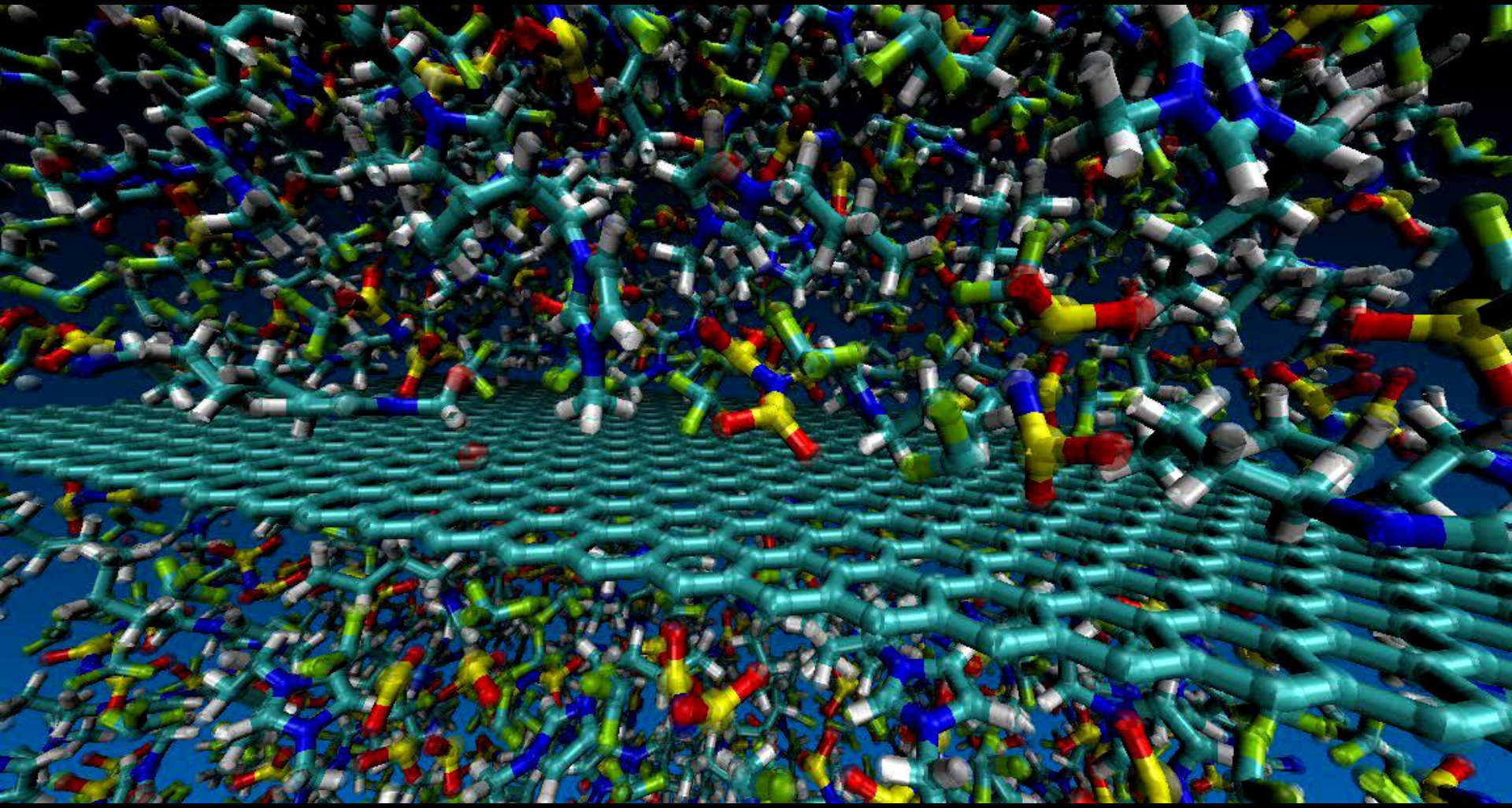
Ab Initio Molecular Dynamics

Free Energies for Complex Solution/Metal Interfaces



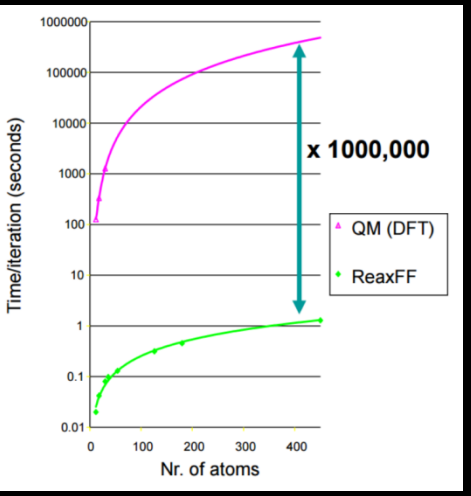
Ring Opening of THFA over Metal Alloys in Water

Advances in CPU and Methods: Significant Advances in Simulation Environments

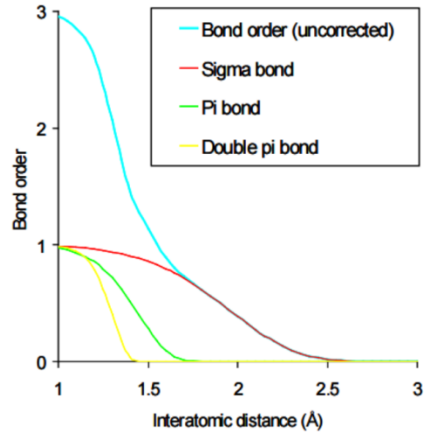


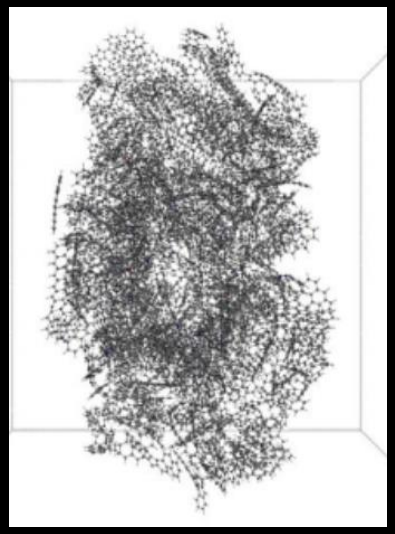
P. Cummings, Vanderbilt University.

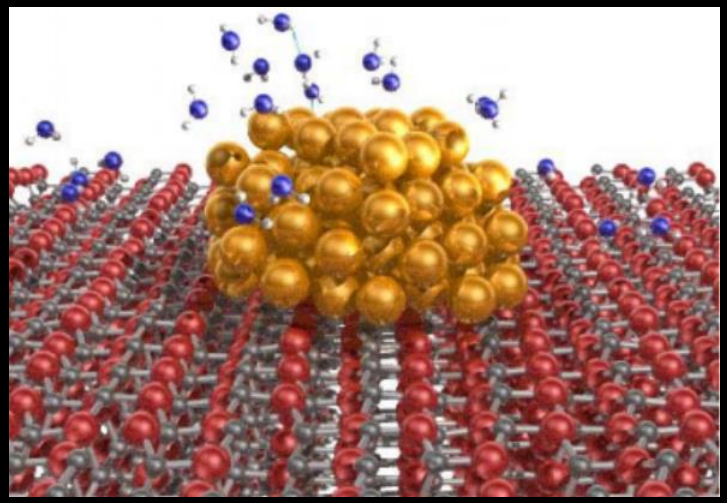
Reactive Force Fields - Molecular Dynamics



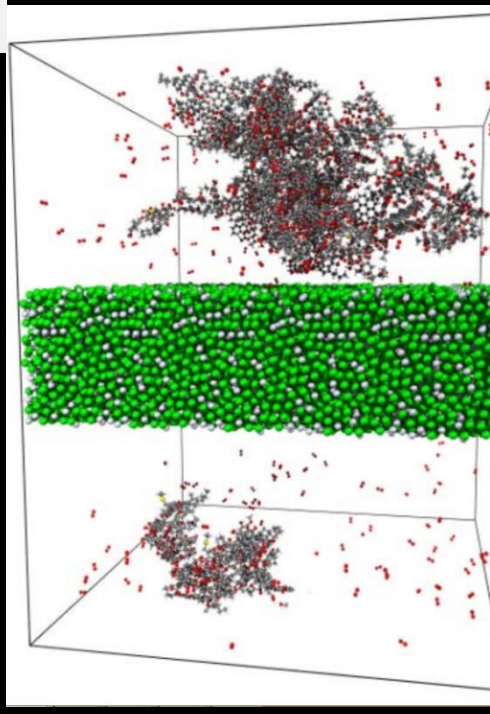
$$BO'_{ij} = \exp\left[p_{bo,1}\cdot\left(\frac{r_{ij}}{r_o^{\sigma}}\right)^{p_{bo,2}}\right] + \exp\left[p_{bo,3}\cdot\left(\frac{r_{ij}}{r_o^{\pi}}\right)^{p_{bo,4}}\right] + \exp\left[p_{bo,5}\cdot\left(\frac{r_{ij}}{r_o^{\pi\pi}}\right)^{p_{bo,6}}\right]$$







A. Van Dyne (PSU), W. Goddard (Caltech)



Computational Catalysis

Where Are We Today?

Prediction of Structure and Properties.

Connection with Spectroscopy

Determination of Energetics

Elucidation of Mechanism

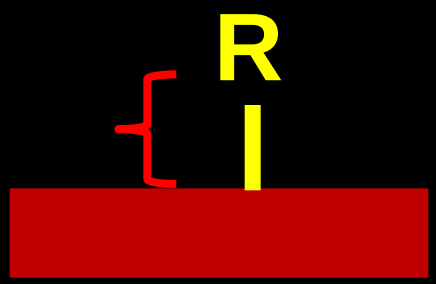
Initial Stages of Catalyst Design

Metals, Composition, Support, Surface Structure, Promoters

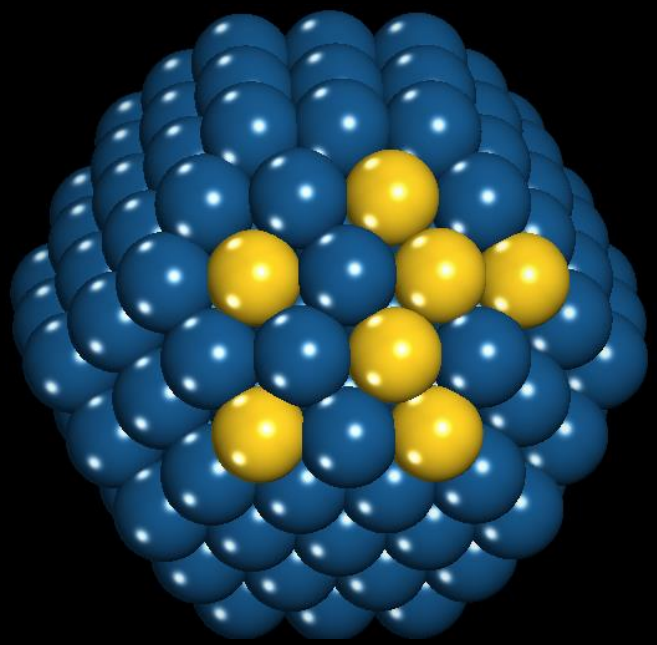
NSF Report, "An International Assessment of Research in Catalysis by Nanostructured Materials", (http://www.wtec.org/catalysis/)

Controlling Design

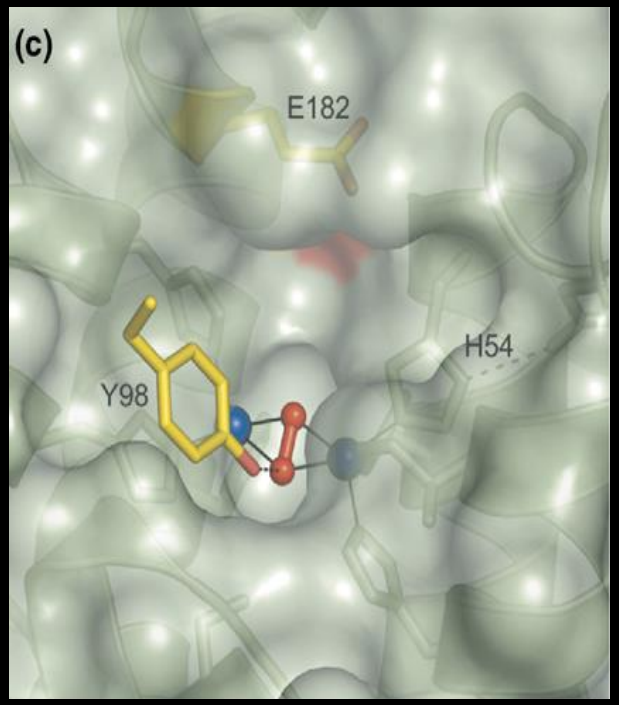
1D



2D



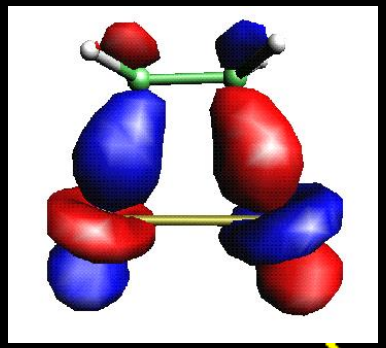
3D



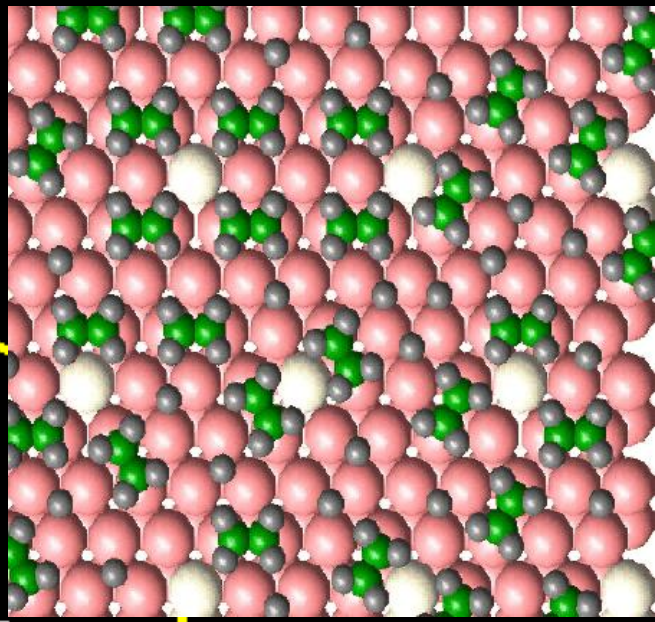
Reaction Environment Effects Catalyst Performance

