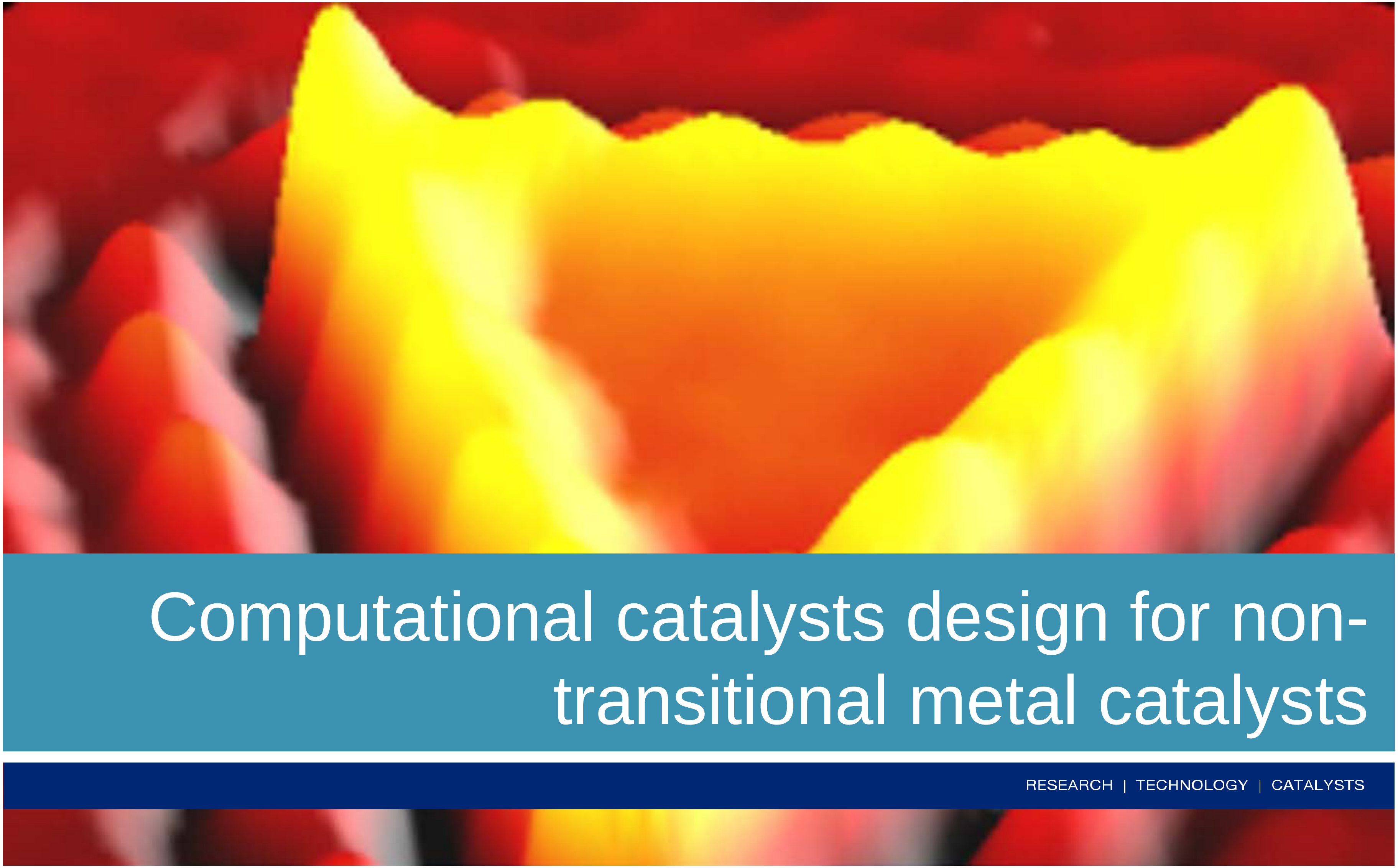


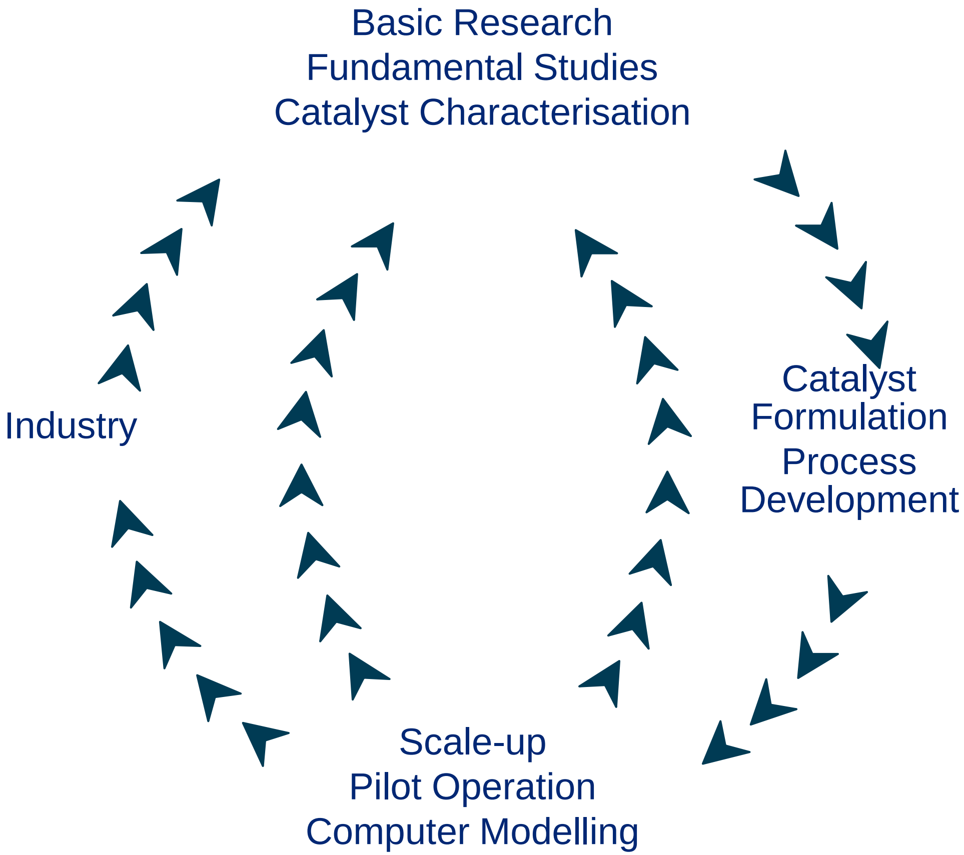
Computational catalysts design for non-transitional metal catalysts

RESEARCH | TECHNOLOGY | CATALYSTS

Poul Georg Moses

HALDOR TOPSØE

Research and development at HTAS



Basic Research
Fundamental Studies
Catalyst Characterisation

Industry

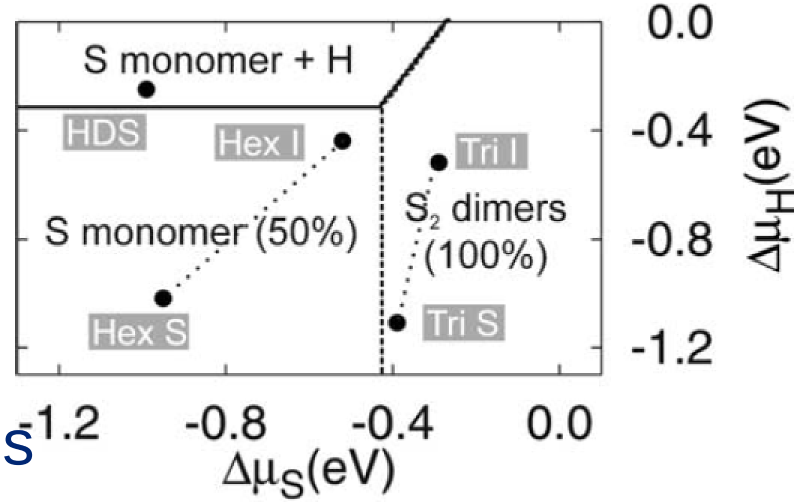
Catalyst
Formulation
Process
Development

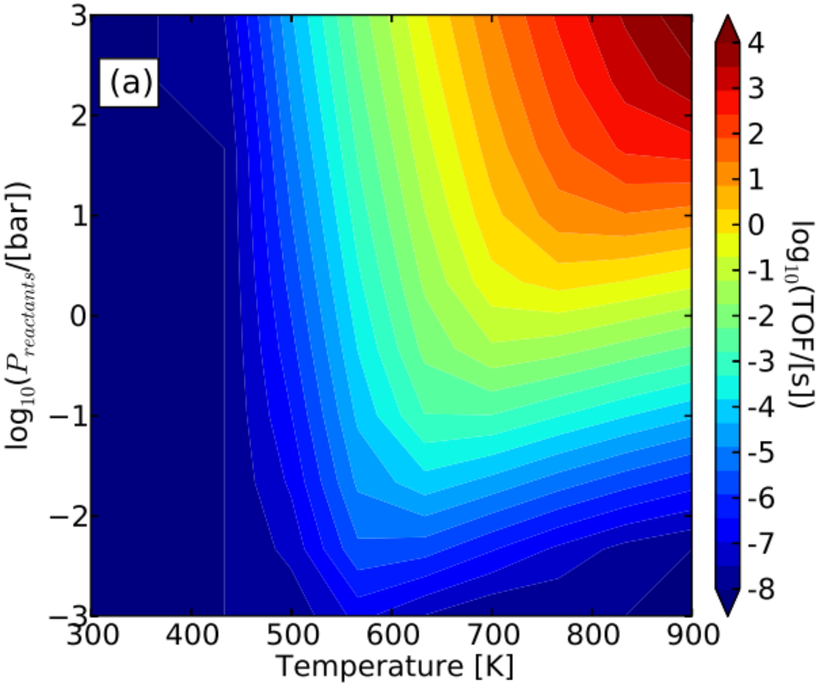
Scale-up
Pilot Operation
Computer Modelling

GIER 1 at HTAS ca. 1960

Standard tools in design of metal based catalysts

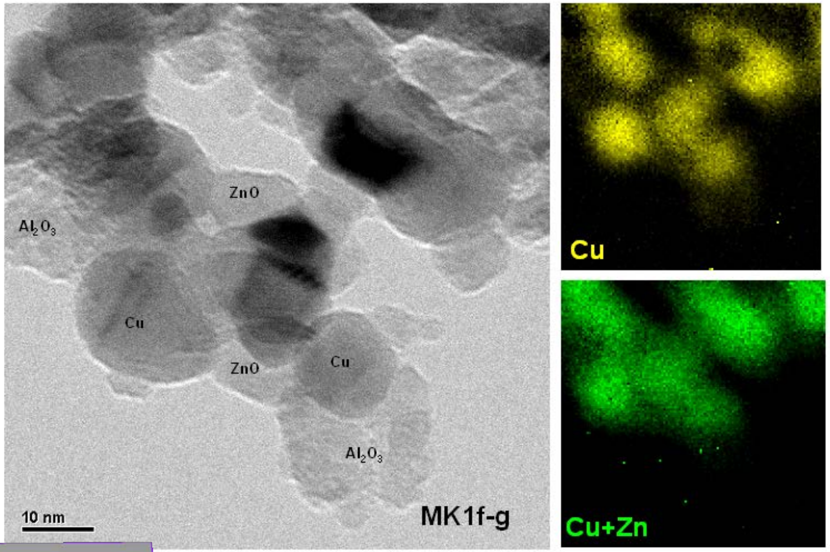
- Thermodynamics
- (Micro)kinetic modeling
- Data bases of DFT values
- (Linear) correlations to fill the gaps

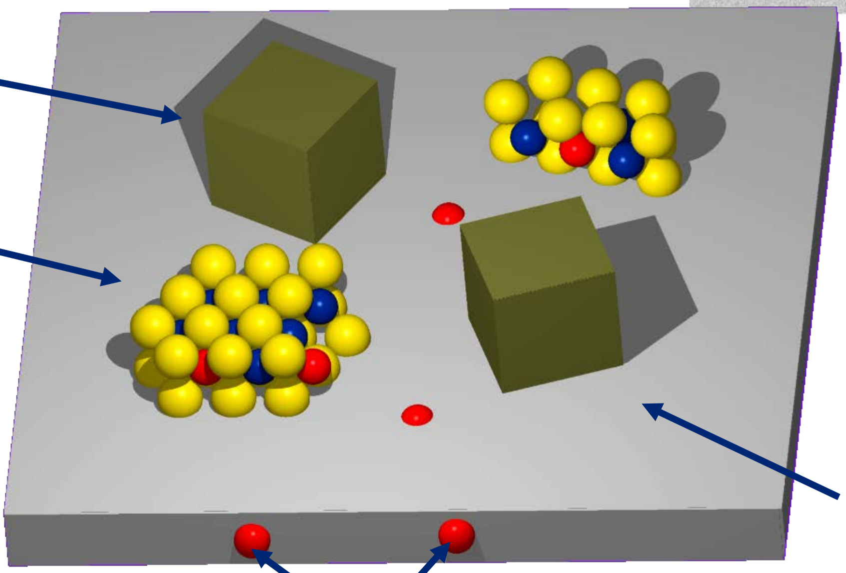




Standard tools applied to non-metal systems

- ZnO as a methanol catalysts
- Trends in HDS catalysis





Co_9S_8

MoS_2-like nanoparticles ”Co-Mo-S”