Simulating Catalytic Kinetics

Ab Initio Periodic DFT Methods



Reaction Mechanism
Adsorption Energies
Activation Barriers
Rate Constants
Equilibrium Constants

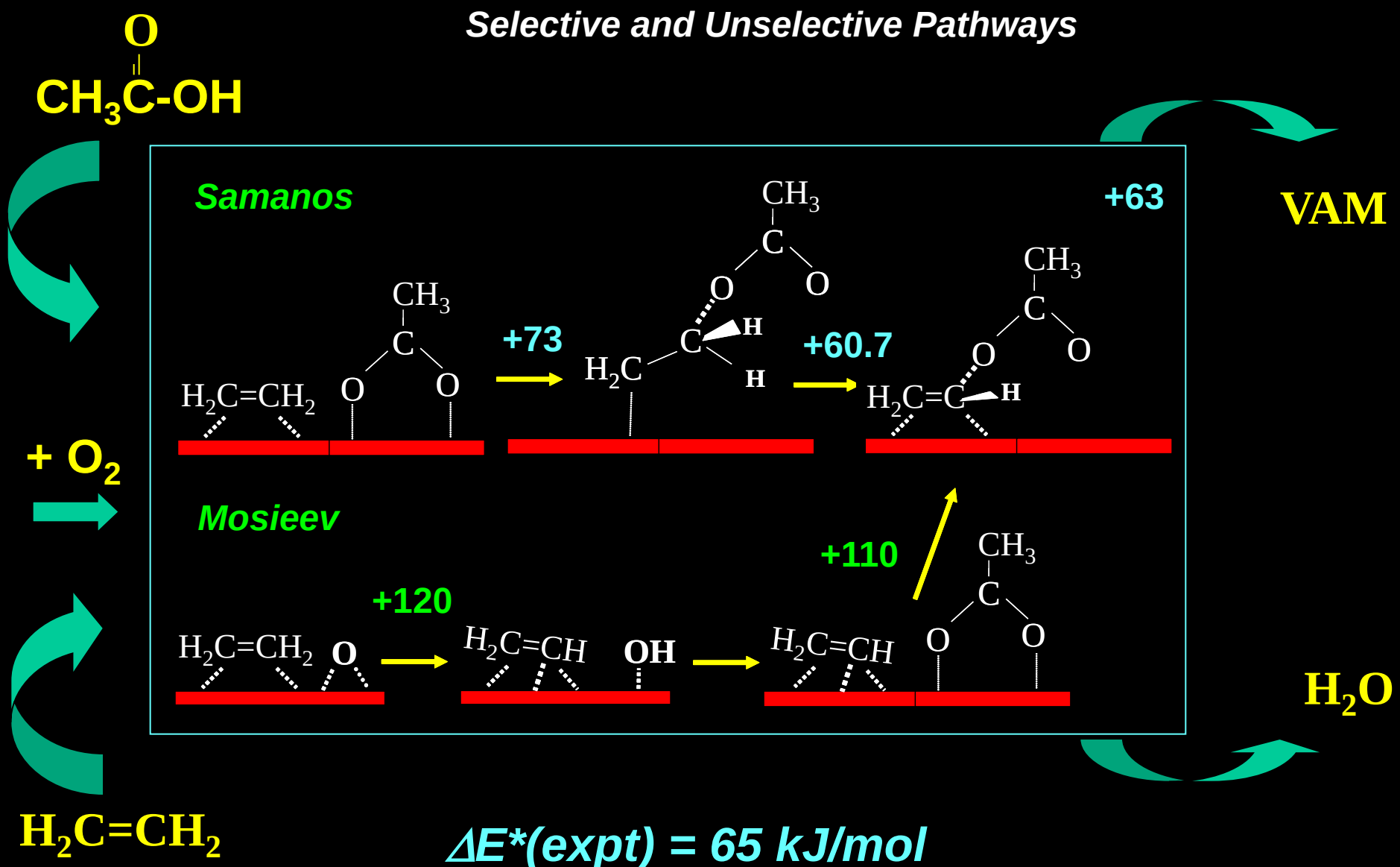


Reactivity

Monte Carlo Simulation

Vinyl Acetate Synthesis

Selective and Unselective Pathways



ΔE*(expt) = 65 kJ/mol

M. Neurock and W. Tysoe.

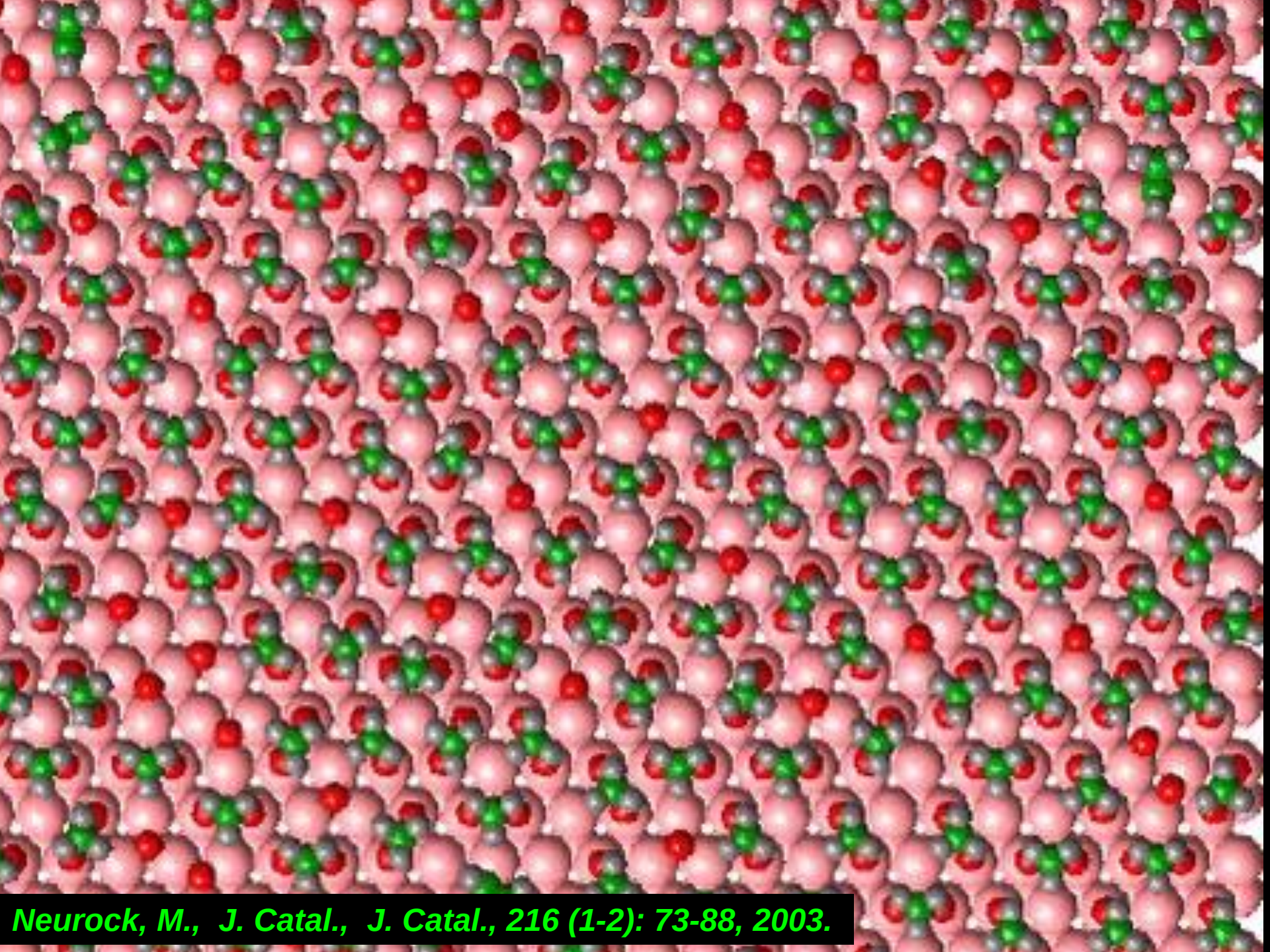
Reaction Kinetics

Vinyl Acetate Synthesis

	ν_{for}	ν_{rev}	E_{for}	E_{rev}
$O_2 = O^* + O^*$	1	10^{13}	0.0	42.4
$H_2 = H^* + H^*$	0.1	10^{13}	6.9	19.7
$C_2H_4 = C_2H_4^*$	1	10^{9}	0.0	14.0
$MeCO_2H = MeCO_2H^*$	1	10^{13}	0.0	11.9
$MeCO_2H = MeCO_2^* + H^*$	1	10^{13}	0.0	14.3
$MeCO_2H + O^* = MeCO_2^* + OH^*$	1	10^{13}	0.0	20.1
$CO = CO^*$	1	10^{13}	0.0	35.1
$CO_2 = CO_2^*$	1	10^{13}	0.0	5.6
$H_2O = H_2O^*$	1	10^{13}	0.0	9.6
$MeCO_2CHCH_2 = MeCO_2^* + CHCH_2^*$	1	10^{13}	5.6	15.8
$MeCO_2CHCH_2 + H^* = MeCO_2^* + CHCH_2^*$	1	10^{13}	0.	25.3
$C_2H_4 = CHCH_2^* + H^*$	1	10^{13}	8.1	7.0
$C_2H_4 + O^* = CHCH_2^* + OH^*$	1	10^{13}	3.6	8.3
$OH^* = O^* + H^*$	10^{13}	10^{13}	20.8	15.0
$2\,OH^* = O^* + H_2O^*$	10^{13}	10^{13}	5.6	19.4
$CH^* = C^* + H^*$	10^{13}	10^{13}	32.5	11.2
$CH^* + O^* = C^* + OH^*$	10^{13}	10^{13}	34.0	18.4
$CH_2^* = CH^* + H^*$	10^{13}	10^{13}	17.3	26.2

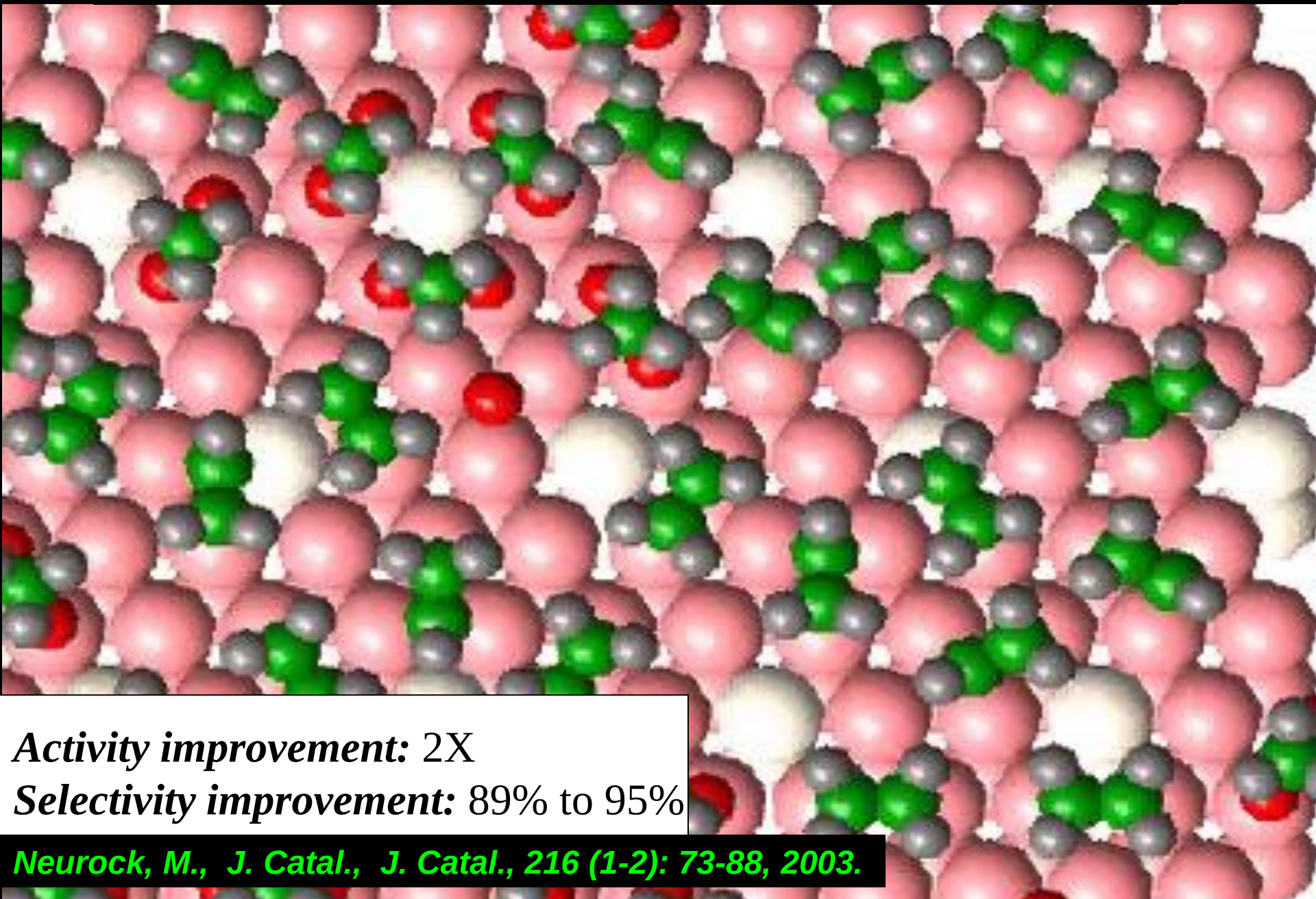
	ν_{for}	ν_{rev}	E_{for}	E_{rev}
$CH_2^* + O^* = CH^* + OH^*$	10^{13}	10^{13}	11.1	25.8
$C_2H_4^* + O^* = CHCH_2^* + OH^*$	10^{13}	10^{13}	17.7	8.3
$C_2H_4^* = CHCH_2^* + H^*$	10^{13}	10^{13}	22.1	7.0
$CHCH_2^* = CH^* + CH_2^*$	10^{13}	10^{13}	27.9	24.3
$CHCH_2^* = H^* + CCH_2^*$	10^{13}	10^{13}	24.6	16.3
$CHCH_2^* + O^* = OH^* + CCH_2^*$	10^{13}	10^{13}	18.8	16.2
$MeCO_2H^* = MeCO_2^* + H^*$	10^{13}	10^{13}	12.8	15.2
$MeCO_2H^* + O^* = MeCO_2^* + OH^*$	10^{13}	10^{13}	1.1	9.3
$MeCO_2^* + O^* = CH_2CO_2^* + OH^*$	10^{13}	10^{13}	18.7	12.1
$MeCO_2^* = CH_2CO_2^* + H^*$	10^{13}	10^{13}	23.9	11.5
$CH_2CO_2^* = CH_2 + CO_2^*$	10^{13}	10^{13}	6.3	0.0
$CHCH_3^* = CHCH_2^* + H^*$	10^{13}	10^{13}	15.7	13.3
$CHCH_3^* + O^* = CHCH_2^* + OH^*$	10^{13}	10^{13}	17.5	20.9
$CHCH_3^* = CCH_3^* + H^*$	10^{13}	10^{13}	14.8	29.6
$CHCH_3^* + O^* = CCH_3^* + OH^*$	10^{13}	10^{13}	8.5	29.1
$CCH_3^* = CCH_2^* + H^*$	10^{13}	10^{13}	33.2	7.7
$CCH_3^* + O^* = CCH_2^* + OH^*$	10^{13}	10^{13}	36.7	16.9
$CO^* = C^* + O^*$	10^{13}	10^{13}	70.6	0.0
$CCH_2^* = CH_2^* + C^*$	10^{13}	10^{13}	34.5	18.0
$CO_2^* = CO^* + O^*$	10^{13}	10^{13}	32.6	0.0

Neurock, M., J. Catal., J. Catal., 216 (1-2): 73-88, 2003



Neurock, M., J. Catal., J. Catal., 216 (1-2): 73-88, 2003.

Ensemble and Ligand Effects

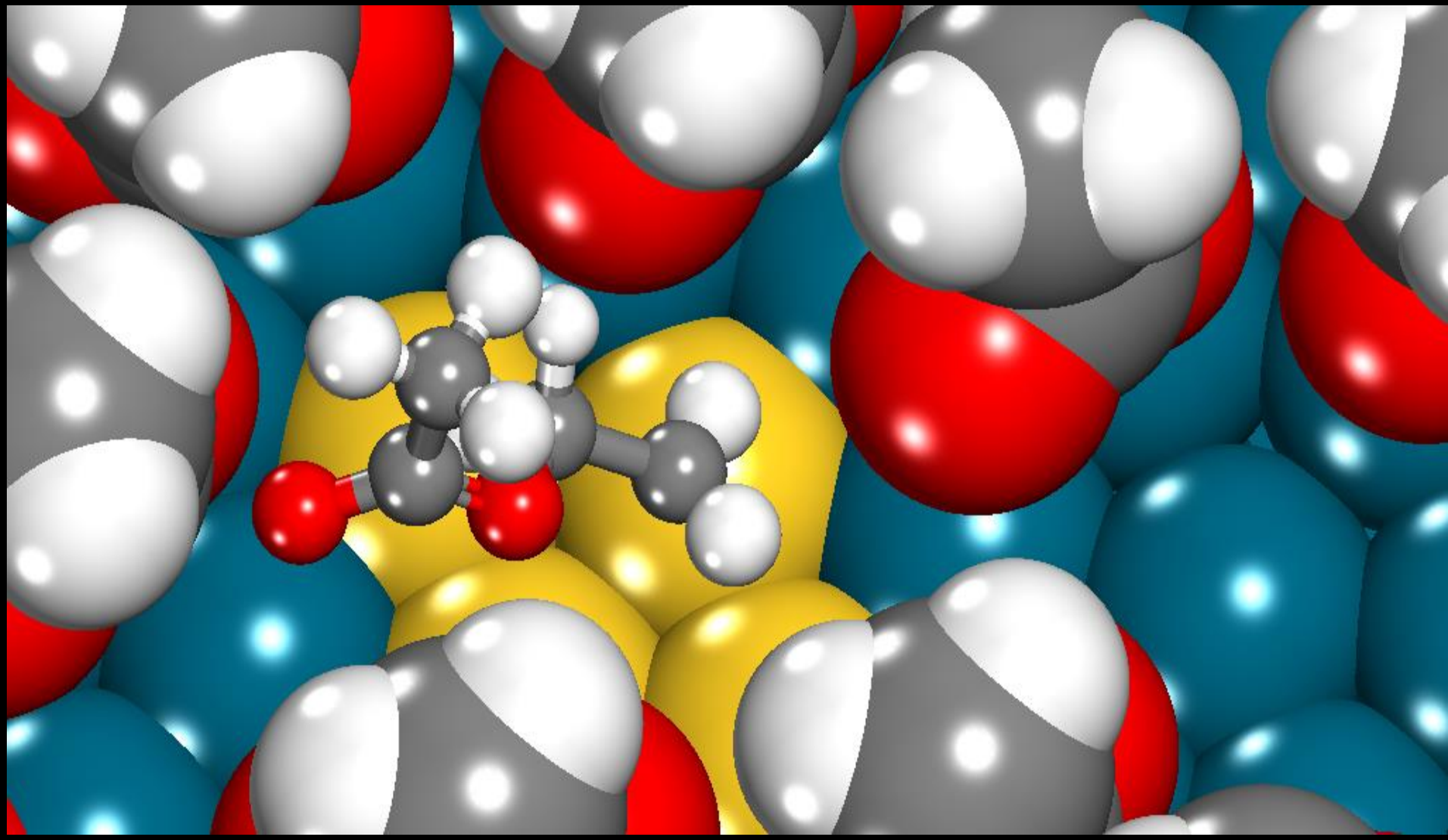


Activity improvement: 2X

Selectivity improvement: 89% to 95%

Neurock, M., J. Catal., J. Catal., 216 (1-2): 73-88, 2003.

Design of Site and Ensemble to Control Self Assembly



M. Neurock

Kinetic Consequences of Chemisorbed O*

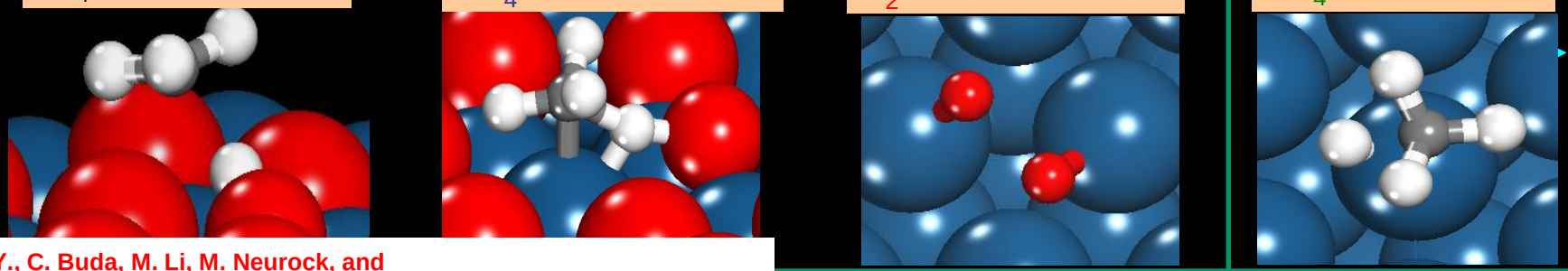
1 2 3 4

$CH_4 + O^* + O^* \xrightarrow{k_{1a}}$

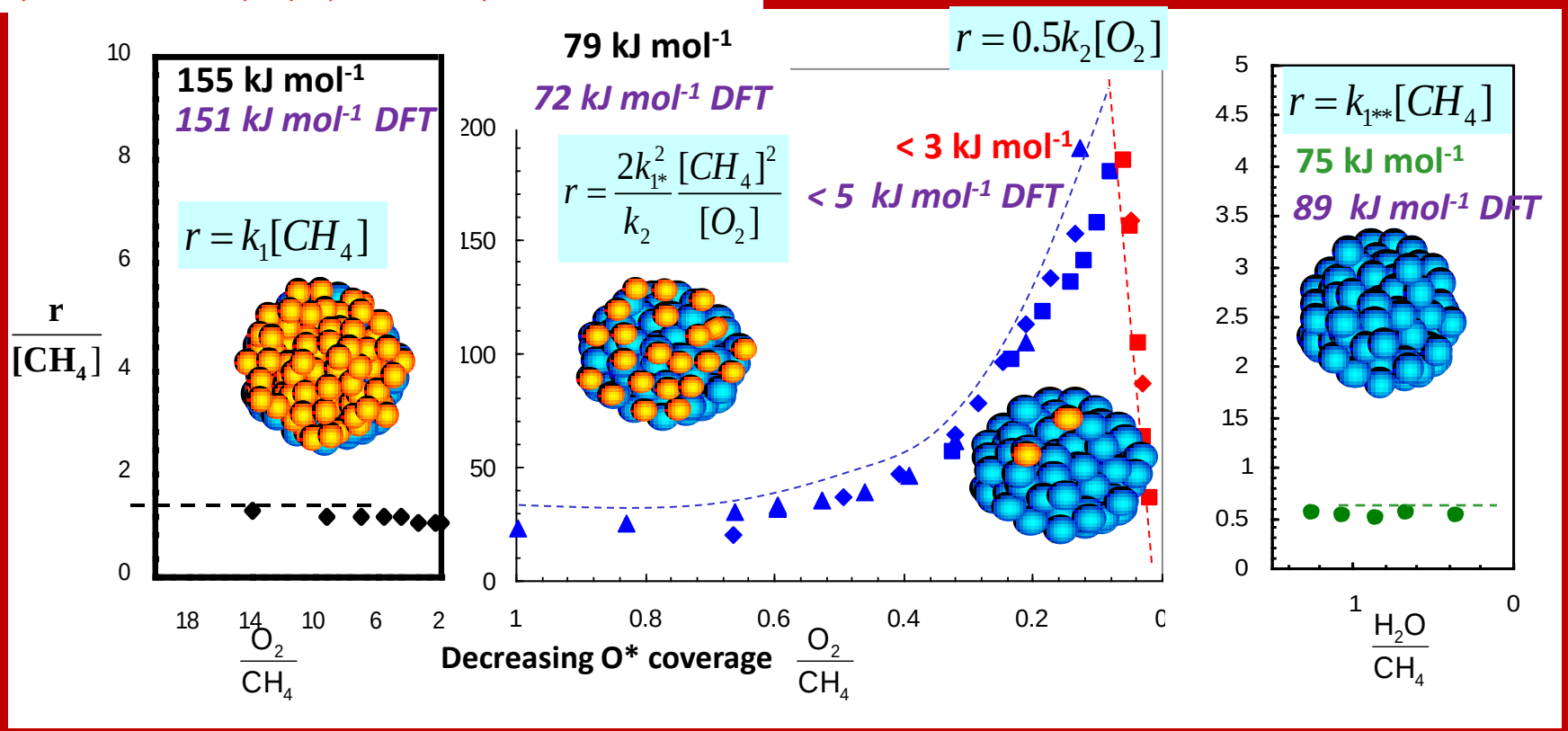
$CH_4 + O^* + * \xrightarrow{k_{1b}}$

$O_2 + 2^* \xrightarrow{k_2} 2O^*$

$CH_4 + * + * \xrightarrow{k_{1c}}$



Chin, Y., C. Buda, M. Li, M. Neurock, and E. Iglesia, *J. Am. Chem. Soc.*,133, 40, 15958-15978, 2011.