● S

● Mo

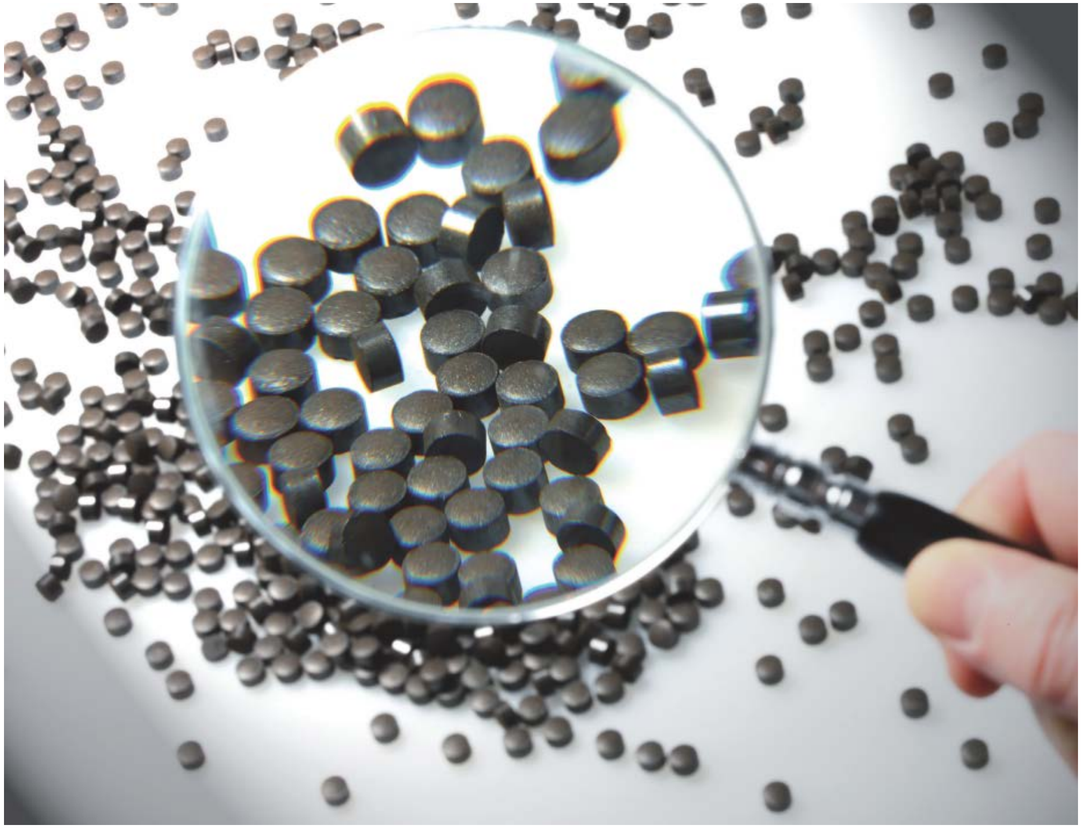
● Co

Al_2O_3 (alumina) support

Co:Al_2O_3

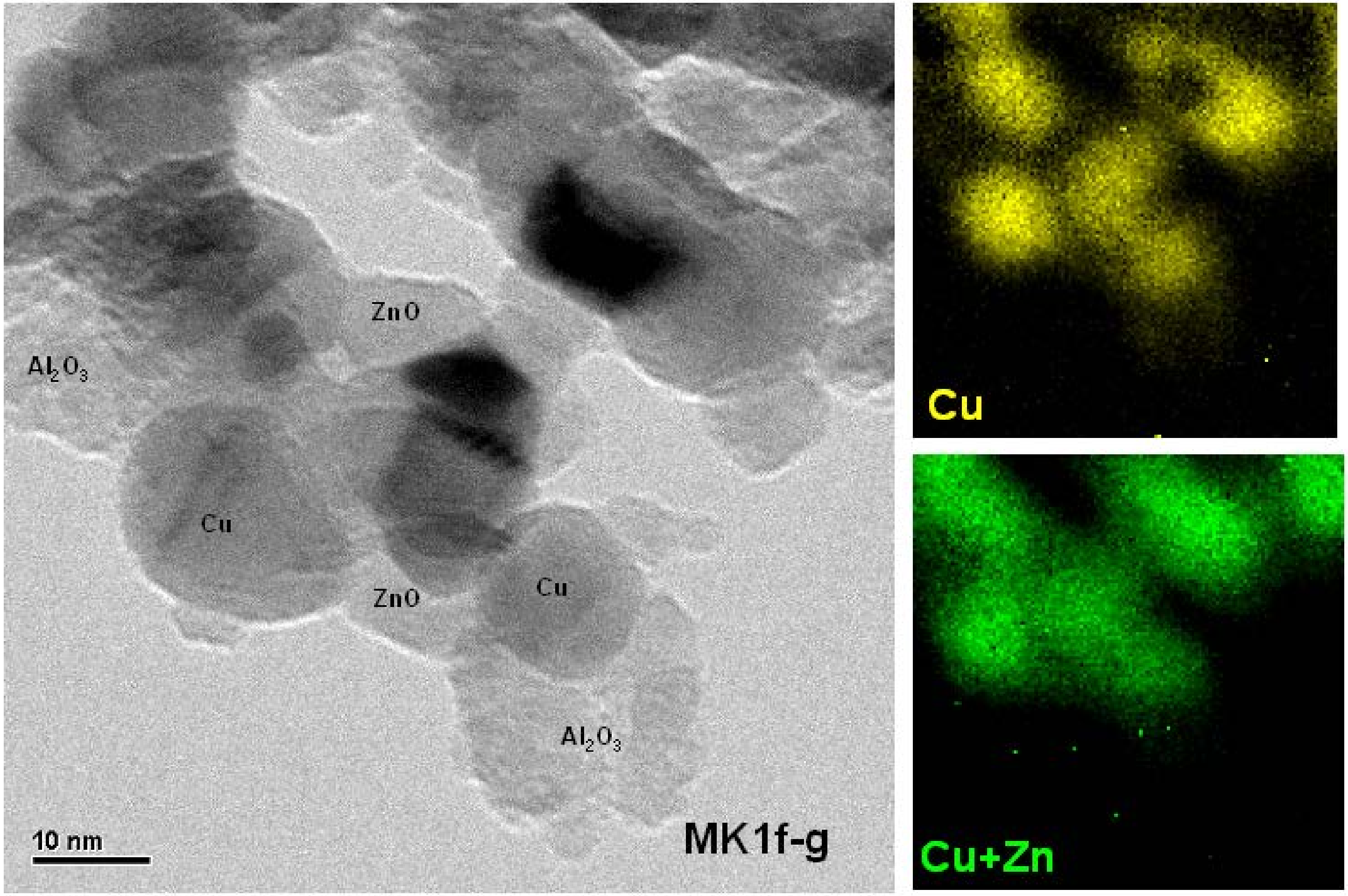
Methanol synthesis

- $Cu/ZnO/Al_2O_3$
- T= 220 – 300 °C ,
- P=50 – 100 Bar



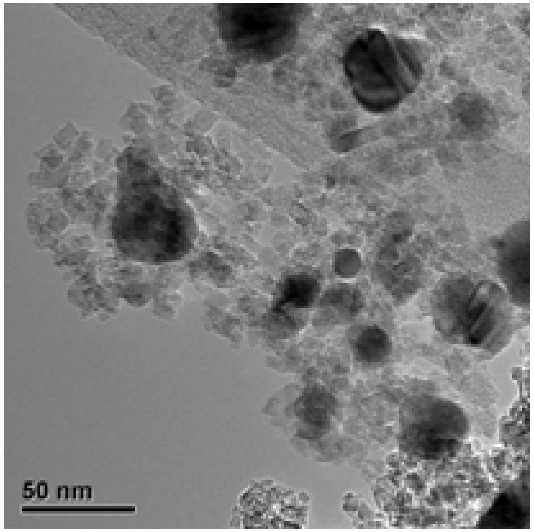
- $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$
- $CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(g)$
- $H_2O(g) + CO(g) \rightarrow CO_2(g) + H_2(g)$ (Water gas shift)

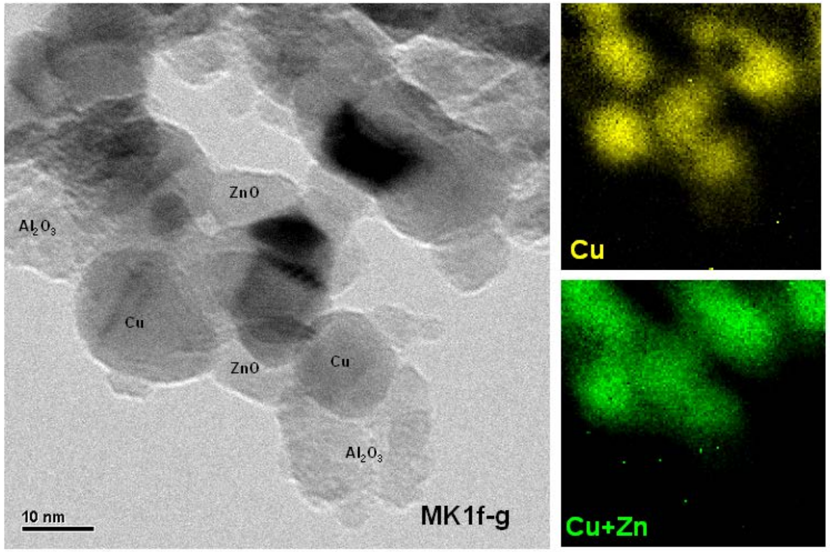
$Cu/ZnO/Al_2O_3$ Energy filtered TEM imaging



Three important questions in MeOH catalysis

1. What affects the stability of MeOH Cat.?
2. Is MeOH formed from CO, CO_2 or both?
3. What is the role of ZnO in MeOH catalysis?





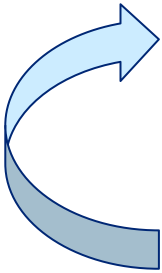
ZnO as a methanol catalysts

- ZnO original Methanol catalysts
- T= 600 – 700 °C , P=200 – 300 Bar
- $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$ Dominating pathway
- $CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(g)$
- $H_2O(g) + CO(g) \rightarrow CO_2(g) + H_2(g)$ (Water gas shift)

M. Kurtz, J. Strunk, O. Hinrichsen, M. Muhler, K. Fink, B. Meyer, and C. Wöll. Angew. Chem. Int. Ed. 2005, 44, 2790

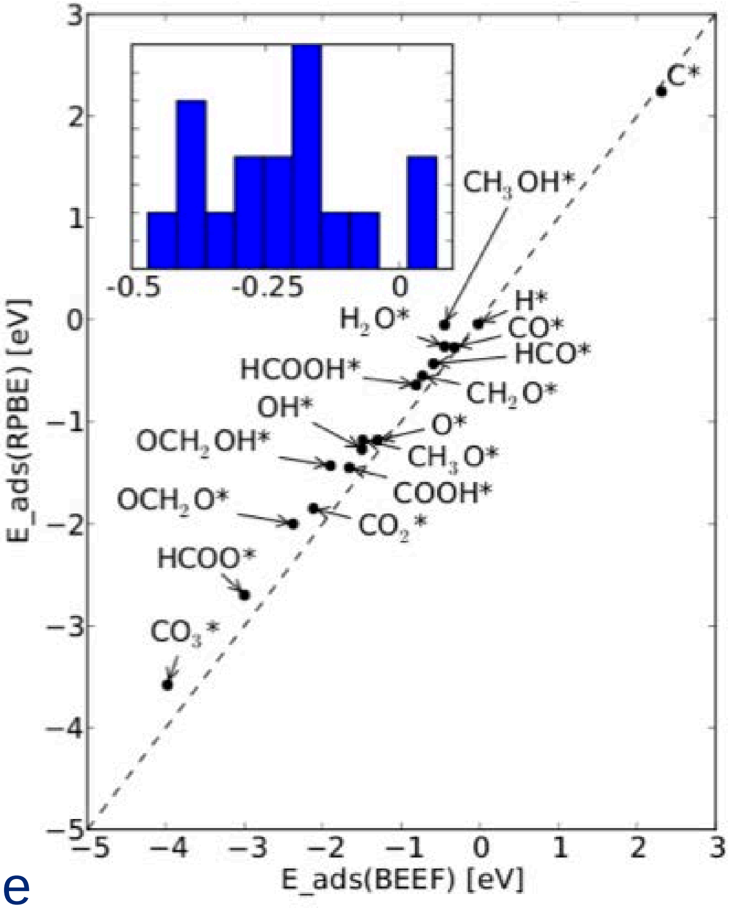
Methods

- Approach



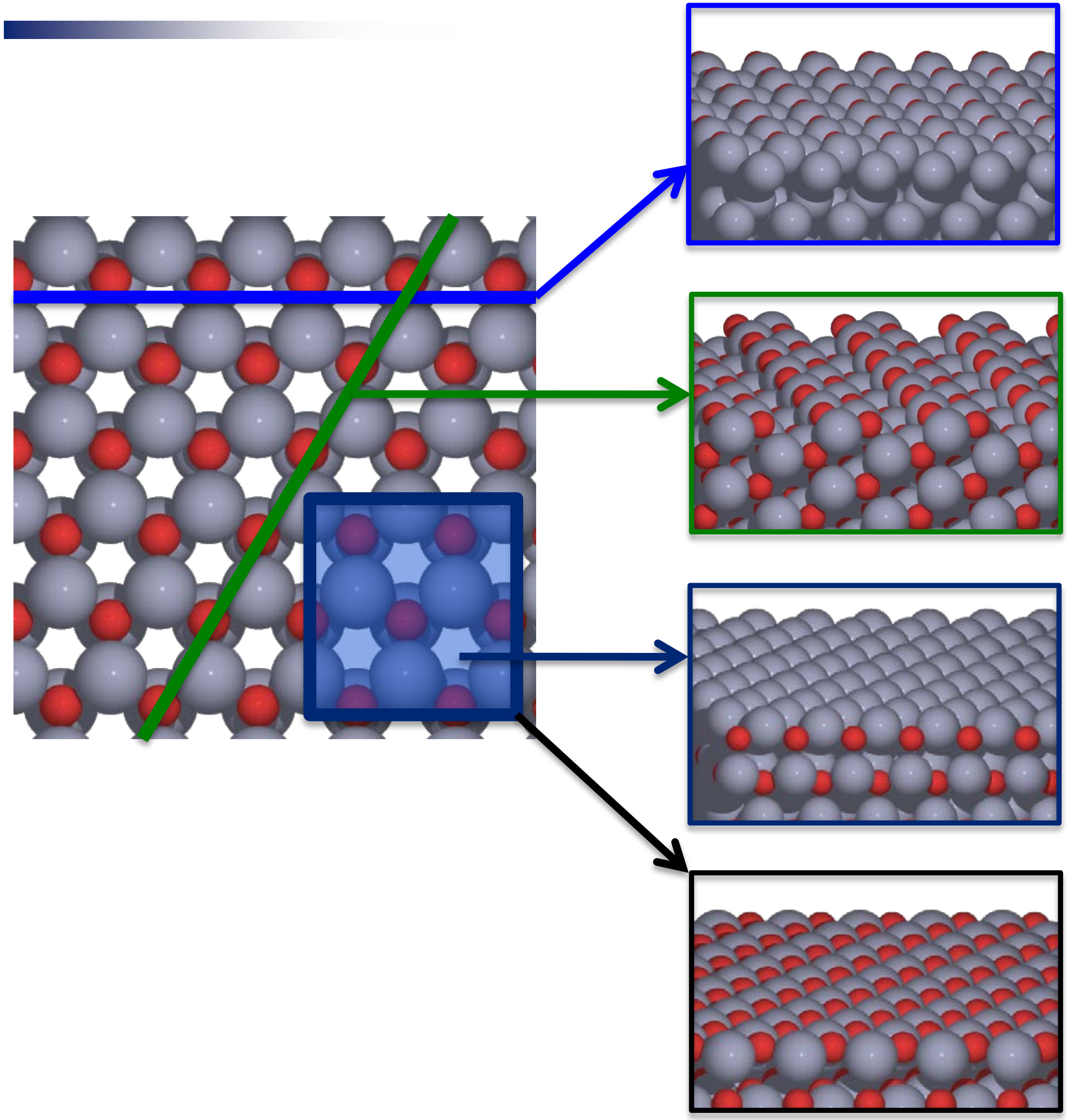
  - Determine model surface
  - Calculate reaction thermodynamics
  - Estimate reaction barriers
  - Analyze with kinetic model
- Details
  - Use GPAW+BEEF-vdW
  - Use Shomate equation (harmonic approx.) for gas (adsorbate) thermal contribution.
  - Apply O=C=O correction for gas phase HCOOH,CO_2,H_2^a)

RPBE vs. BEEF



a) F. Studt, F. Abild-Pedersen, J.B. Varley, J.K. Nørskov Catal. Lett 143, 2012, 71

Model Surface



ZnO(100)
$\sim 1.8\ \mathrm{J/m^2}$

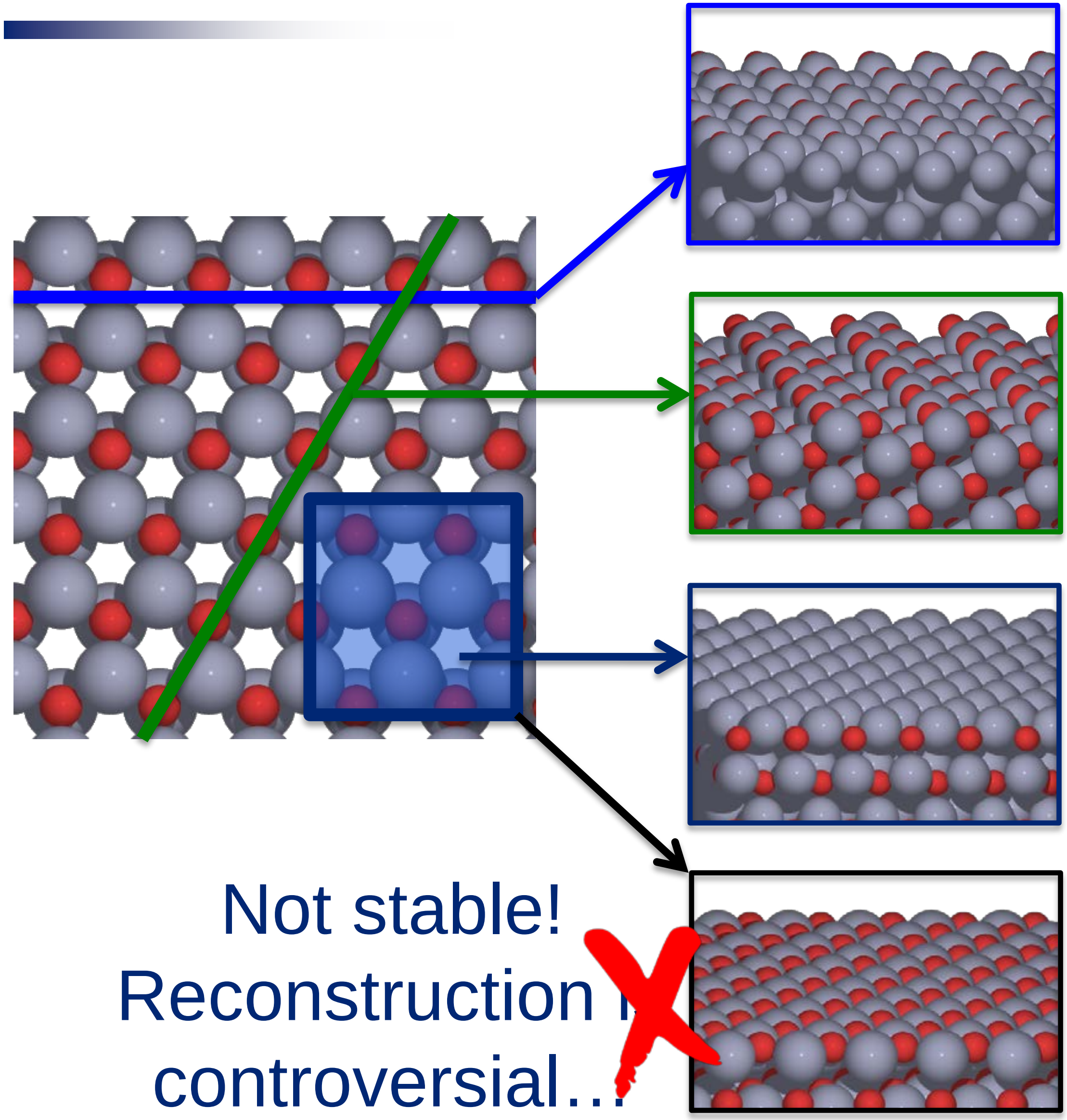
ZnO(110)
$\sim 1.9\ \mathrm{J/m^2}$

ZnO(001)
$\sim 3.5\ \mathrm{J/m^2}$

ZnO(00-1)
$\sim 4.3\ \mathrm{J/m^2}$

Diebold, App. Surf. Sci. 237 (2004

Model Surface



ZnO(100)
~1.8 J/m^2

ZnO(110)
~1.9 J/m^2

ZnO(001)
~3.5 J/m^2

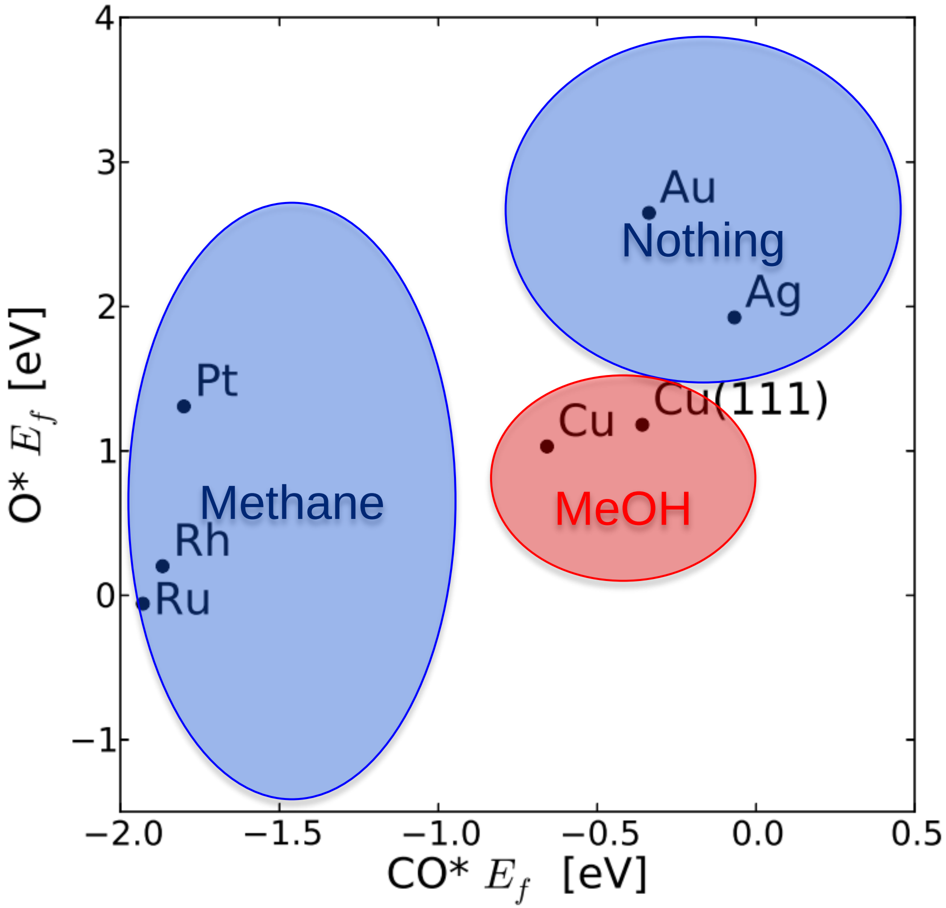
ZnO(00-1)
~4.3 J/m^2

Not stable!
Reconstruction i
controversial…

Diebold, App. Surf. Sci. 237 (2004

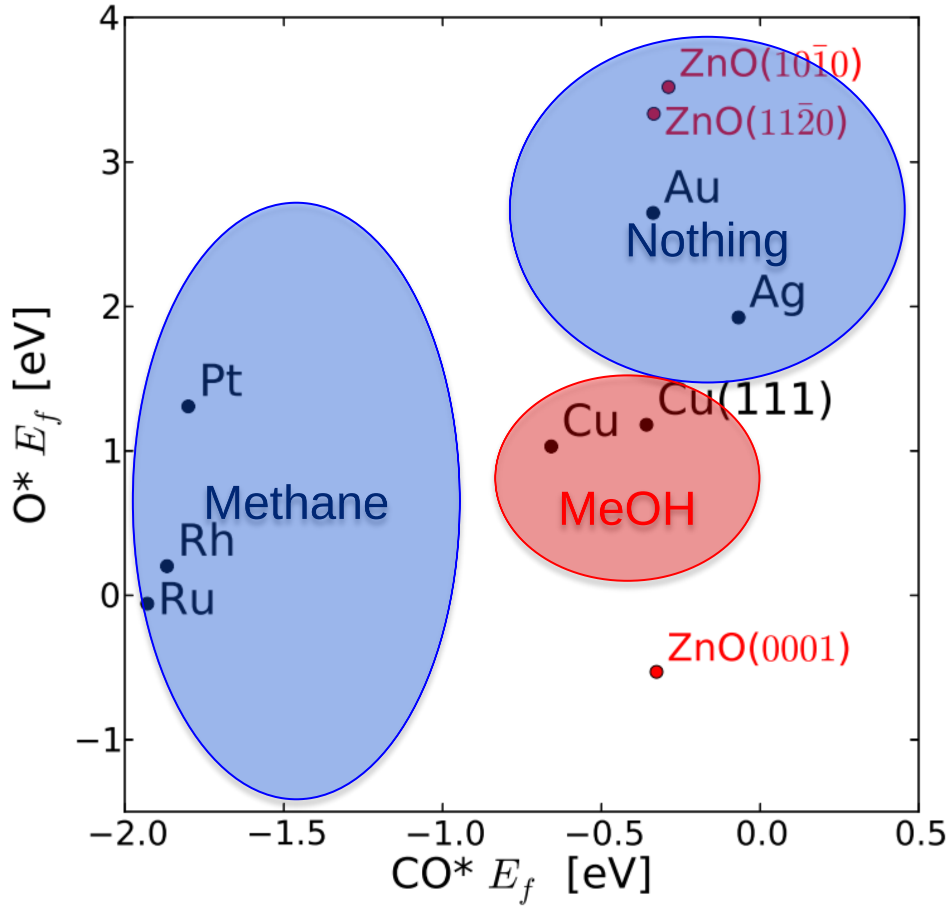
Model Surface

- Assume scaling relations are similar to metals
- Use O and CO binding as probes for reactivity of surfaces



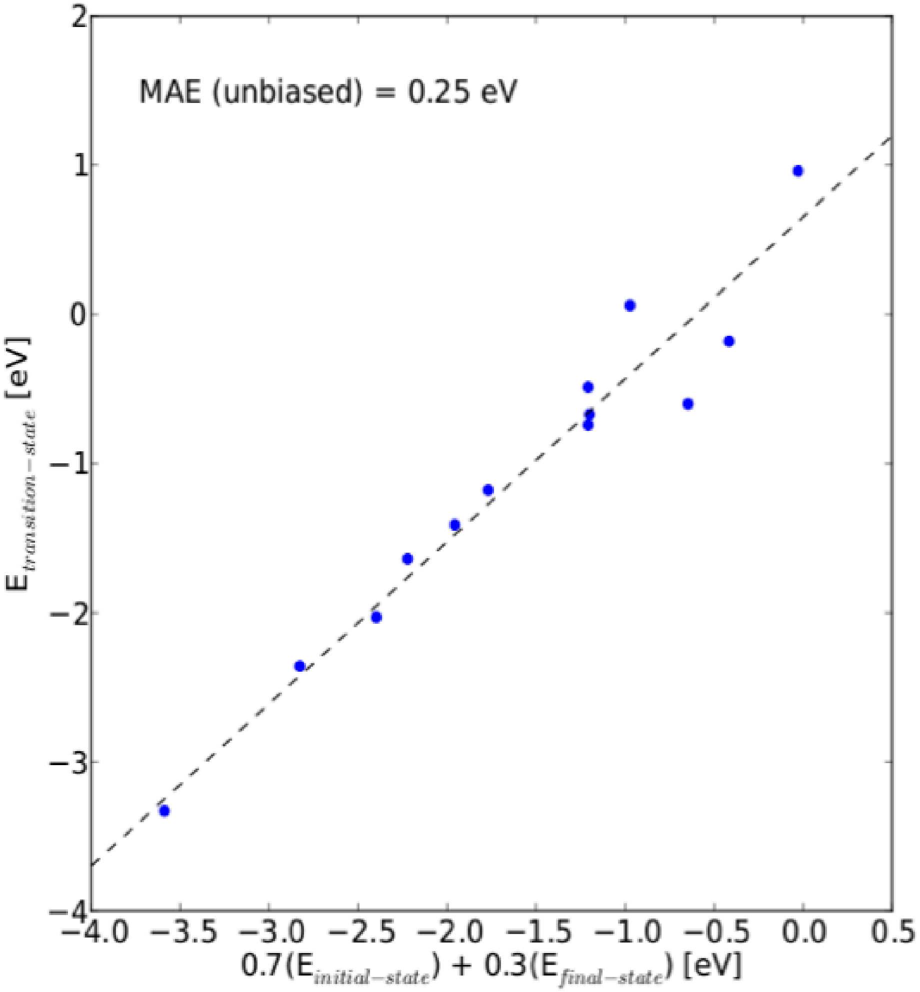
Model Surface

- Non-polar surfaces are more noble than gold!
- Zn-terminated 001 surface looks interesting
- Defects on (001) are likely too reactive
- Defects on non-polar surfaces could be interesting, but complex to model.



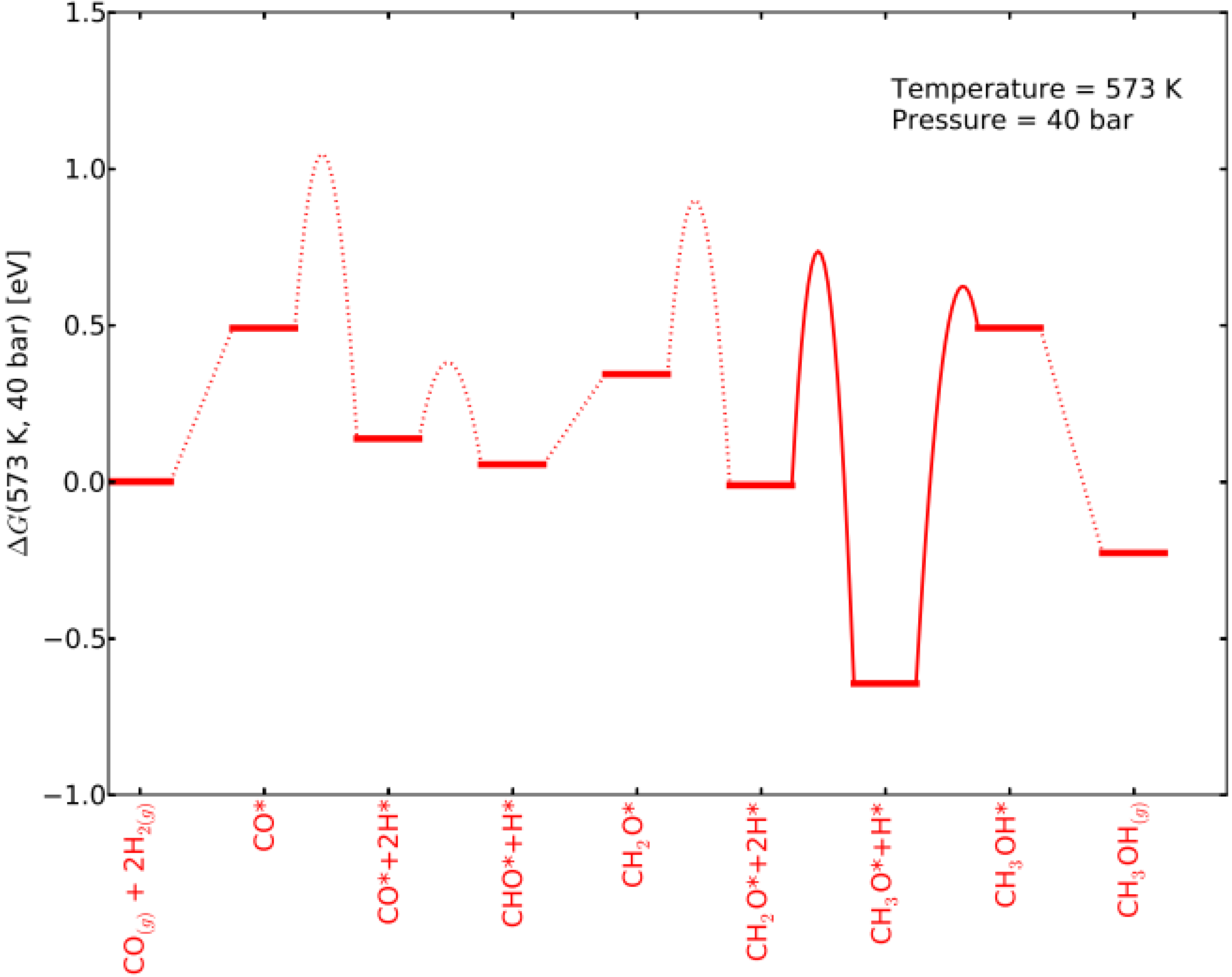
Barrier Estimation

- Take available barriers from literature
    - Calculated with PBE/LCAO
- Use transition-state scaling to estimate few remaining barriers
- Very crude and very fast
- Trends hold as long as barriers don’t change RDS