Kinetic Consequences of Chemisorbed O*

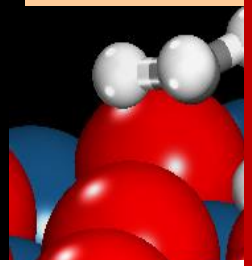
1 2 3 4

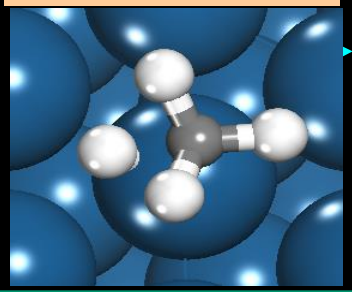
$CH_4 + O^* + O^* \xrightarrow{k_{1a}}$

$CH_4 + O^* + * \xrightarrow{k_{1b}}$

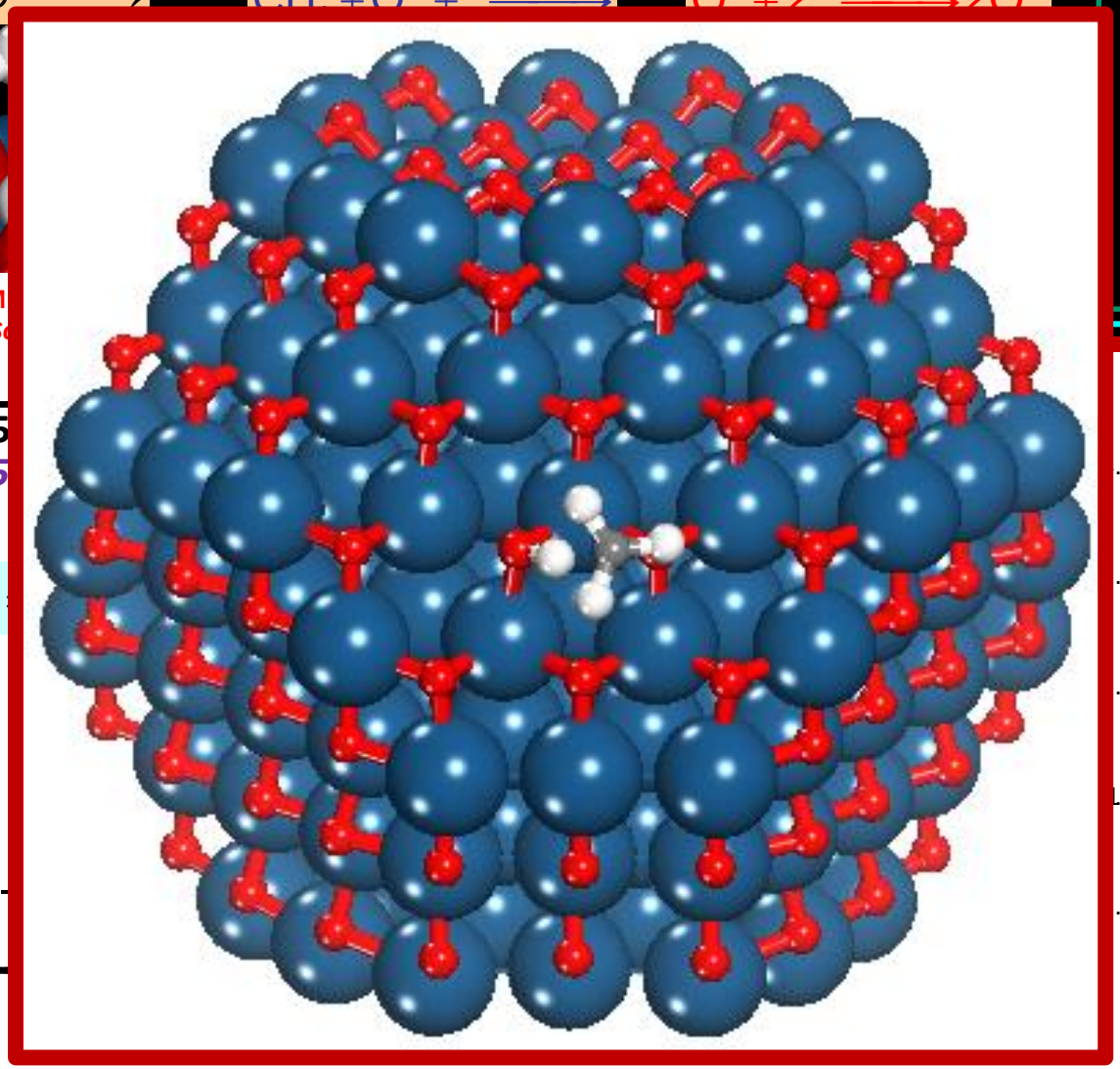
$O_2 + 2^* \xrightarrow{k_2} 2O^*$

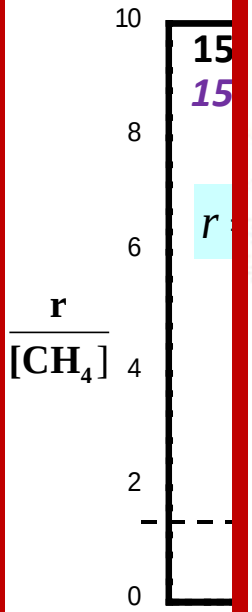
$CH_4 + * + * \xrightarrow{k_{1c}}$

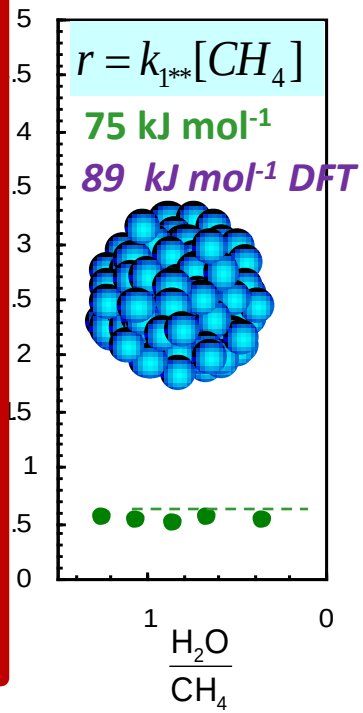




Chin, Y., C. Buda, M. Li, M
E. Iglesia, *J. Am. Chem. S*

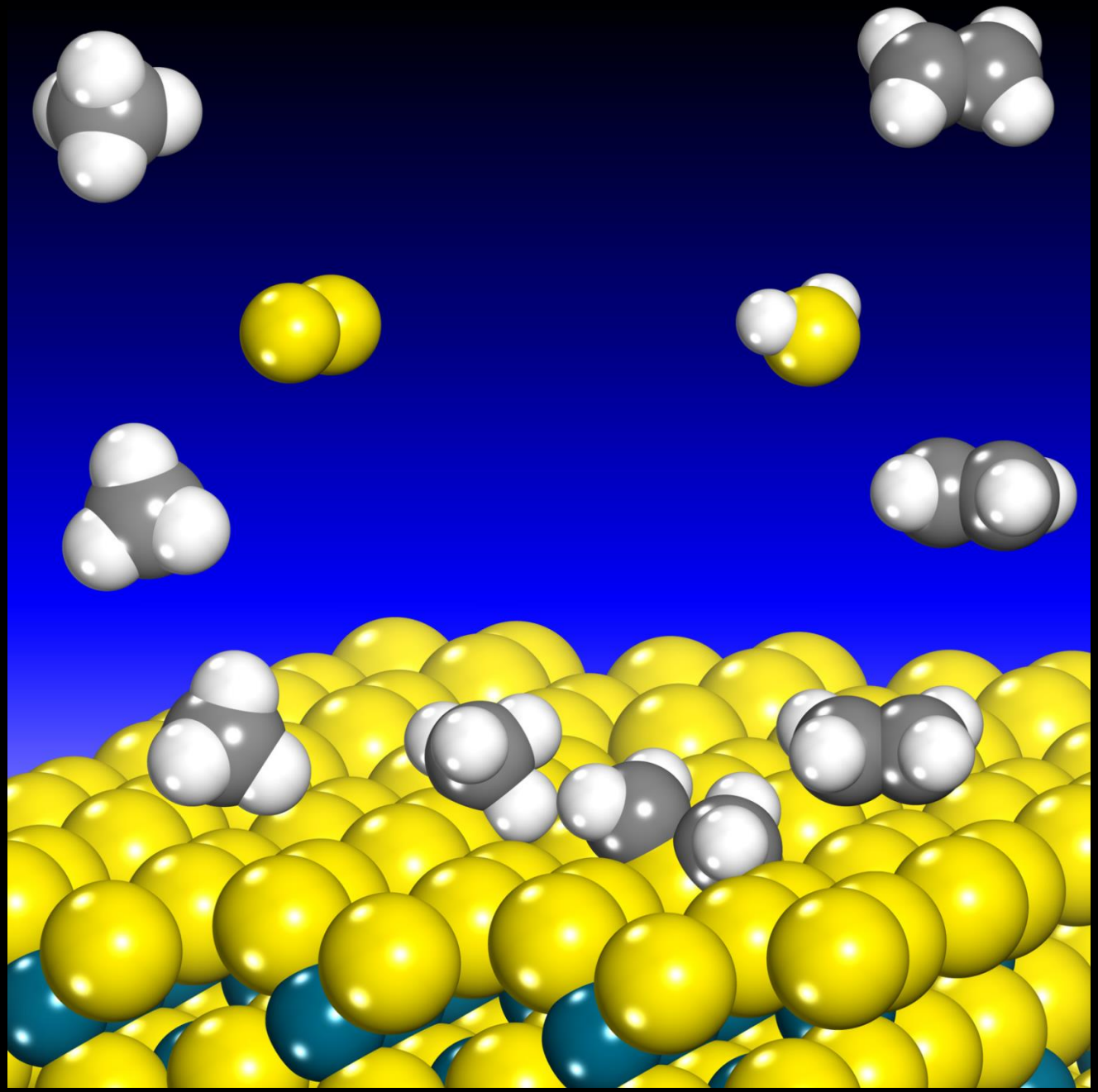






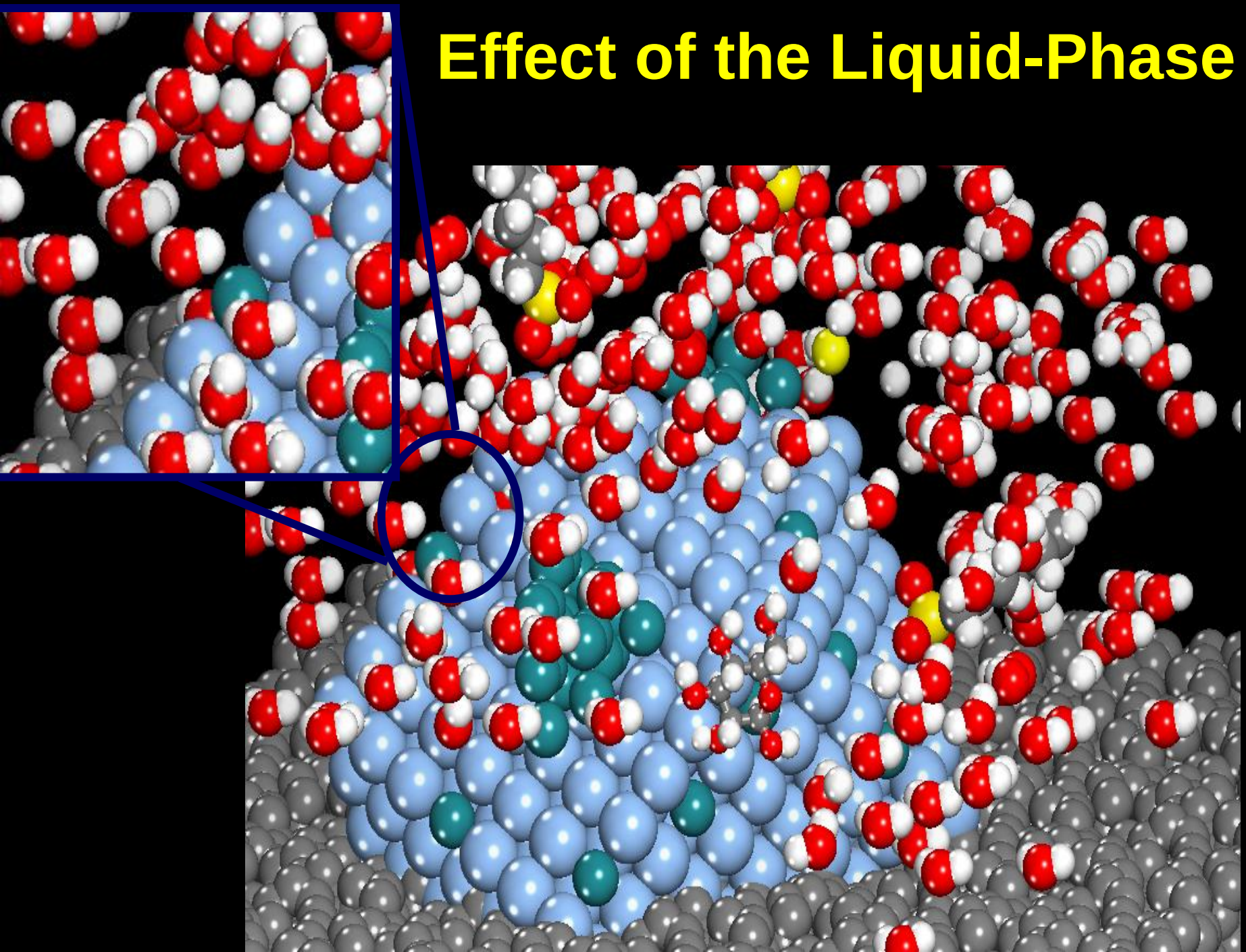
CH_4 CH_4

Decreasing O* coverage



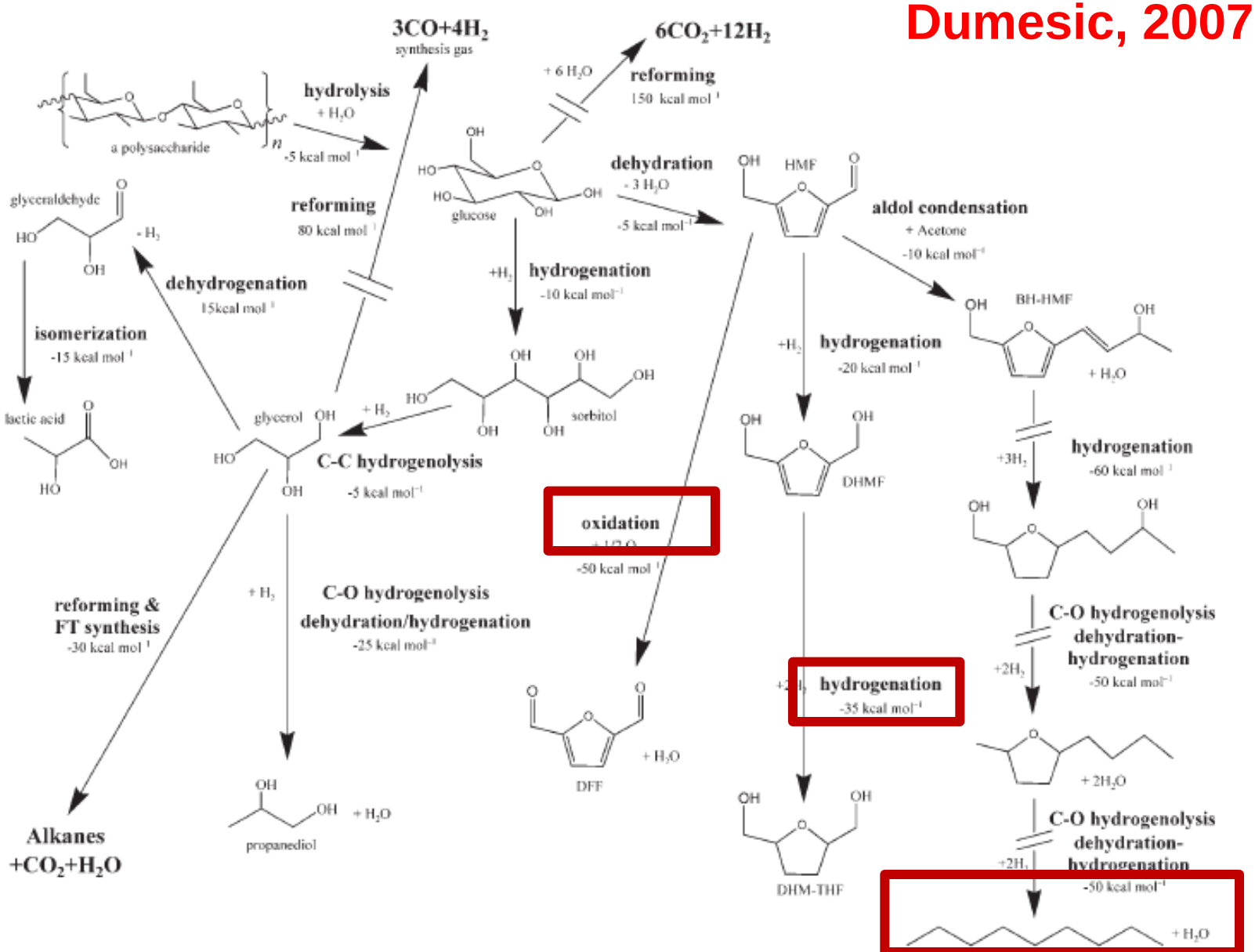
Zhu, Q., S.L. Wegener, C. Xie, O. Uuche, M. Neurock, and T. J. Marks, Nature Chem.,5, 2, 104-109, 2013.