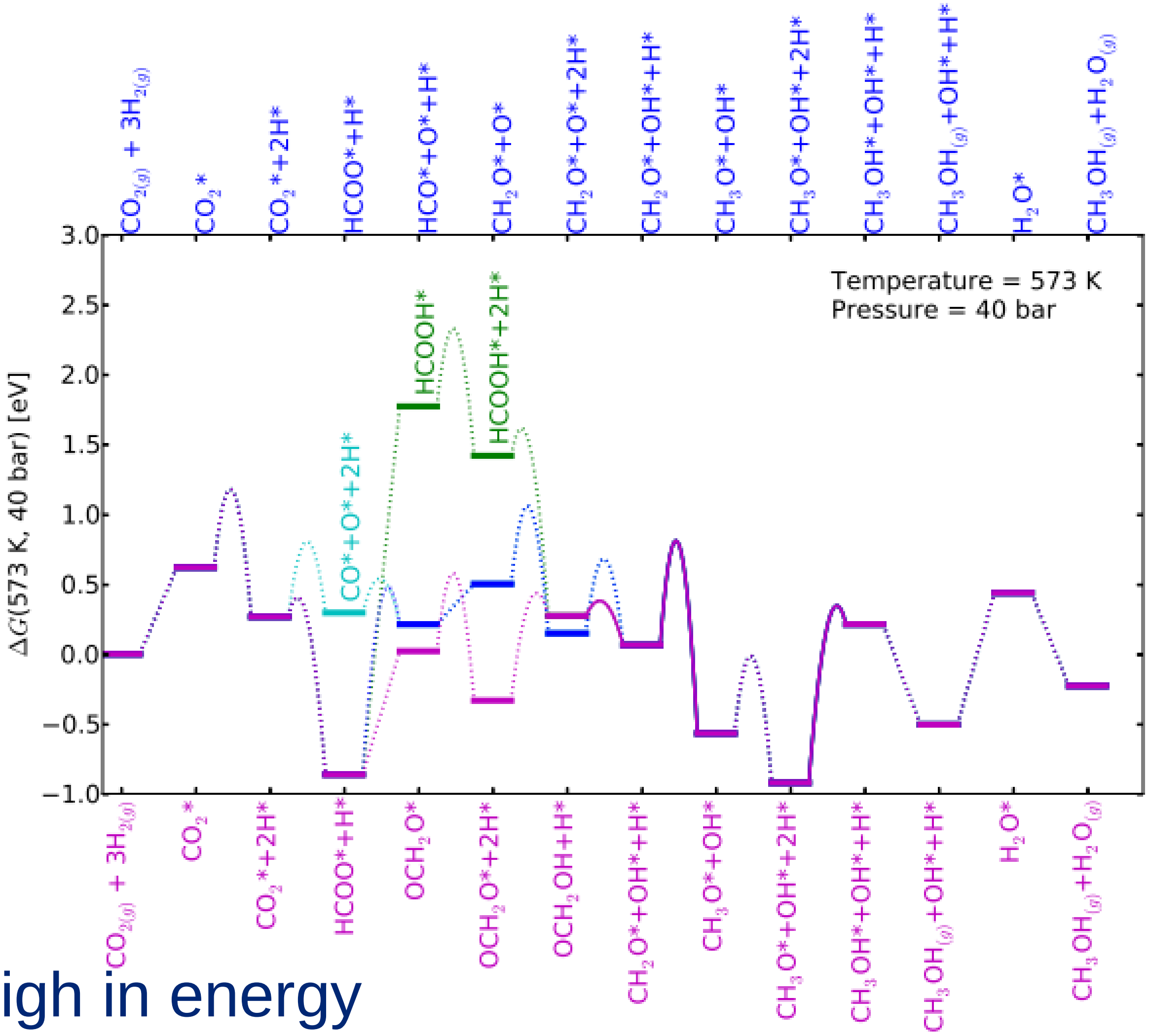
Y. Zhao, R. Rousseau, J. Li, D. Mei J. Phys Chem C 116, (2012) 15952
G. K. Smith, S. Lin, W. Lai, A. Datye, D. Xie, H. Guo, Surface Science 605 (2011) 750

CO Hydrogenation: CO + H_2 → CH_3OH



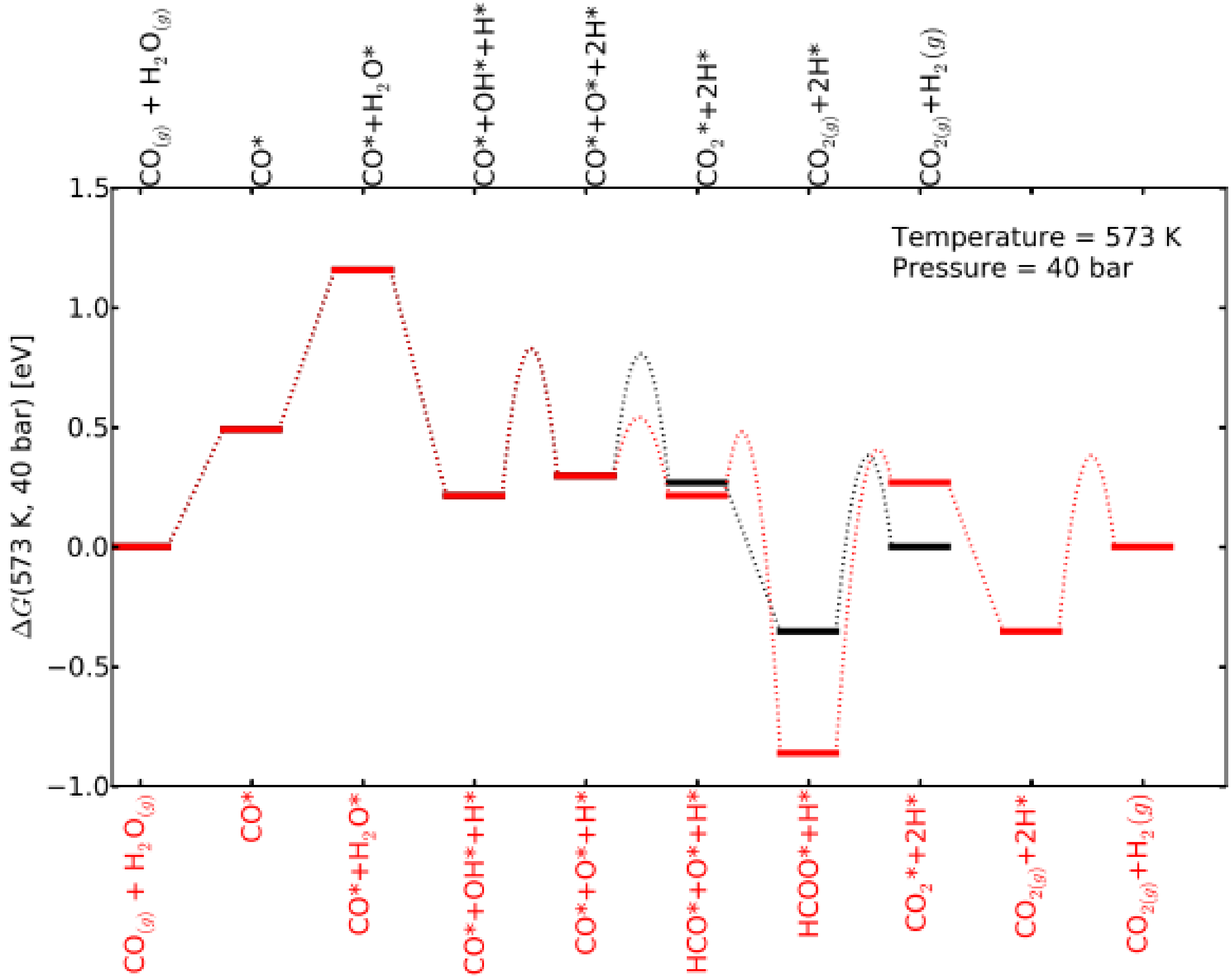
- RDS appears to be methoxy removal
- CO hydrogenation appears very facile… why are high temperatures needed?

CO_2 Hydrogenation: $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$

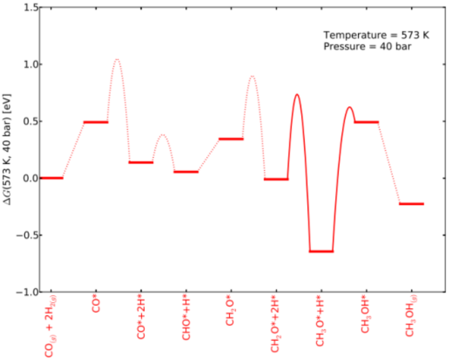


- Formic acid route is high in energy
- Formate species are very stable
- Mechanism is not clear

Water Gas Shift $CO + H_2O \rightarrow CO_2 + H_2$



Free energy diagram algebra



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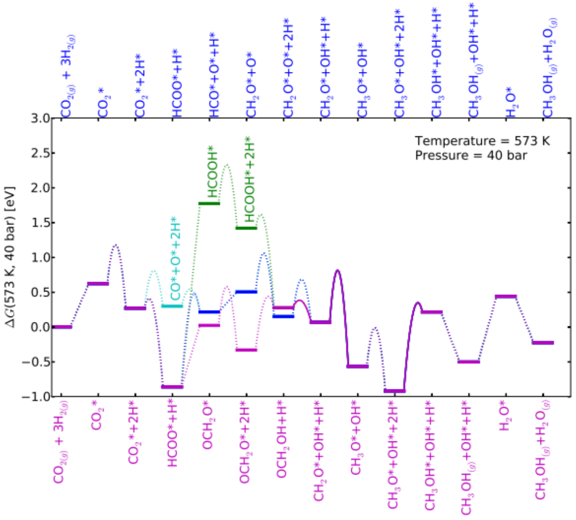

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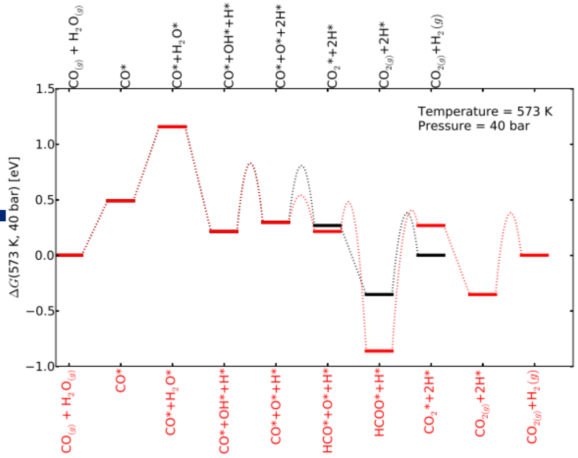

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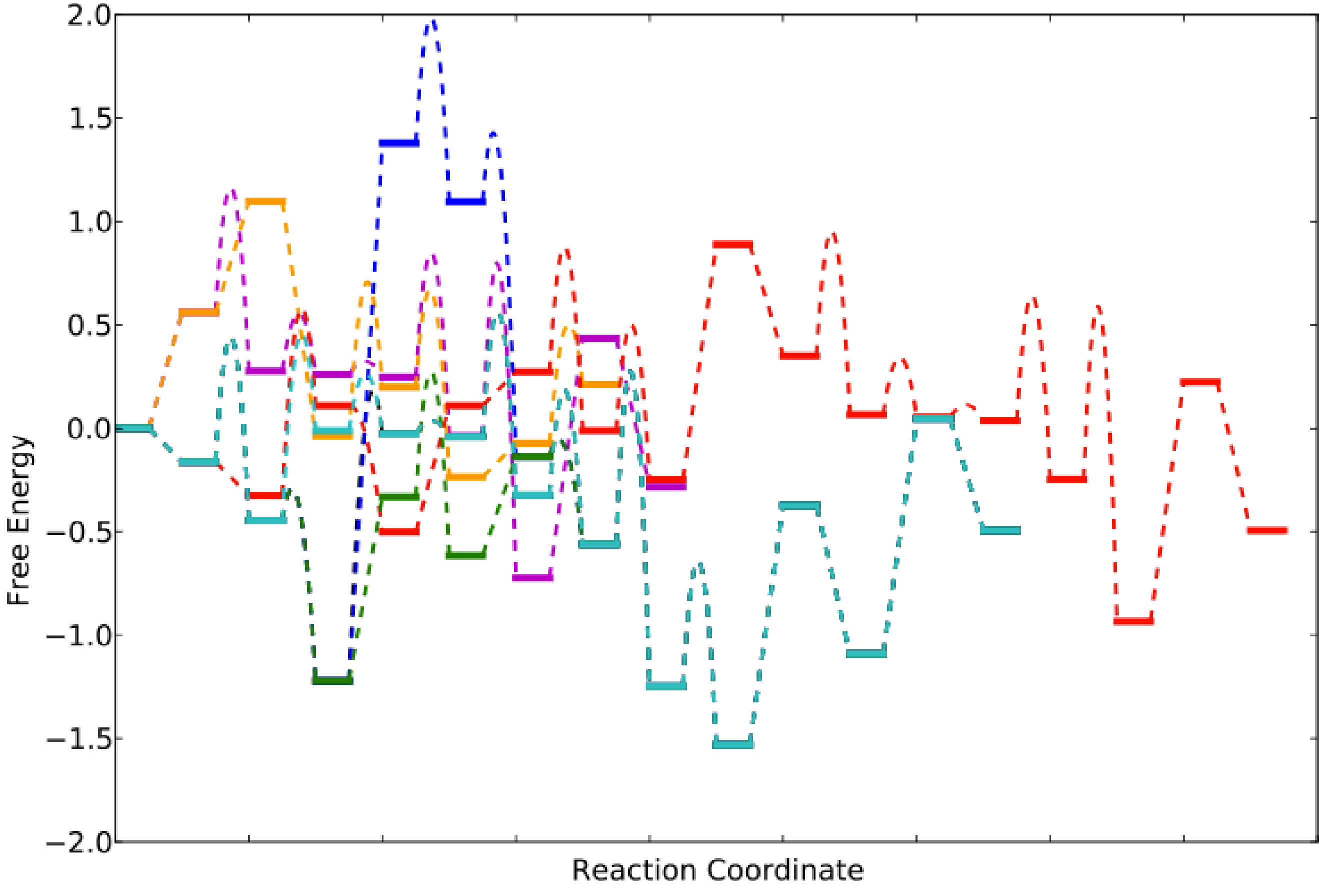
Free Energy Spaghetti Diagram

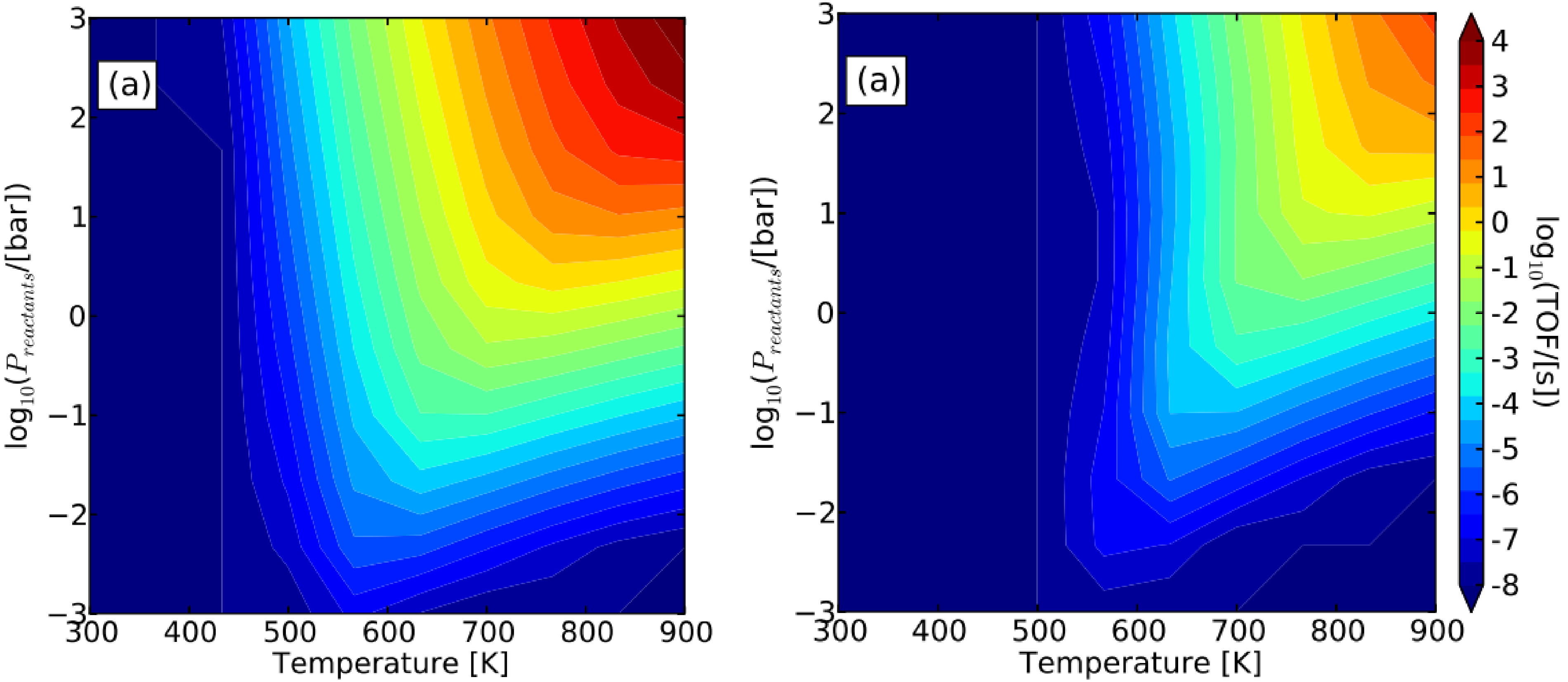


- Need a method for gaining intuition from complex reaction network!

Micro-kinetic model

CO hydrogenation

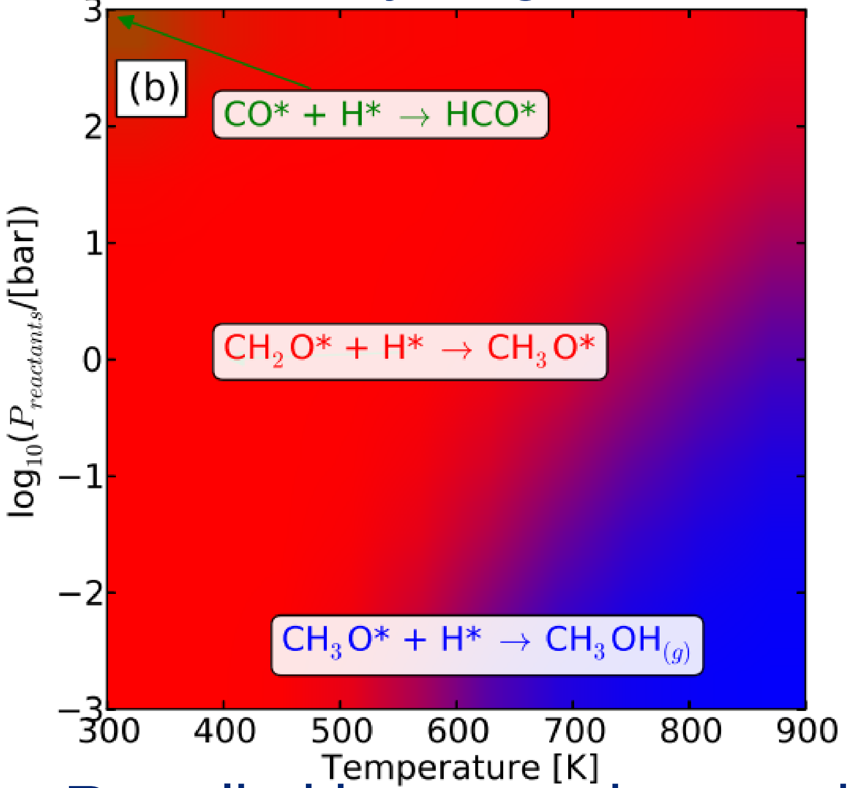
CO_2 hydrogenation



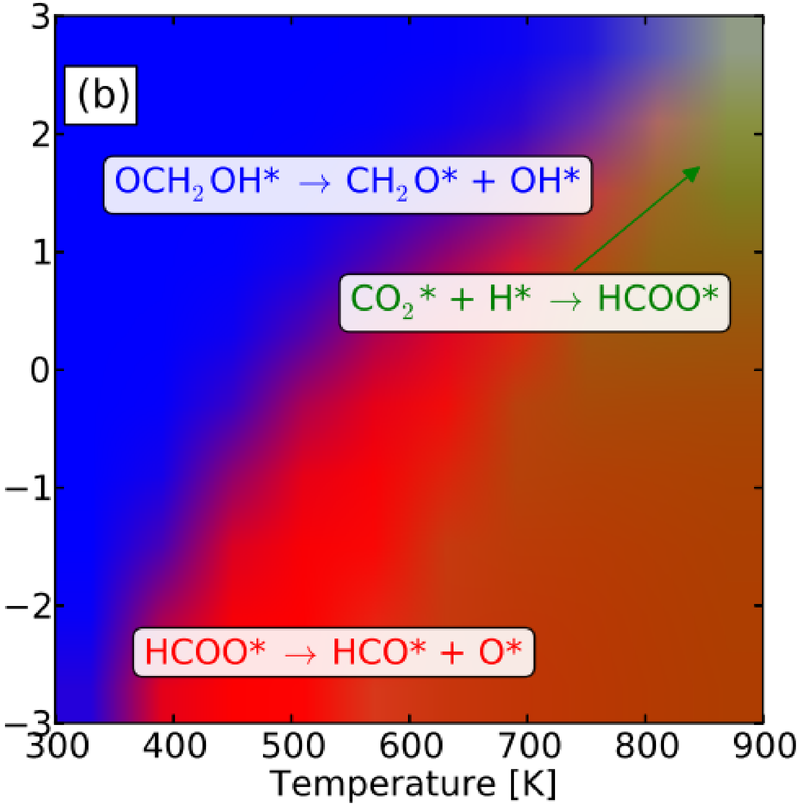
- $CO:H_2 = 7:1$, $P_{CO2} = 0.001$ %, 1% of equilibrium conversion to MeOH and H_2O
- CO hydrogenation is dominant for ZnO
- High temperatures and pressures are needed for significant rates

Rate-limiting Steps

CO hydrogenation

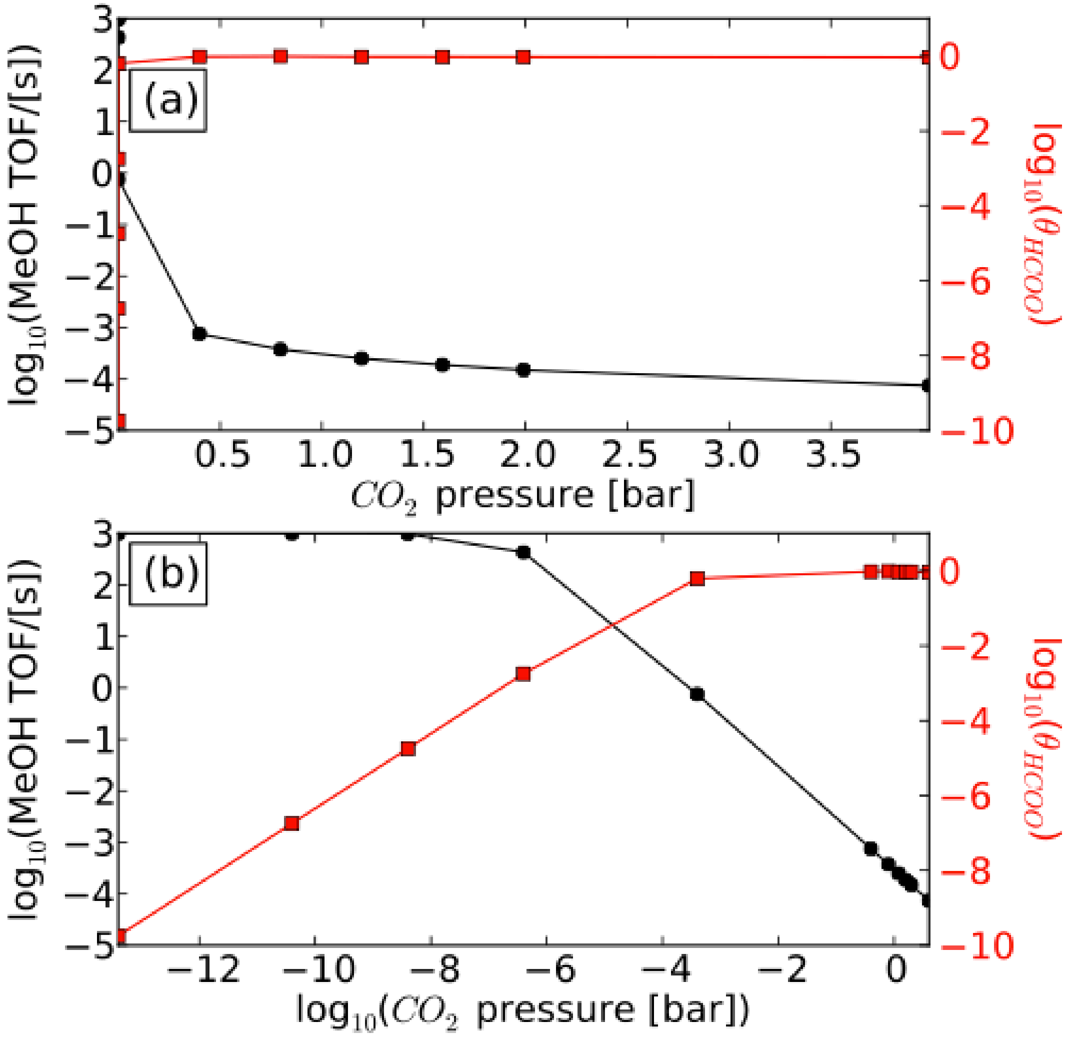


CO_2 hydrogenation



- Rate-limiting step changes between formaldehyde and methoxy hydrogenation for CO hydrogenation
- Formate or OCH_2OH decomposition is rate-limiting for CO_2 hydrogenation

CO_2 Poisoning



- CO_2 poisoning is due to strong formate binding
- Rate is not just CO + CO_2 hydrogenation!
- Site competition is important

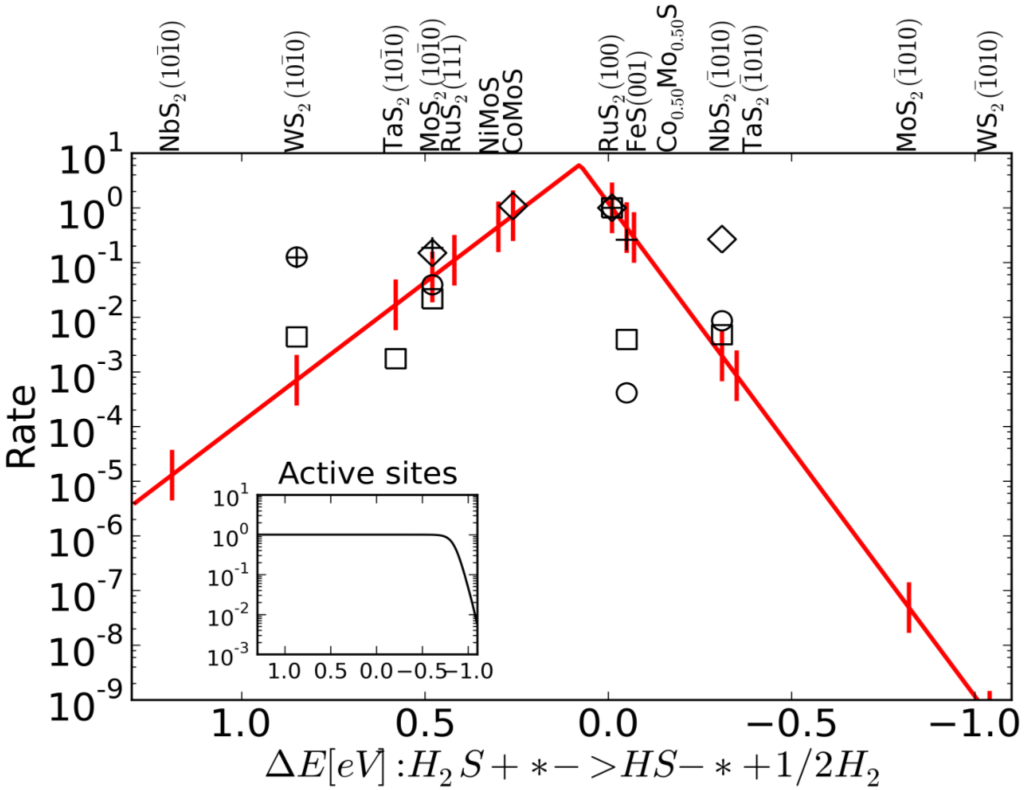
Conclusions on methanol synthesis over ZnO

- Polar surfaces of ZnO are likely the most important for catalysis
- Kinetic models provide an intuitive way of analyzing complex reaction networks
- MeOH synthesis is limited by removal of formate from the surface, leading to high temperature/pressure requirements and low CO_2 concentrations

Andrew Medford; Jens Sehested, Jan Rossmeisl, Ib Chorkendorff, Felix Studt, Jens K Nørskov, Poul G Moses, Journal of catalysis, accepted

Trends in HDS catalysis over sulfides

- Provide guidelines
- Identify key descriptors
- Ultimately predict



Green is very dirty

- Pyrolysis oil contain 0-0.05wt % S
- EU and US regulations are 0.0010-0.0015 wt % S in diesel
- Hydrotreating is needed