Effect of the Liquid-Phase

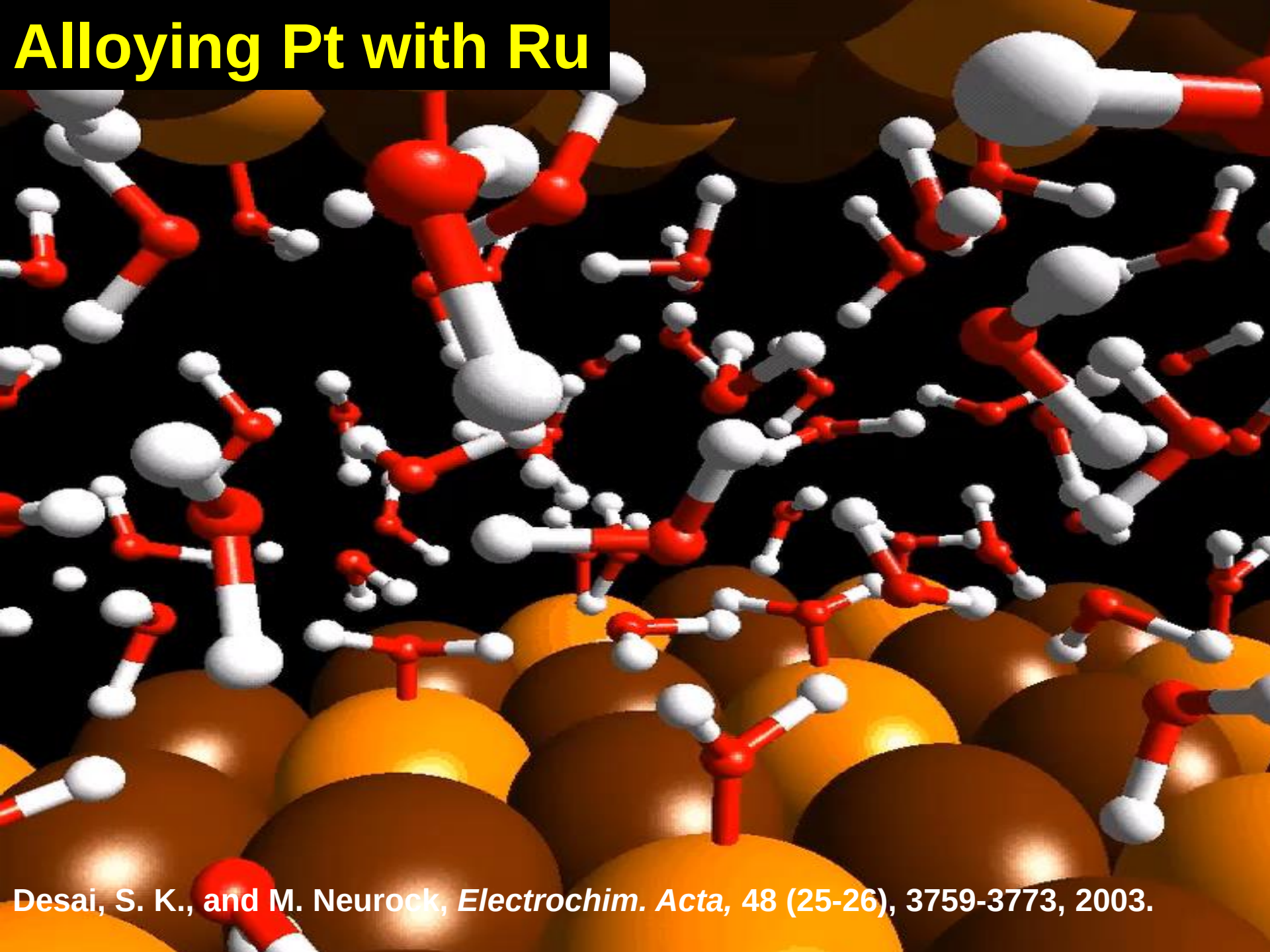


Paths in the Conversion of Carbohydrates to Chemicals and Fuels

Dumesic, 2007



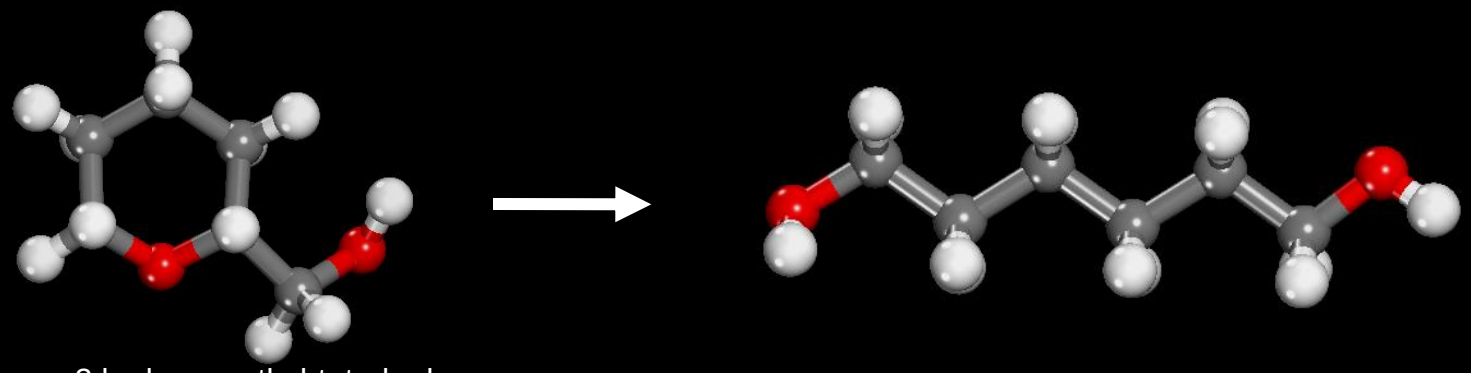
Alloying Pt with Ru



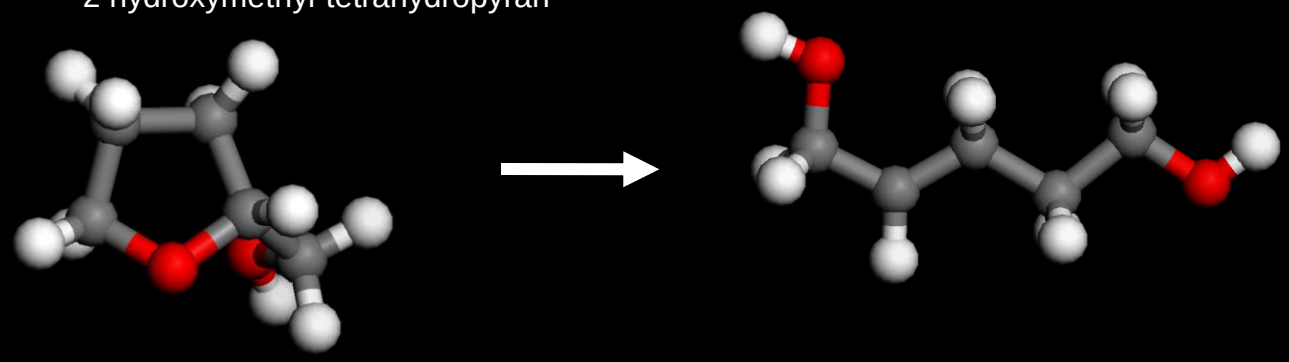
Desai, S. K., and M. Neurock, *Electrochim. Acta,* 48 (25-26), 3759-3773, 2003.

Hydrogenolysis for Selective Removal of Oxygen from Biomass

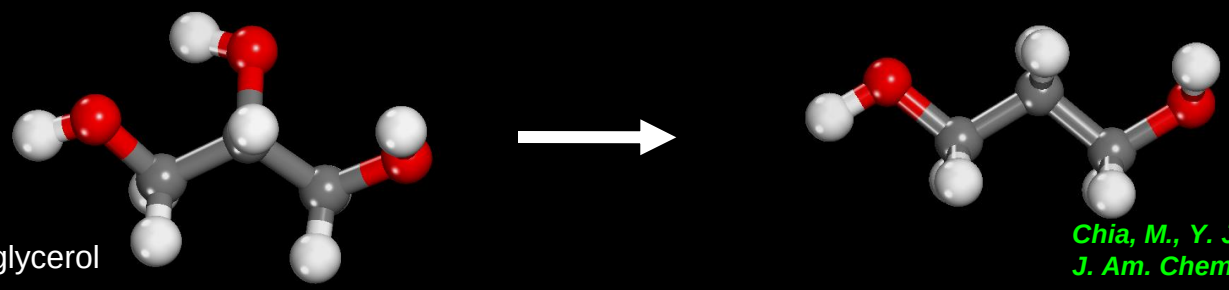
Conversion of Polyols to High Value Chemicals