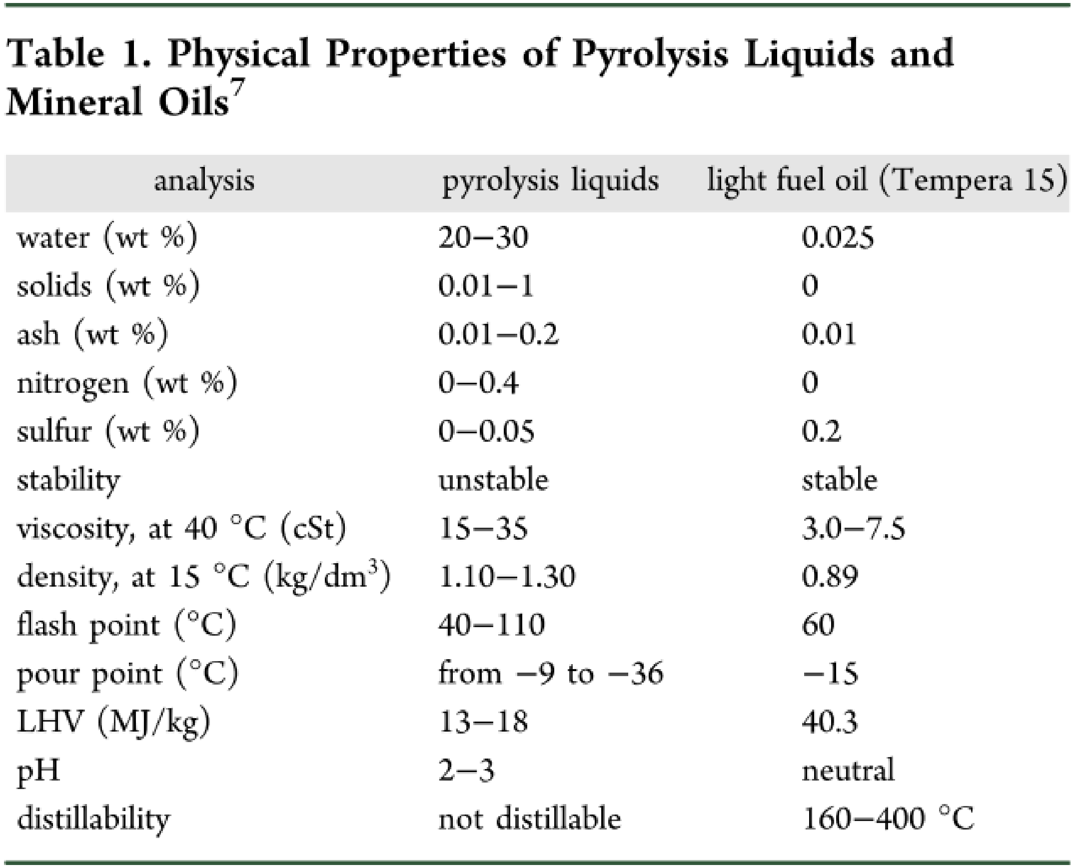


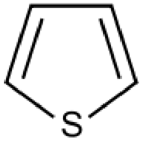
Table 1. Physical Properties of Pyrolysis Liquids and Mineral Oils[7]

analysis	pyrolysis liquids	light fuel oil (Tempera 15)
water (wt %)	20–30	0.025
solids (wt %)	0.01–1	0
ash (wt %)	0.01–0.2	0.01
nitrogen (wt %)	0–0.4	0
sulfur (wt %)	0–0.05	0.2
stability	unstable	stable
viscosity, at 40 °C (cSt)	15–35	3.0–7.5
density, at 15 °C (kg/dm^3)	1.10–1.30	0.89
flash point (°C)	40–110	60
pour point (°C)	from −9 to −36	−15
LHV (MJ/kg)	13–18	40.3
pH	2–3	neutral
distillability	not distillable	160–400 °C

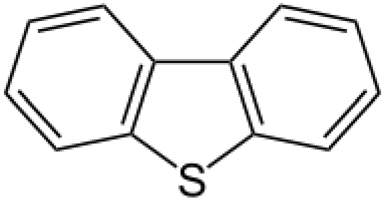
A. Oasmaa, E. Kuoppala, D.C. Elliott Energy and Fuels, 2012,26,2454

Hydrodesulfurization (HDS)

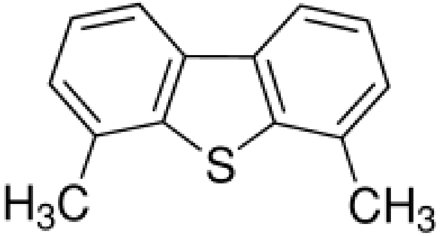
(Sulfur-containing organic compound) + H_2 → (Desulfurized organic compound) + H_2S



thiophene

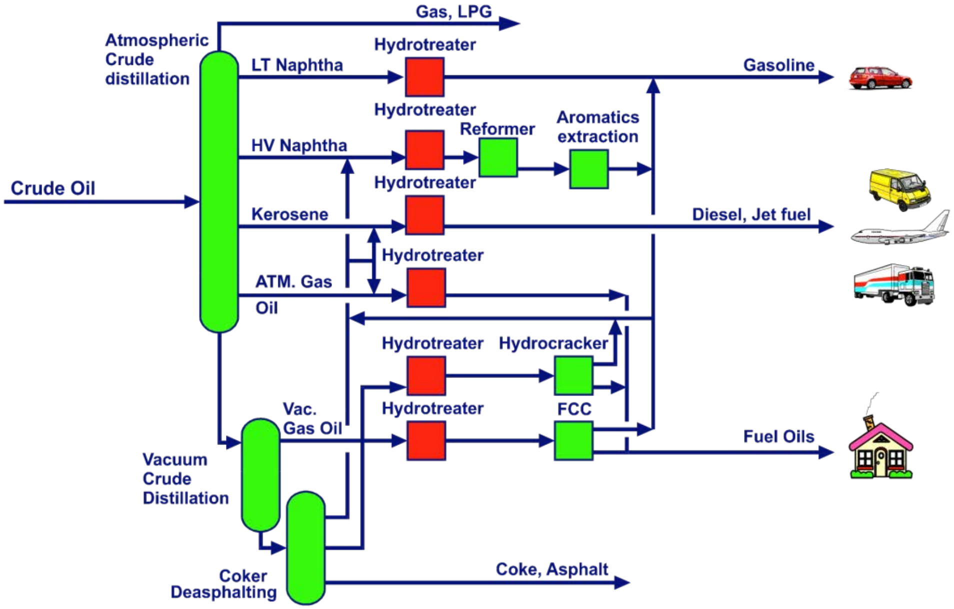


dibenzothiophene



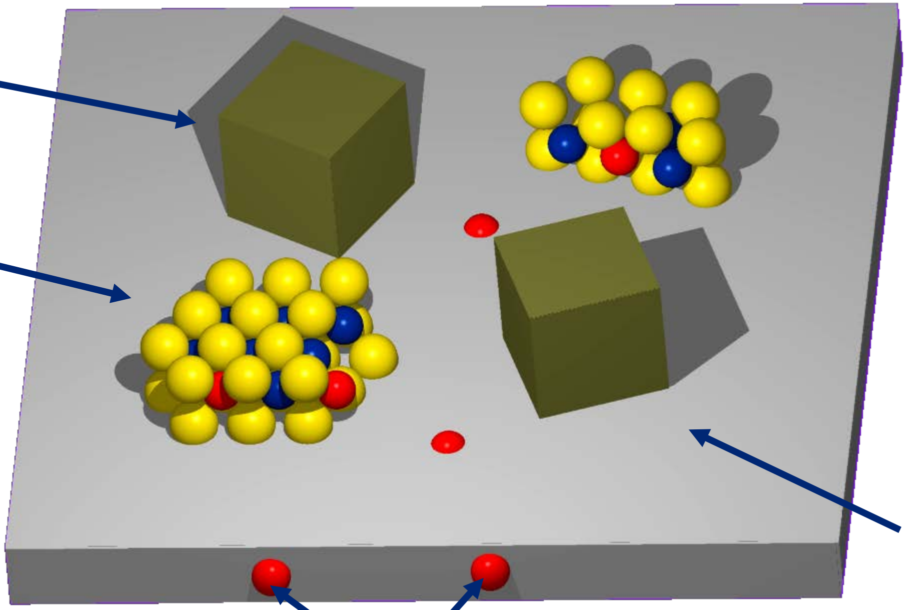
4,6-dimethyl dibenzothiophene

Naphta: 1.4-5.2 MPa, 290-370 °C



HALDOR TOPSØE

Catalysts structure



Co_9S_8

MoS_2-like nanoparticles ”Co-Mo-S”

● S

● Mo

● Co

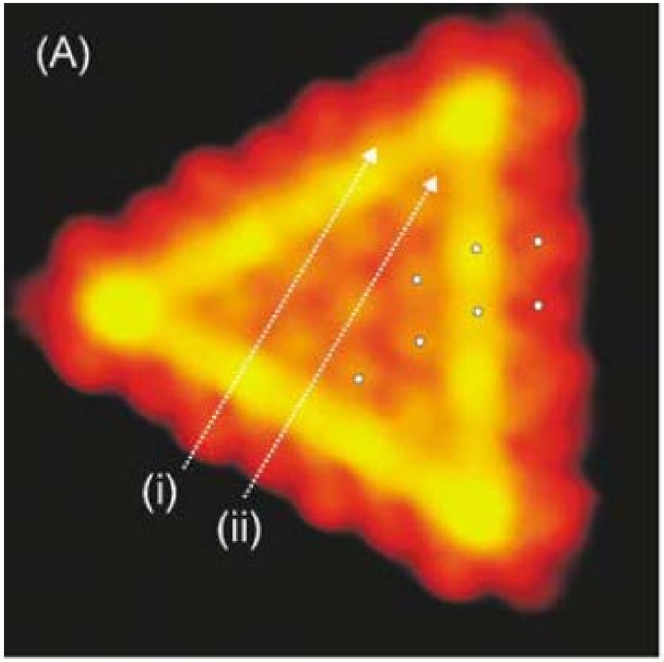
Al_2O_3 (alumina) support

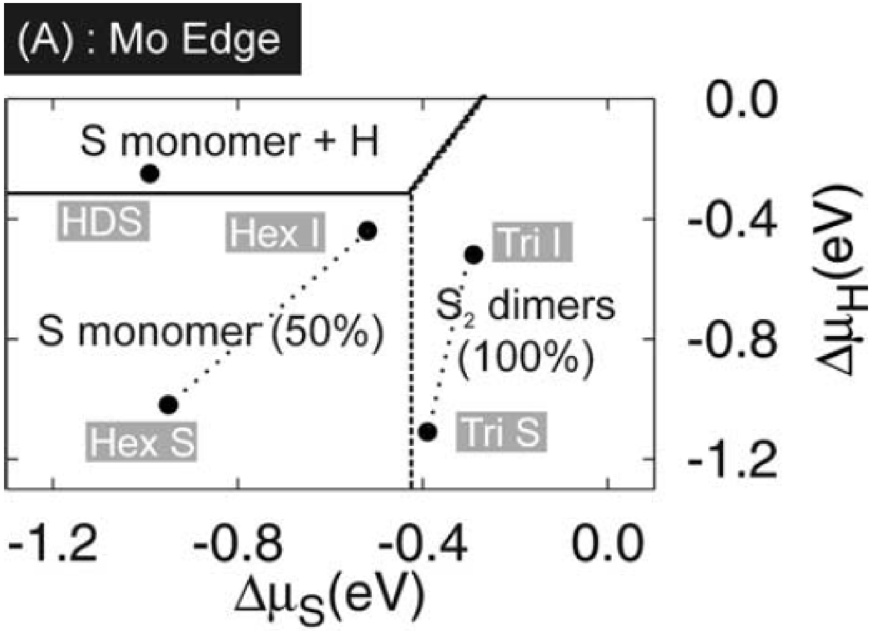
$Co:Al_2O_3$

- Co, Ni Promoters is located at the S edge

H. Topsøe, B.S. Clausen, R. Candia, C. Wivel, S. Mørup, J. Catal. 68 (1981) 433

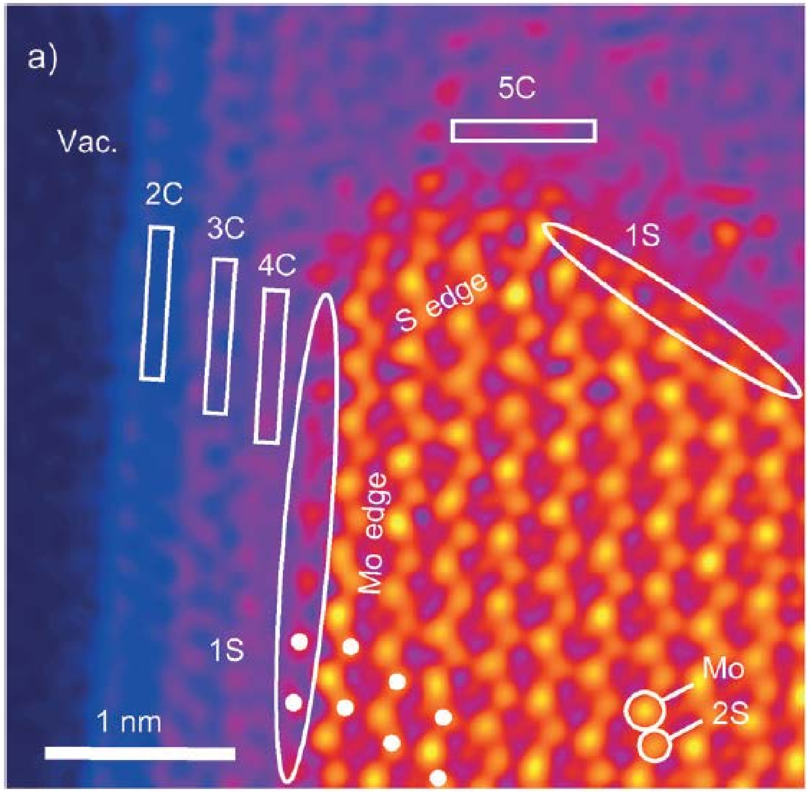
Atomic scale structural insight : STM confirms DFT prediction

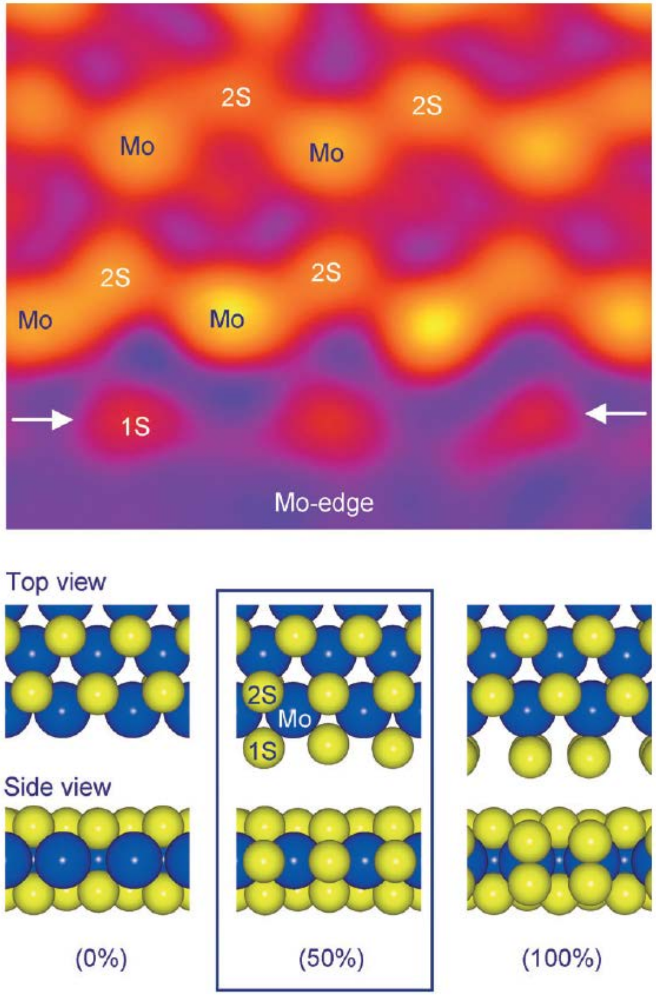




J.V. Lauritsen, M.V. Bollinger, E. Lægsgaard, K.W. Jacobsen, J.K. Nørskov, B.S. Clausen, H. Topsøe, F. Besenbacher J. Catal 221 (2004) 510

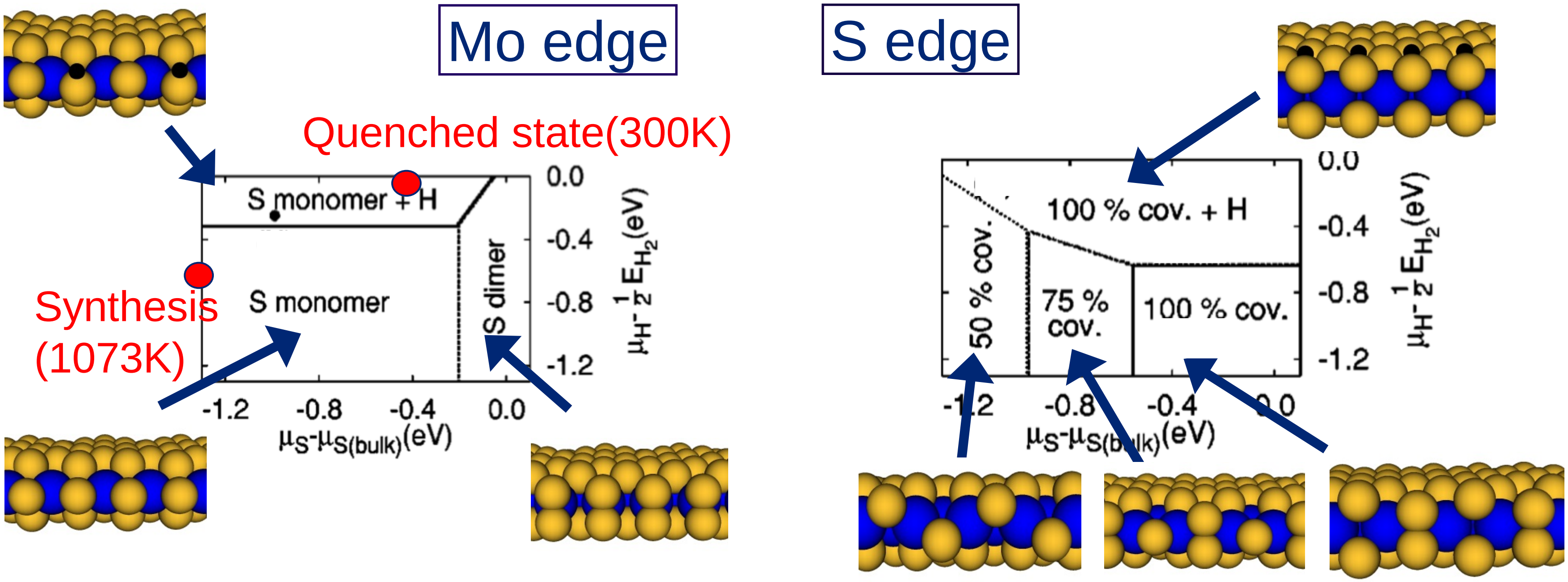
Atomic scale structural insight
Transmission electron microscopy





L.P. Hansen, Q.M. Ramasse, C. Kisielowski, M. Brorson, E. Johnson, H. Topsøe, and S. Helveg. Angew. Chem. Int. Ed. 2011, 50 10153

STEM confirms DFT prediction



Mo edge

S edge

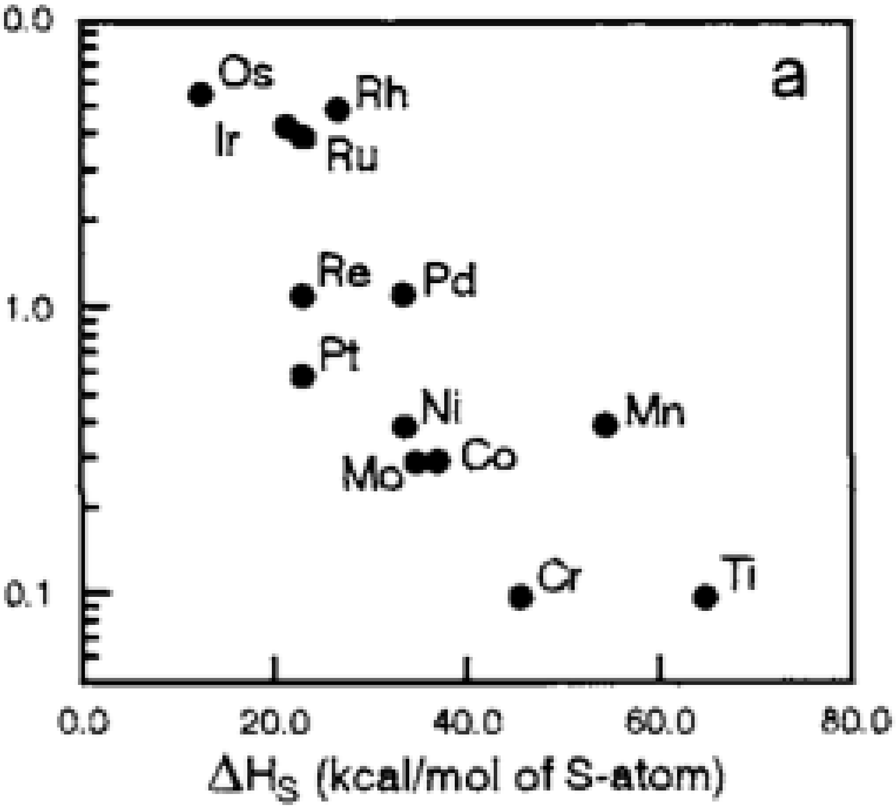
Quenched state(300K)

Synthesis (1073K)

- Edge structure depends on (T,p) of the H_2,H_2S atmosphere
- Synthesis: P_{H2} = 0.9bar, P_{H2S} = 0.1bar at 1073K. Storage: N_2 at 300K

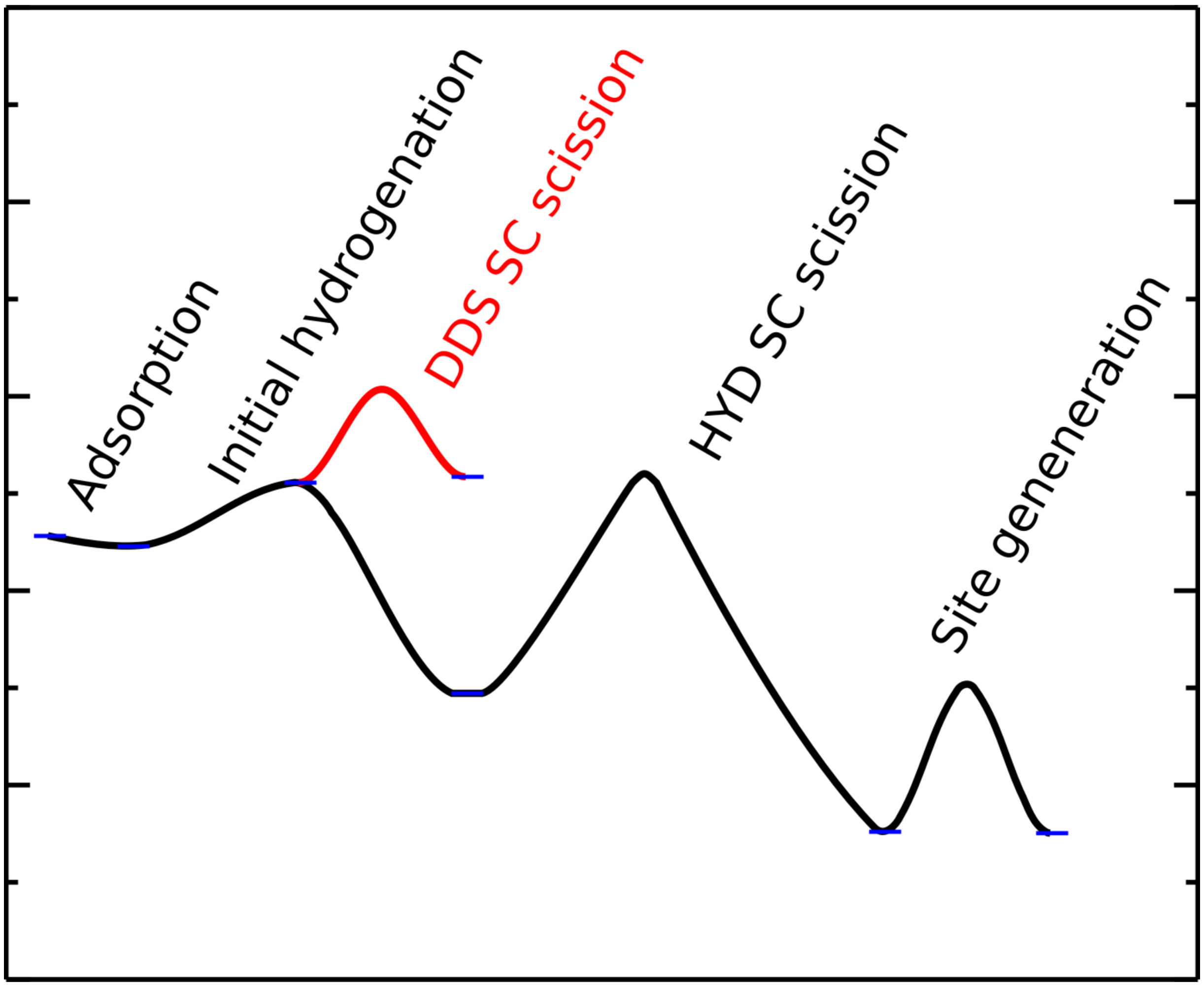
Bollinger, Jacobsen, Nørskov, *Phys. Rev. B* **67**, 085410 (2003).

Trends in HDS activity
Several models based on bulk properties.



H. Topsøe, K. G. Knudsen, L.S. Byskov, J. K. Nørskov, B. S. Clausen Sci. Tech. Cat. 1998 p13

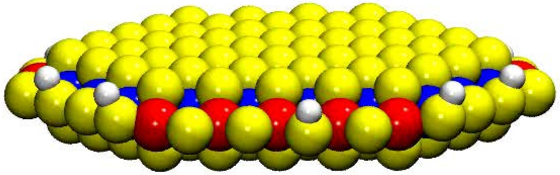
Schematic potential energy diagram



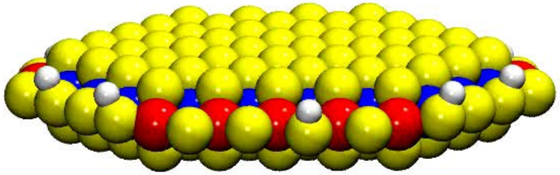
P.G. Moses, B. Hinnemann, H. Topsøe, J.K. Nørskov, J. Catal 248 (2007) 188, 260 (2008) 202