2 hydroxymethyl-tetrahydropyran



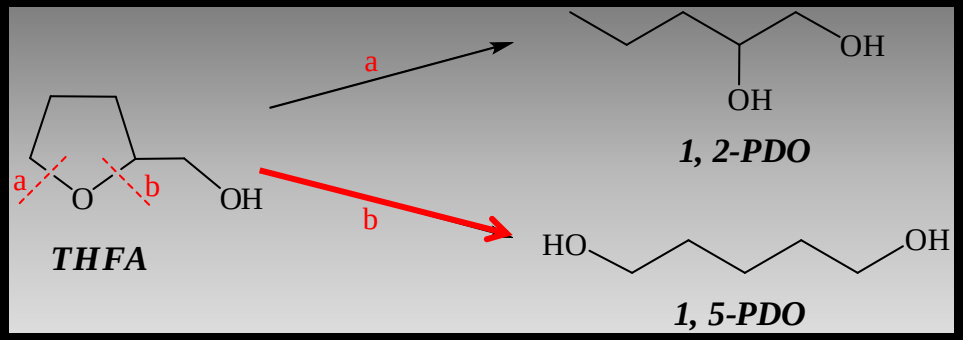
tetrahydrofurfuryl alcohol

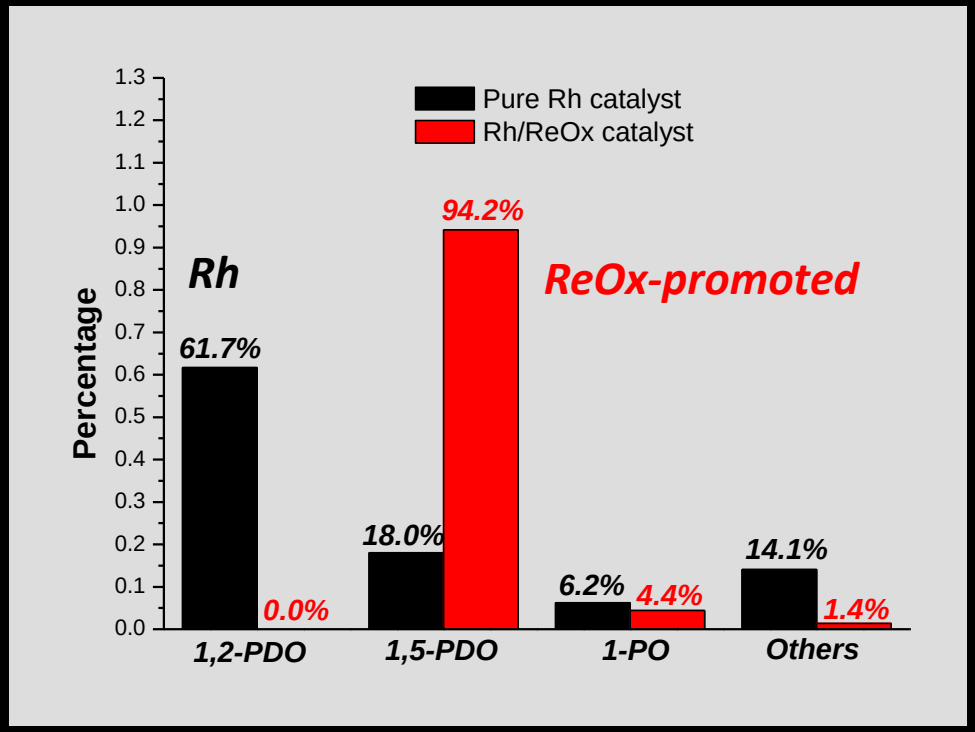


glycerol

Chia, M., Y. J.A. Dumesic, et al.,
J. Am. Chem. Soc., 133, 32, 12675689, 2011

Ring Opening of *THFA over Rh and Re-Promoted Rh*

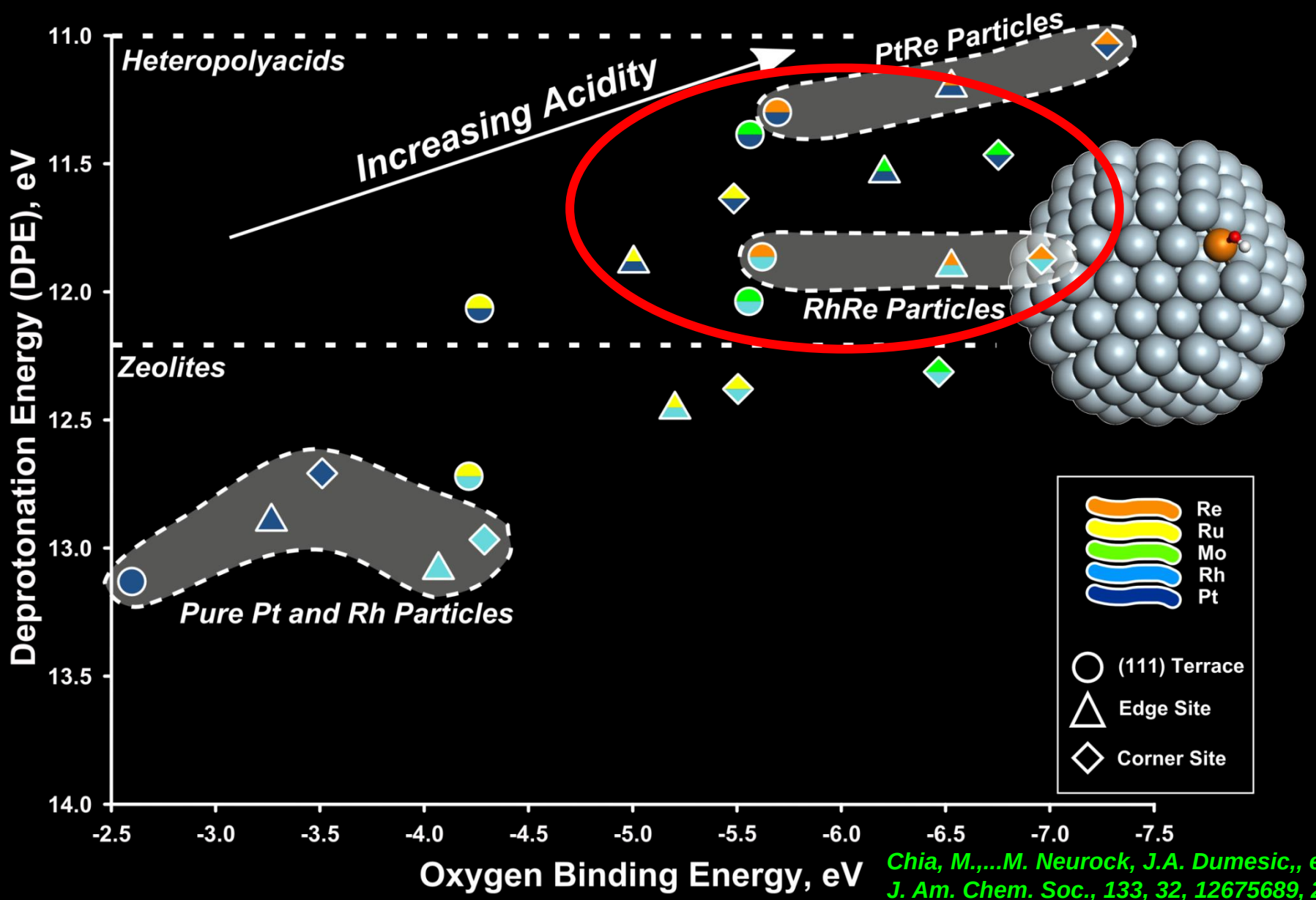




ReOx shifted the selectivity

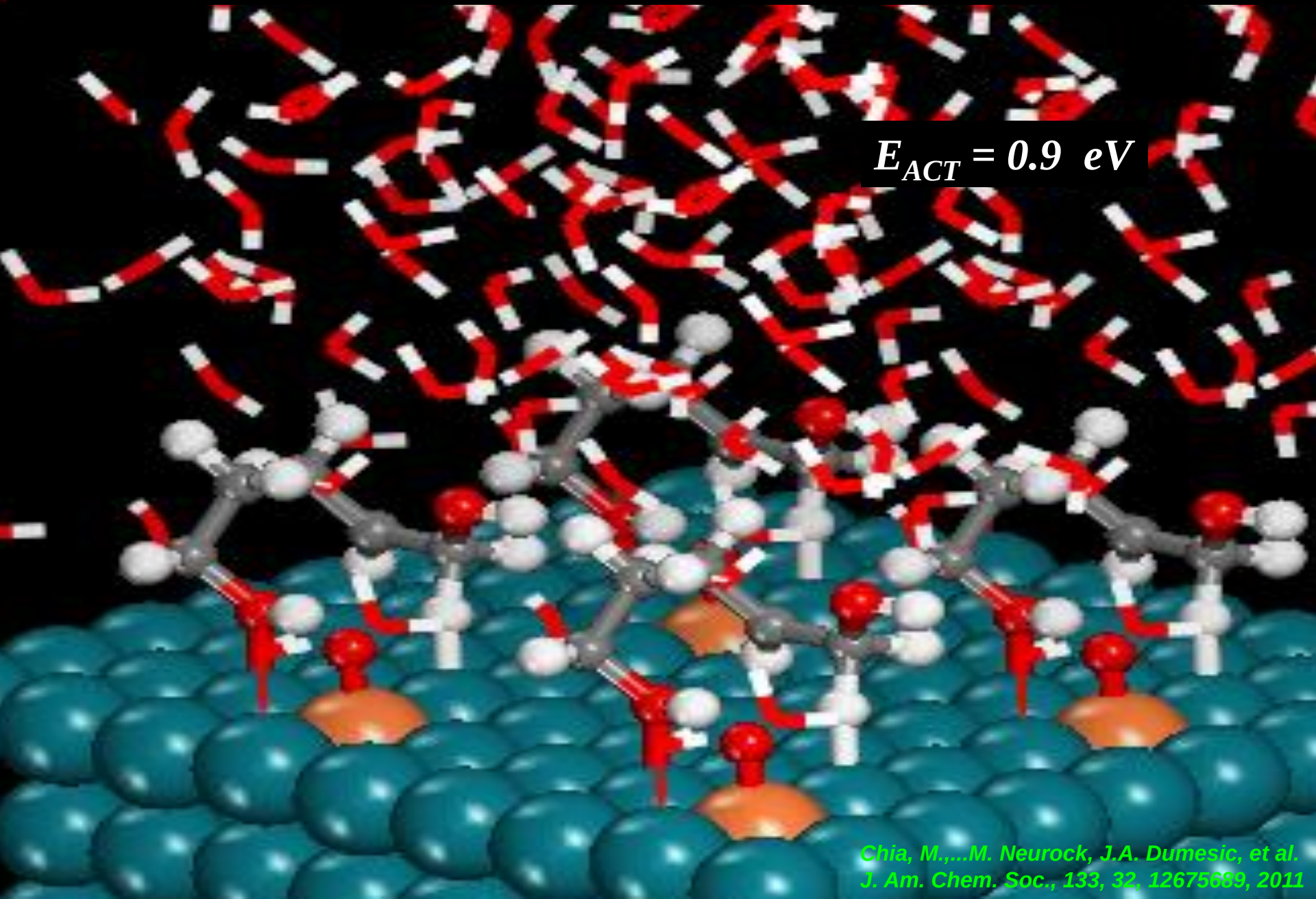
Chia, M., Y. Pagan-Torres, M. Neurock, J.A. Dumesic, et al. J. Am. Chem. Soc., 133, 32, 12675689, 2011

Acidity of MO-H



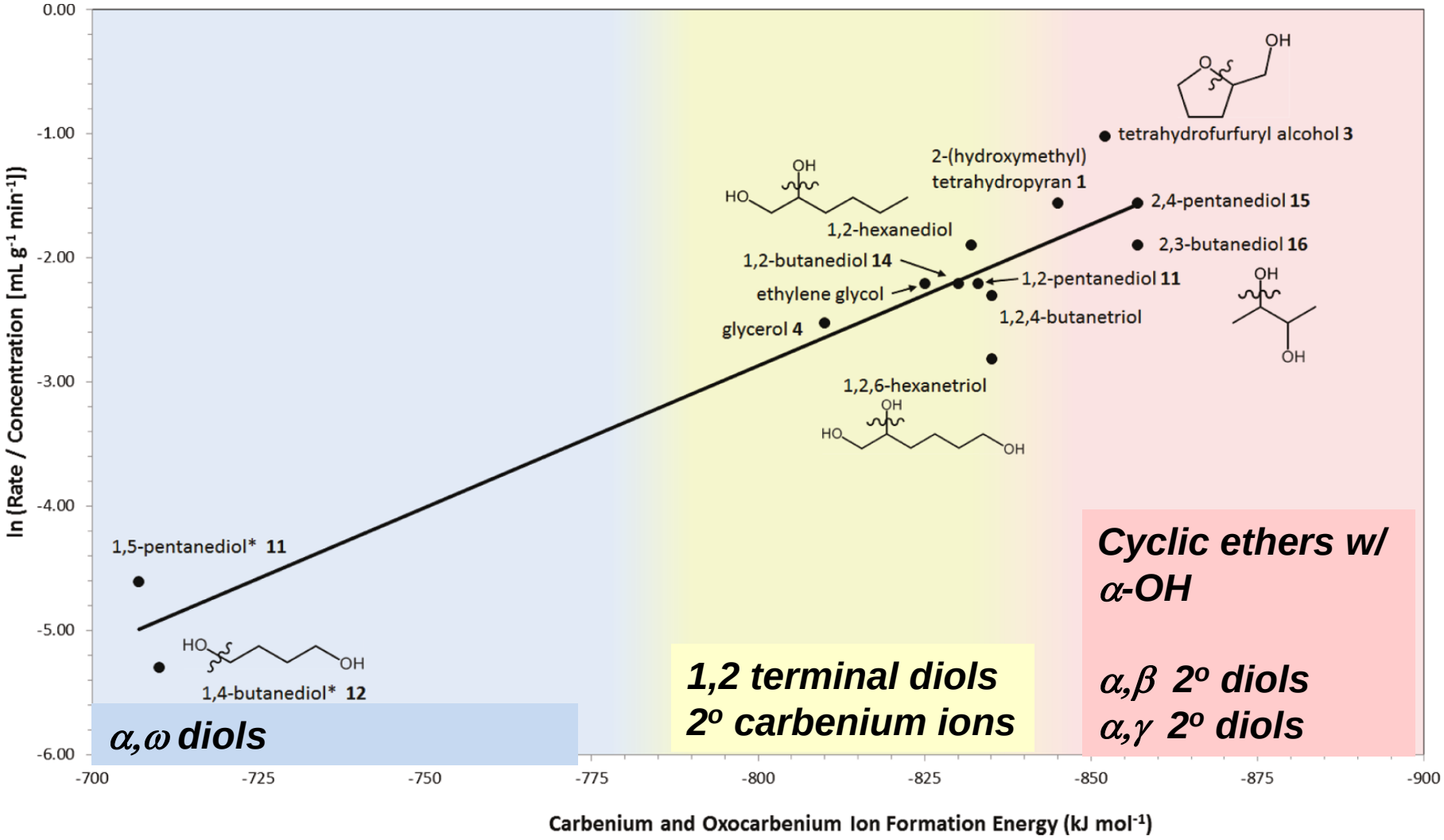
Chia, M.,...M. Neurock, J.A. Dumesic,, et al.
J. Am. Chem. Soc., 133, 32, 12675689, 2011

Ring Opening at Solution/RhReOH Interface



Chia, M.,...M. Neurock, J.A. Dumesic, et al.
J. Am. Chem. Soc., 133, 32, 12675689, 2011

Direct Correlation between Polyol Hydrogenolysis Activity and Carbenium Ion Formation Energies



Chia, M., Y. Pagan-Torres, D. Hibbitts, Q.H. Tan, H.N. Pham, A. Datye, M. Neurock, R.J. Davis, and J.A. Dumesic, *J. Am. Chem. Soc.*, 133, 32, 12675689, 2011

Bifunctional Catalysts

Similar trends for RhMo, PtRe, PtMo, IrRe, etc.

Direct Contact Between:

Reducible Metal - Hydrogenation
Oxophilic Metal - Strong Acidity

Chia, M., Y. Pagan-Torres, D. Hibbitts, Q.H. Tan, H.N. Pham, A. Datye, M. Neurock, R.J. Davis, and J.A. Dumesic, *J. Am. Chem. Soc.*, 133, 32, 12675689, 2011

Opportunities & Challenges

Catalyst Design

Learn from structure and mechanism of enzymes.

Establish atomic features and nanoscale environments that result in active, selective and stable catalysts.

Determine the “rules” that govern the reactivity of different molecular classes.

Challenge

How do we do this for complex feeds and the processing of more complex solids?

- Resilience to S- and N- containing molecules
- Influence of water
- Effects of resulting polymeric liquid phase and solids
- Interactions in complex mixtures

Modeling Reactions of Complex Hydrocarbon Feeds

Feedstock Construction

M. Neurock, M.T. Klein, Chem. Eng. Sci., 49, 24A,4153, 1995.

Feedstock Characterization

Analytical characterization data for an offshore California-derived asphaltene feedstock

Elemental	Wt.%	^{1}H NMR	Wt.%	MW (VPO)
Carbon	80.03	H_α	0.150	2683
Hydrogen	8.20	H_A	0.133	
Sulfur	7.94	H_N	0.211	
Oxygen	1.89	H_{Me}	0.180	
Nitrogen	1.70	H_{My}	0.348	
Vanadium	0.11	H_{My+N}	0.559	
Nickel	0.038			

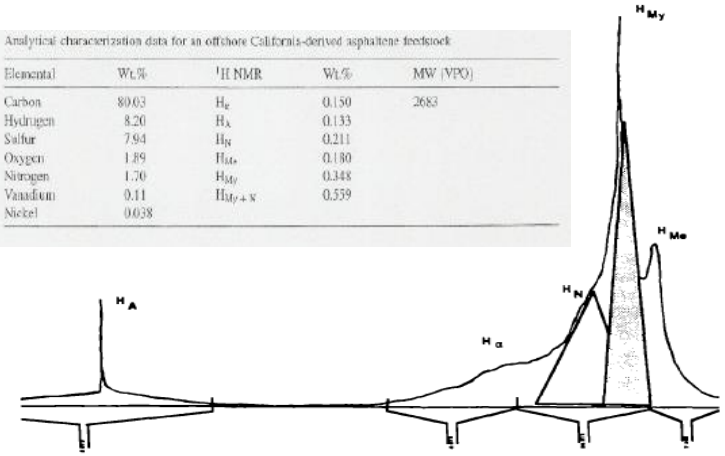
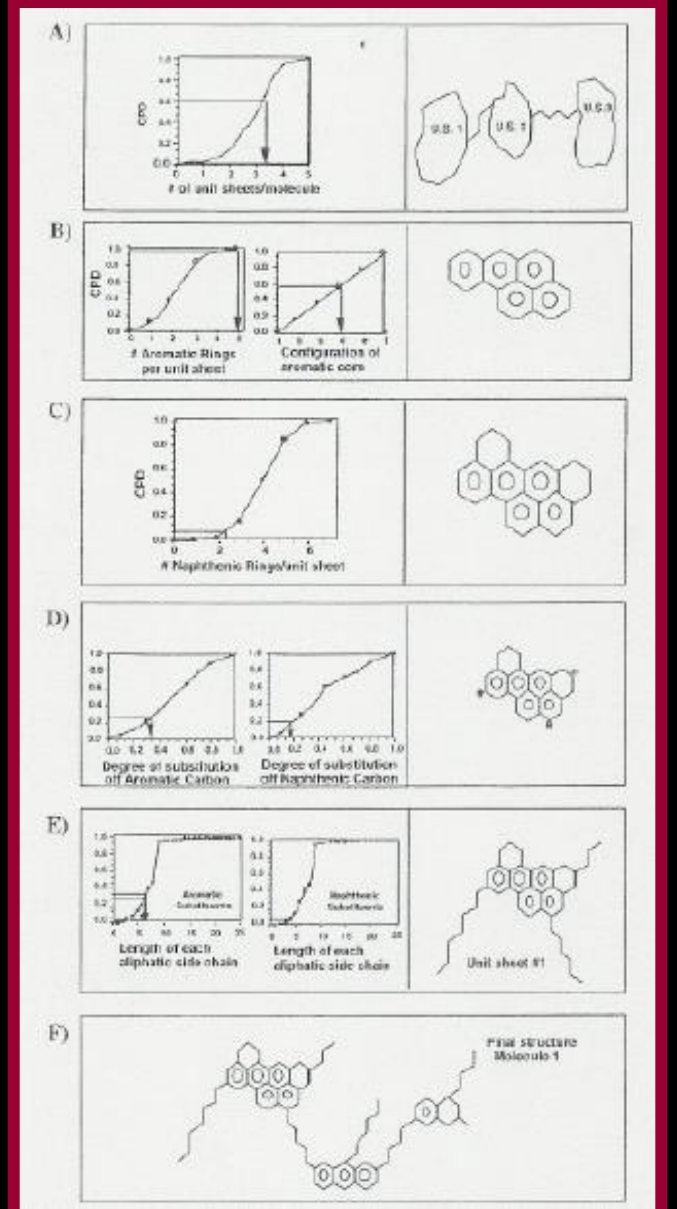


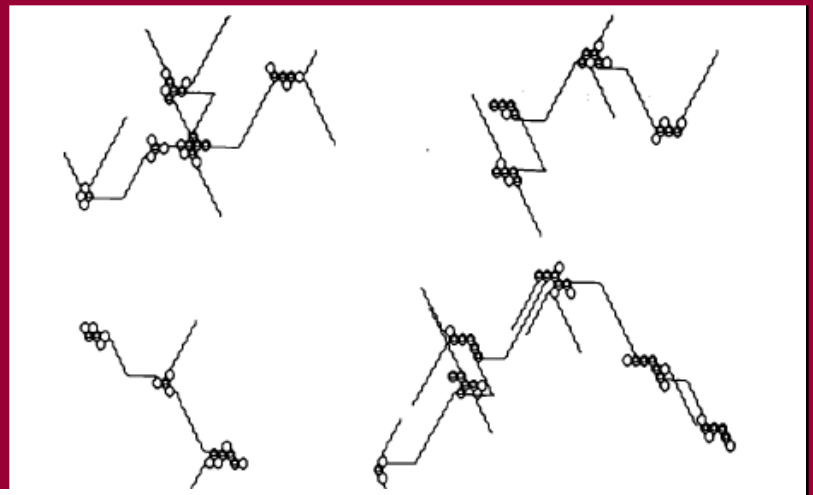
Fig. 7. ^{1}H NMR spectrum of an off-shore California derived asphaltene.

Conversion to Attribute Distributions

Stochastic Molecule Construction



Molecular Feedstock Construction (100,000 Molecules)



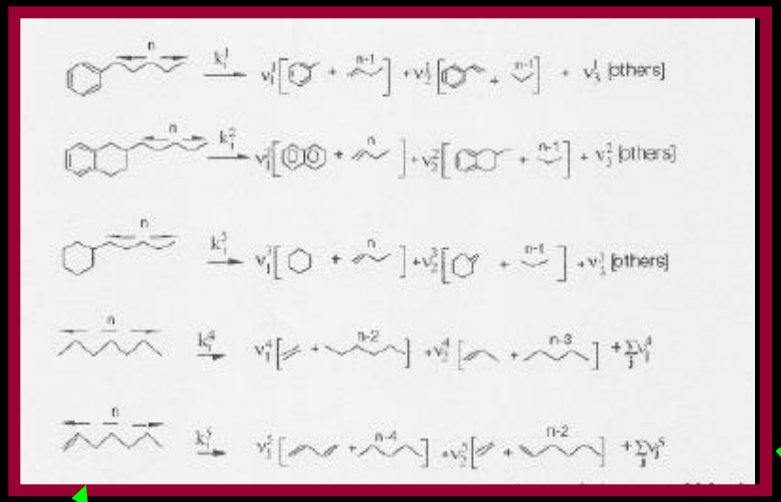
Neurock, M. T. Klein, et al., Chemical Reactions in Complex Mixtures: The Mobil Workshop,126, 1991.

Modeling Reactions of Complex Hydrocarbon Feeds

Reactivity

M. Neurock, M.T. Klein,Chem. Eng. Sci., 49, 24A, 4153, 1995.

Molecular Pathway & Kinetics

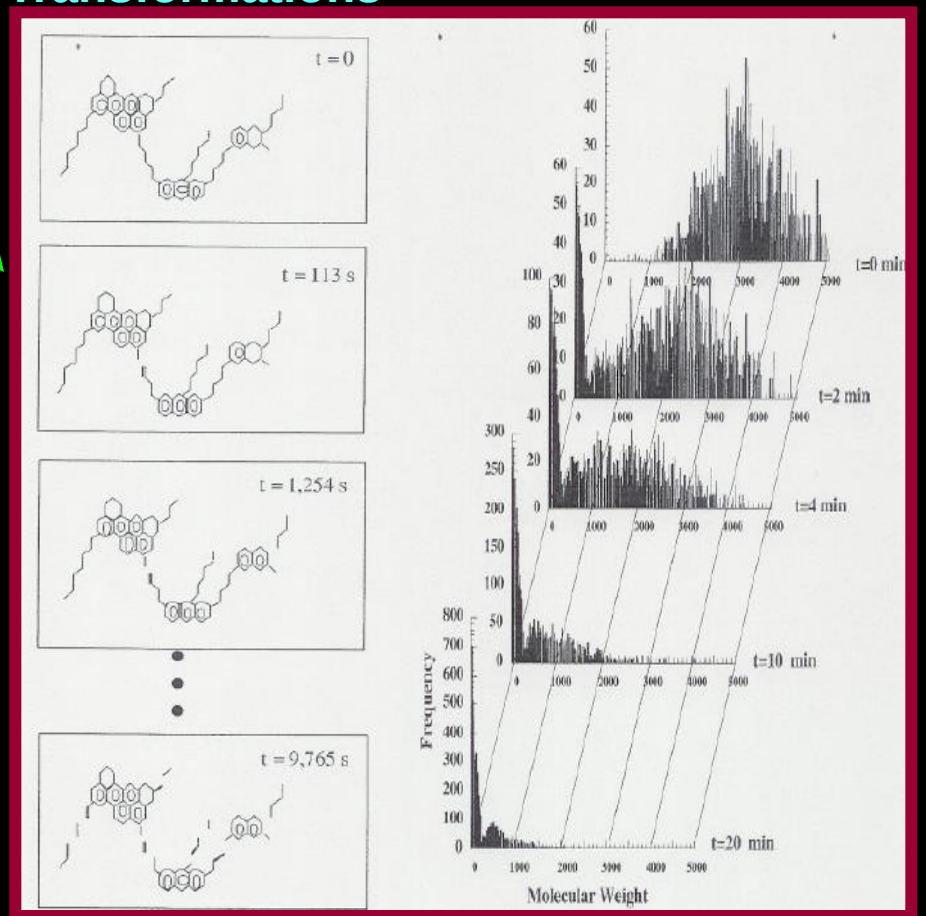


Kinetic Monte Carlo Reaction Simulation

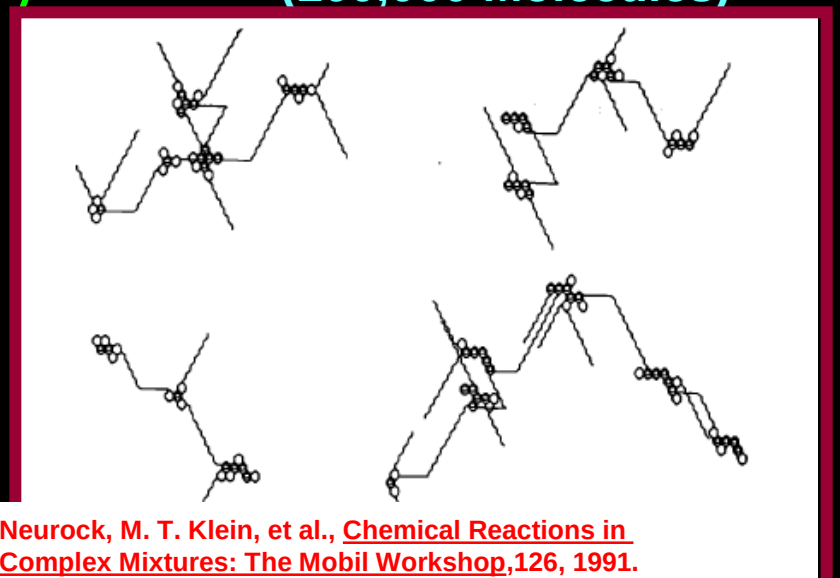
$$\Delta t_v = -\ln(1 - RN) / \left[\sum_{i=1}^{Nevents} k_i \right]$$

Temporal Molecular Transformations

Temporal MW Distribution



Molecular Feedstock Construction (100,000 Molecules)

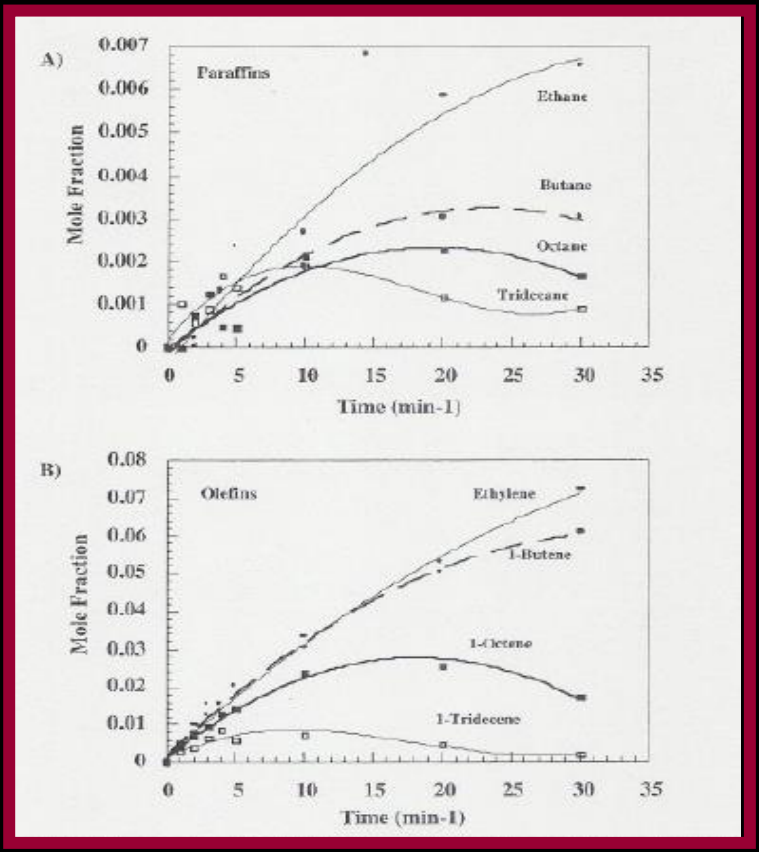


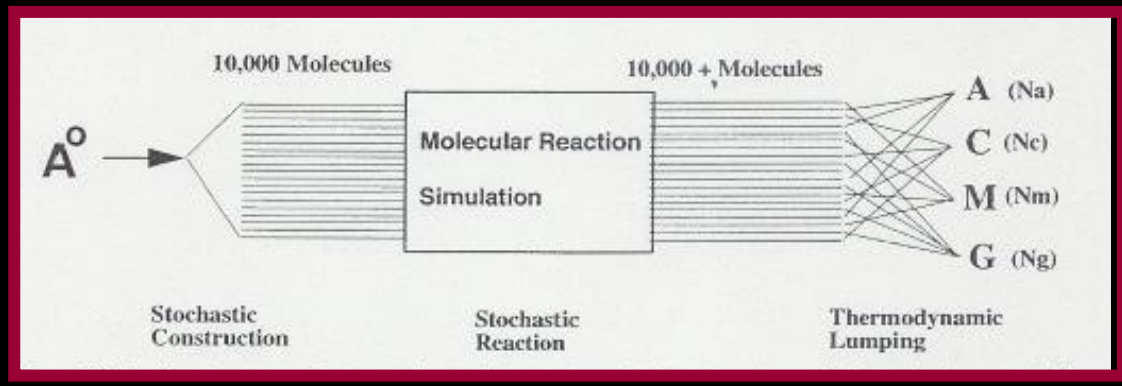
Neurock, M. T. Klein, et al., Chemical Reactions in Complex Mixtures: The Mobil Workshop,126, 1991.

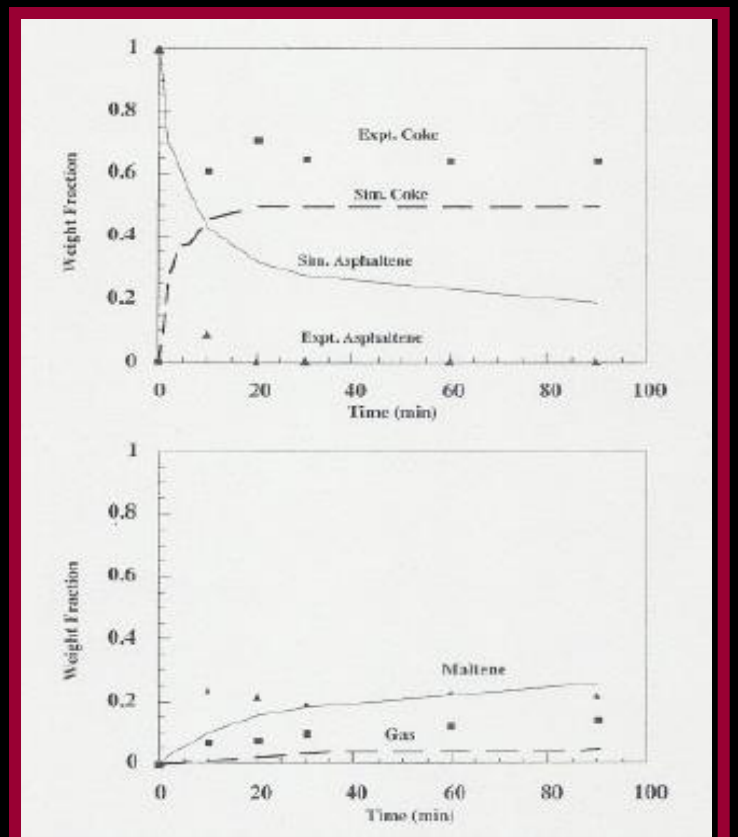
Modeling Reactions of Complex Hydrocarbon Feeds

Product Formation

M. Neurock, M.T. Klein, Chem. Eng. Sci., 49, 24A,4153, 1995.





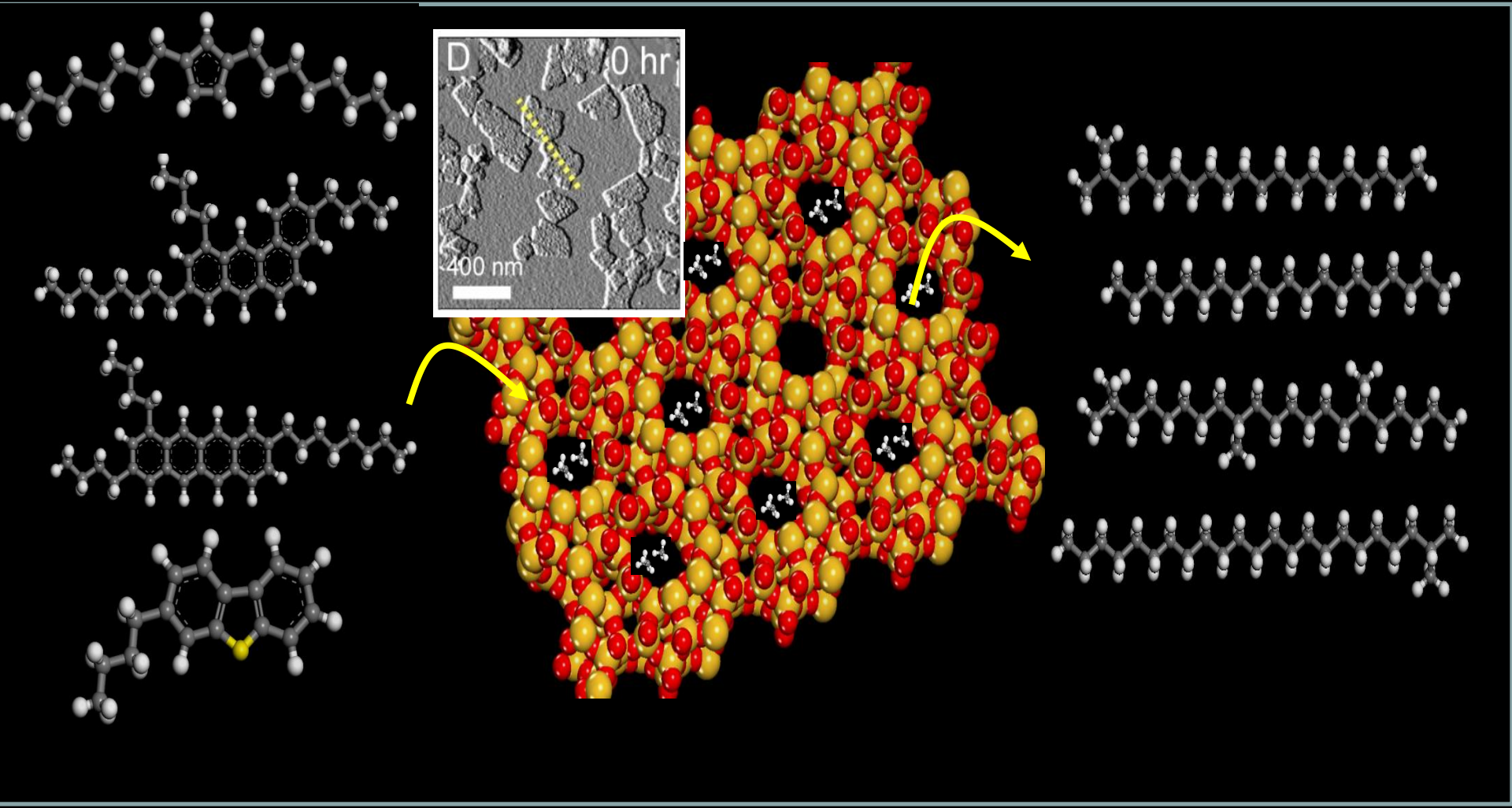


Temporal Molecular Distributions

Temporal Changes in Global Products

Neurock, M. T. Klein, et al., Chemical Reactions in Complex Mixtures: The Mobil Workshop,126, 1991.

Integrating Molecular Kinetic Models and Detailed QM and Catalyst Kinetic Simulations

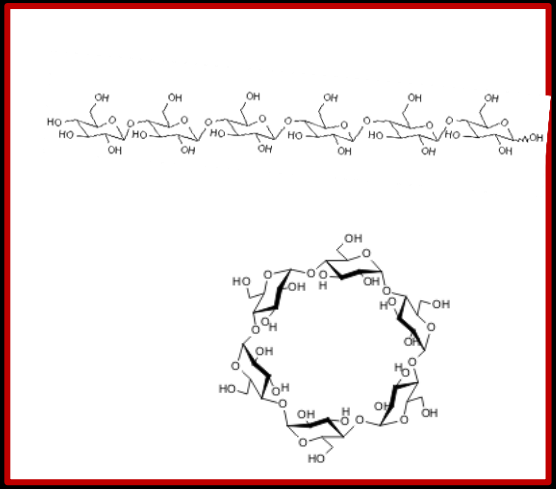


M. Neurock

Future Needs and Opportunities

Needs/Opportunities – Model Systems

Synergistic Experimental and Computational
Model Compound Studies



Synergistic Experimental & Computational
Model Mixtures Studies

Detailed analysis of molecular products

Rigorous kinetics

Isotopic labeling studies

Detailed characterization studies

Needs/Opportunities – Complex Model Systems

Measurements, Theory and Simulation

Characterization of Model Solids and Complex Liquids

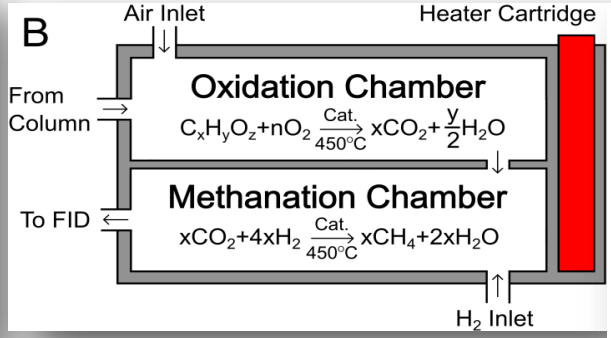
NMR
Quantitative Mass Spec

Needs/Opportunities – Complex Model Systems

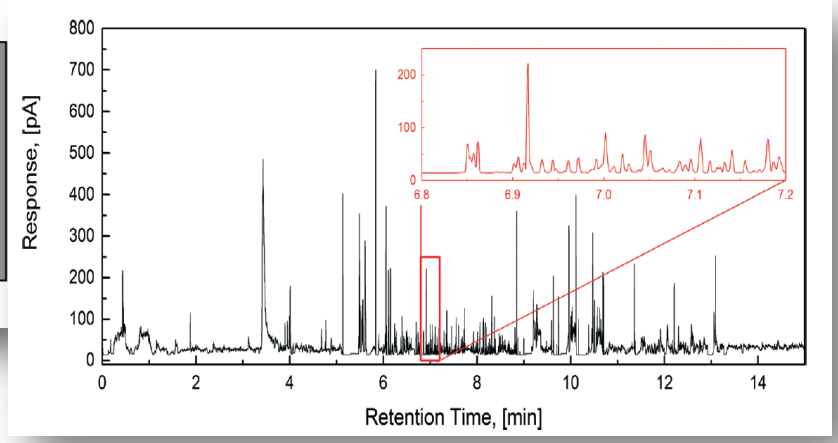
Measurements, Theory and Simulation

Characterization of Model Solids and Complex Liquids

NMR
Quantitative Mass Spec
In-Situ Quantitative Carbon Detection



P. Dauenhauer, UMN.



M. Neurock

Needs/Opportunities – Complex Model Systems

Measurements, Theory and Simulation

Characterization of Model Solids and Complex Liquids

NMR
Quantitative Mass Spec
In-Situ Quantitative Carbon Detection

Reactivity of Model Solids and Complex Liquids

Novel reactors that provide fundamental rigorous kinetics

Needs/Opportunities – Complex Model Systems

Measurements, Theory and Simulation

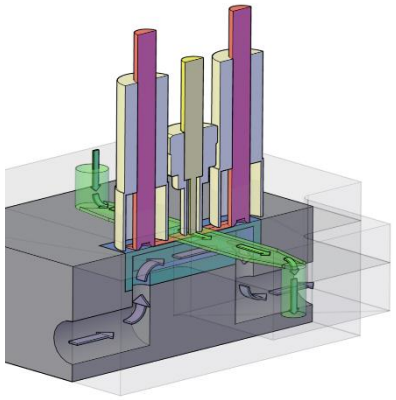
Characterization of Model Solids and Complex Liquids

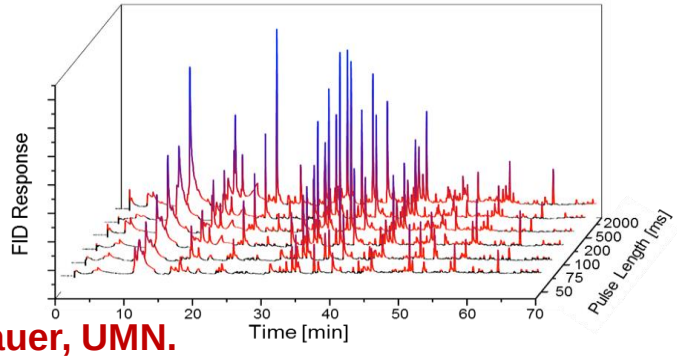
NMR
Quantitative Mass Spec
In-Situ Quantitative Carbon Detection

Reactivity of Model Solids and Complex Liquids

Novel reactors that provide fundamental rigorous kinetics

Pulse Heated Analysis of Solid Reactors





P. Dauenhauer, UMN.

Algorithm Developments

Faster, cheaper, and more accurate methods.

Order N-Scaling, Improved Transition State Search Algorithms, Better DFT Functionals, Improved Property Prediction, Accurate Semiempirical Methods..

Ability to model more realistic reaction environments

Mixtures, Reactivity of Solids, Liquid Phase, Catalytic Poisons, Complex Catalytic Architectures

Better integration between time and length scales.

Electronic, Molecular, Meso, Macro, and Process

Robust force fields for broad application of materials.

Reactive FF, Charge Transfer, Induced Polarization

Acknowledgements

Paul Dauenhauer (UMN)

Robert Davis (UVA)
Jim Dumesic (UW)
Enrique Iglesia (UCB)
Tobin Marks (NWU)

National Science Foundation
Department of Energy
BP