P.G. Moses, B. Hinnemann, H. Topsøe, J.K. Nørskov, J. Catal 268 (2009) 201

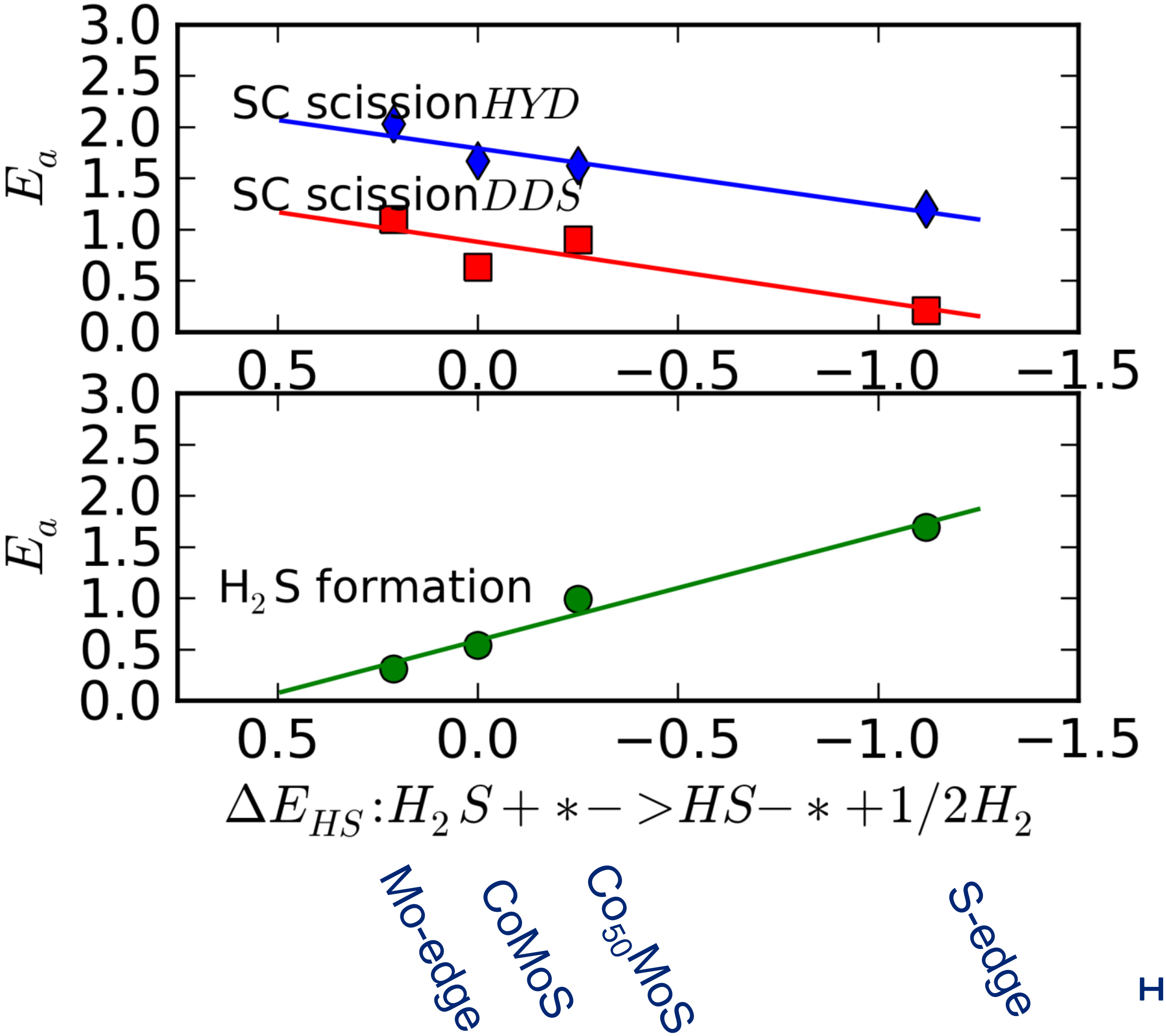
HDS kinetics: Hydrogenation path



HDS kinetics: Direct desulfurization path



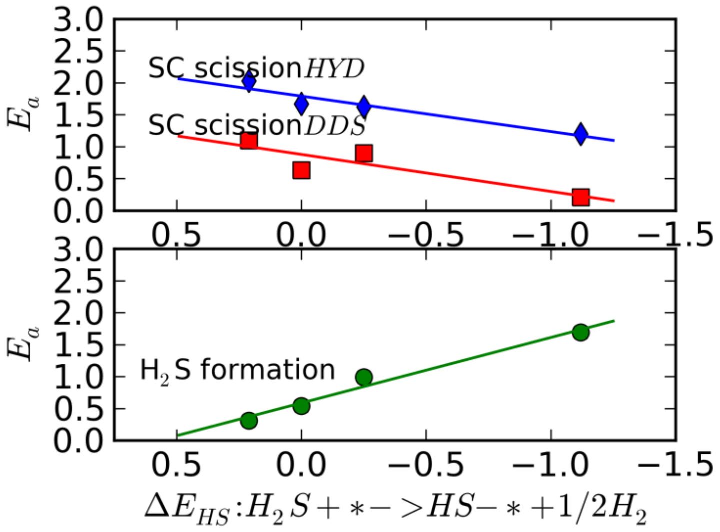
Linear Correlations



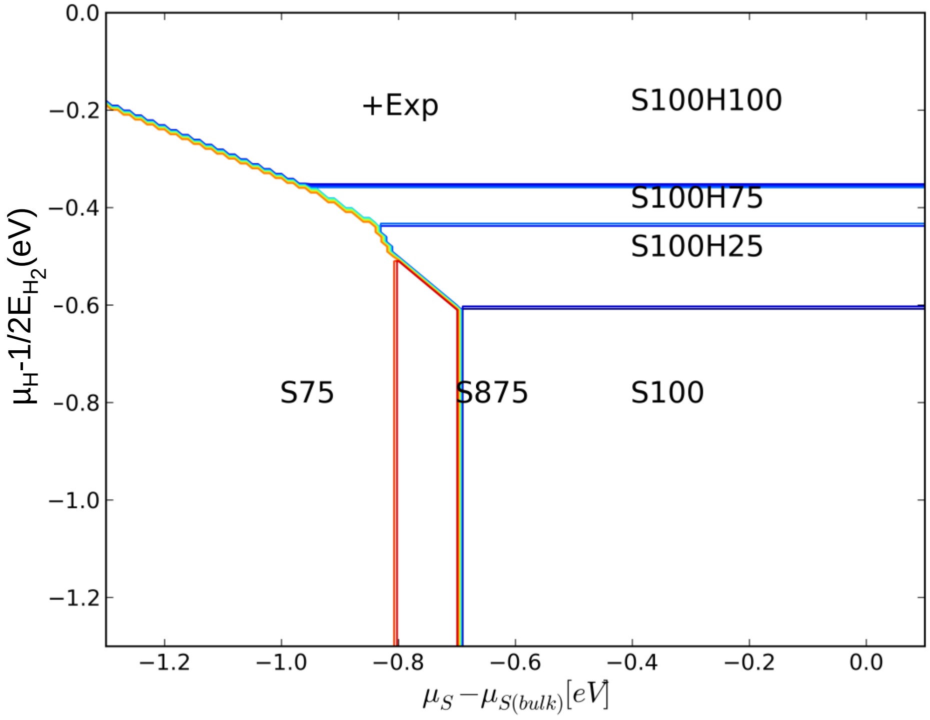
Sabatier analysis

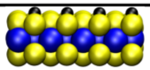
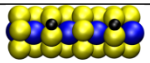
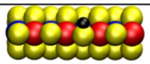
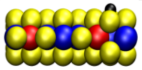
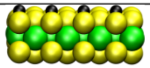
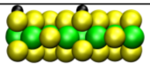
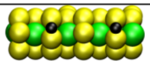
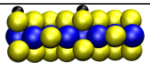
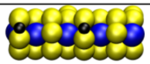
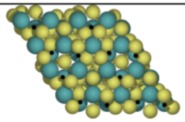
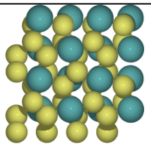
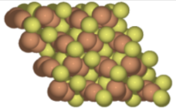
- Assume
  - Optimal coverage

$$rate \propto \min(\max(rate_{SC}), \max(rate_{H_2S})) = \min(\exp(-E_{SC}/k_BT), \exp(-E_{H_2S}/k_BT))$$

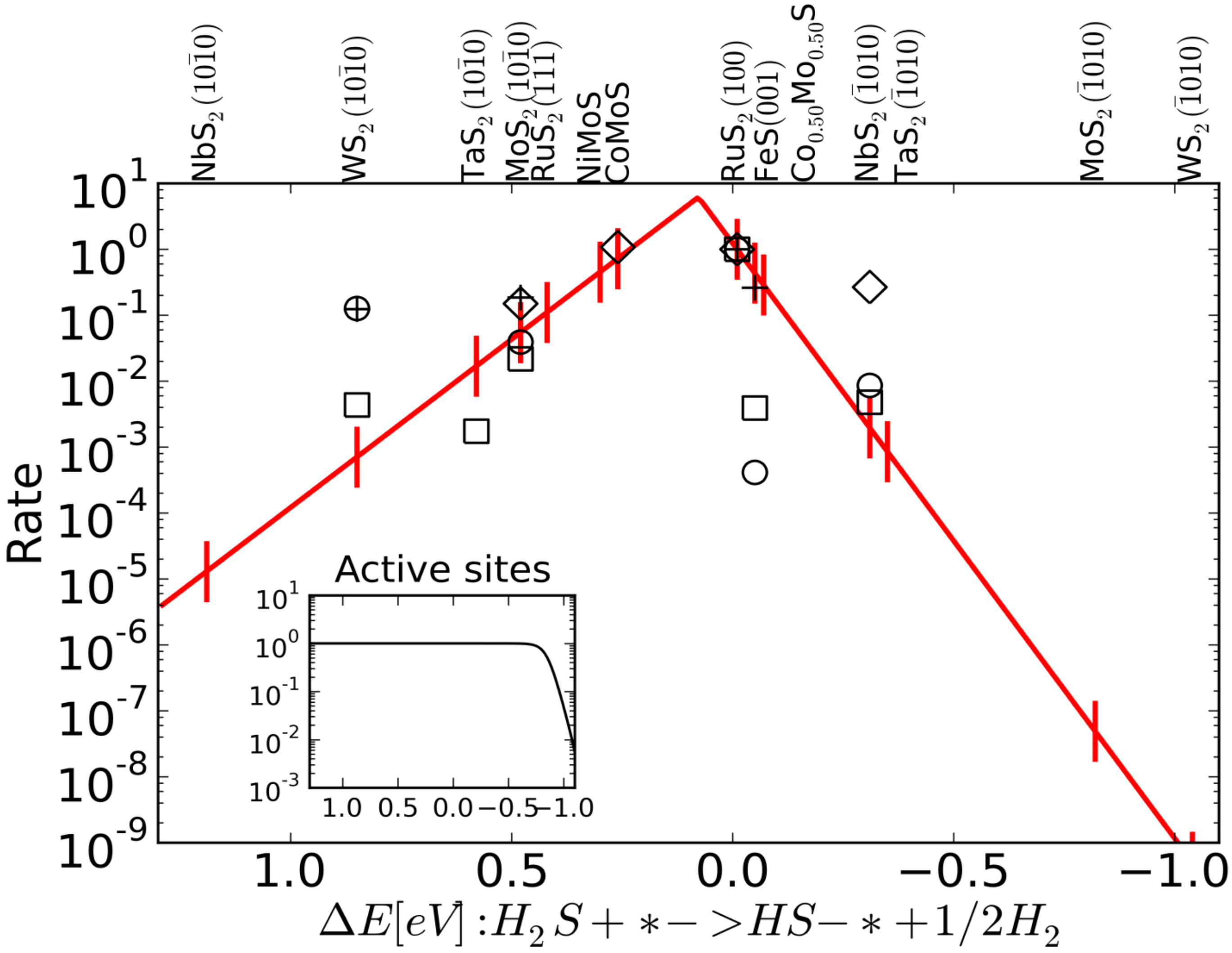


Compounds

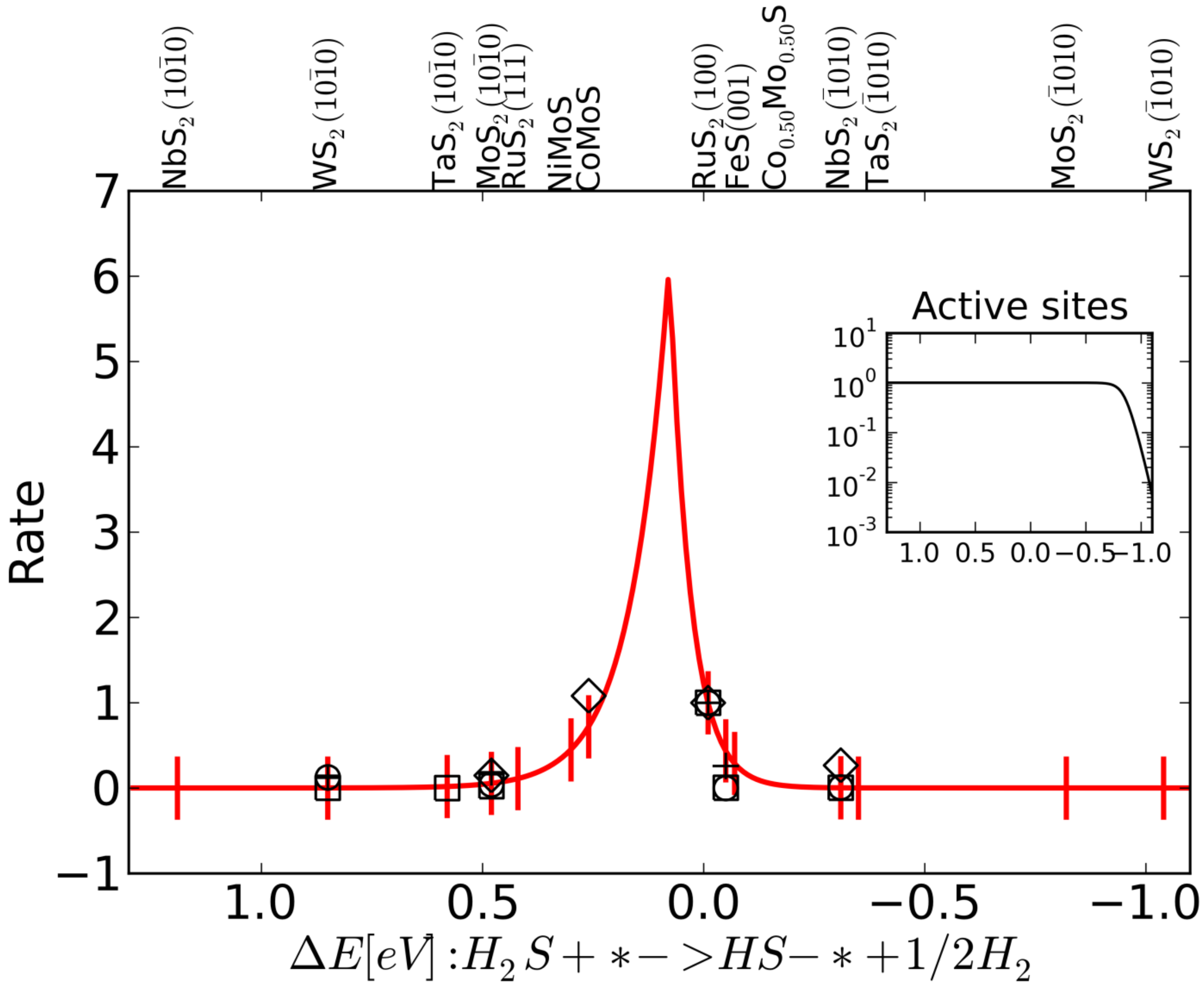


Compound	Surface	Equilibrium structure	ΔE(½H_2)	ΔE(HS, reaction1)
MoS_2	$(\bar{1}010)$		-0.42	-0.82[a]
MoS_2	$(10\bar{1}0)$		-0.24	0.48
Co-Mo-S	$(\bar{1}010)$		-0.19	0.26
$Co_{0.50}$-$Mo_{0.50}$-S	$(\bar{1}010)$		-0.32	-0.07
Ni-Mo-S	$(\bar{1}010)$		-0.38	0.3[b]
WS_2	$(\bar{1}010)$		-0.36	-1.04[a]
WS_2	$(10\bar{1}0)$		-0.07[c]	0.85
TaS_2	$(\bar{1}010)$		-0.29	-0.35
TaS_2	$(10\bar{1}0)$		-0.31	0.58
NbS_2	$(\bar{1}010)$		-0.43	-0.31
NbS_2	$(10\bar{1}0)$		-0.43	1.19
RuS_2	(111)		-0.56	0.42
RuS_2	(100)		0.78[c]	-0.01
FeS	(001)		0.25[c]	-0.05

Activity Volcano



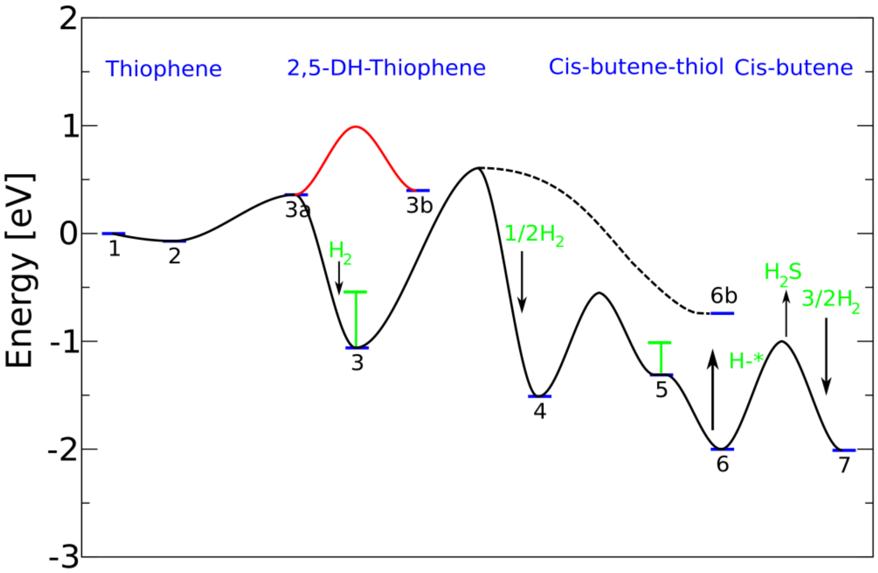
Predict known excelent catalysts

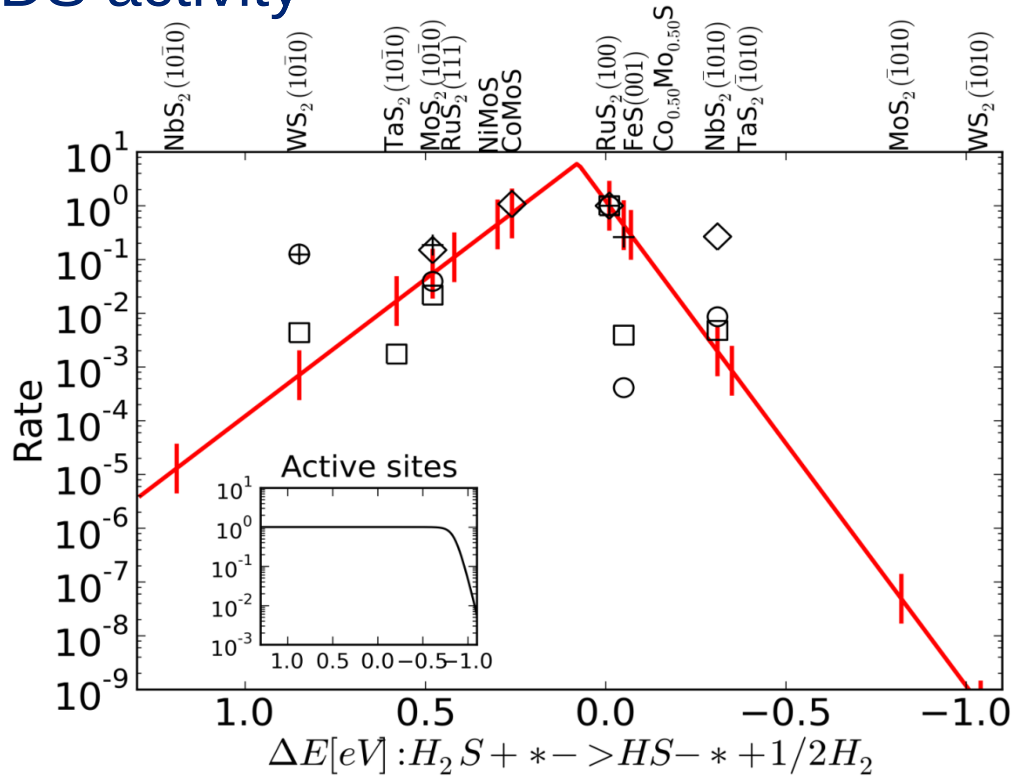


HALDOR TOPSØE

Conclusion on trends in HDS catalysis

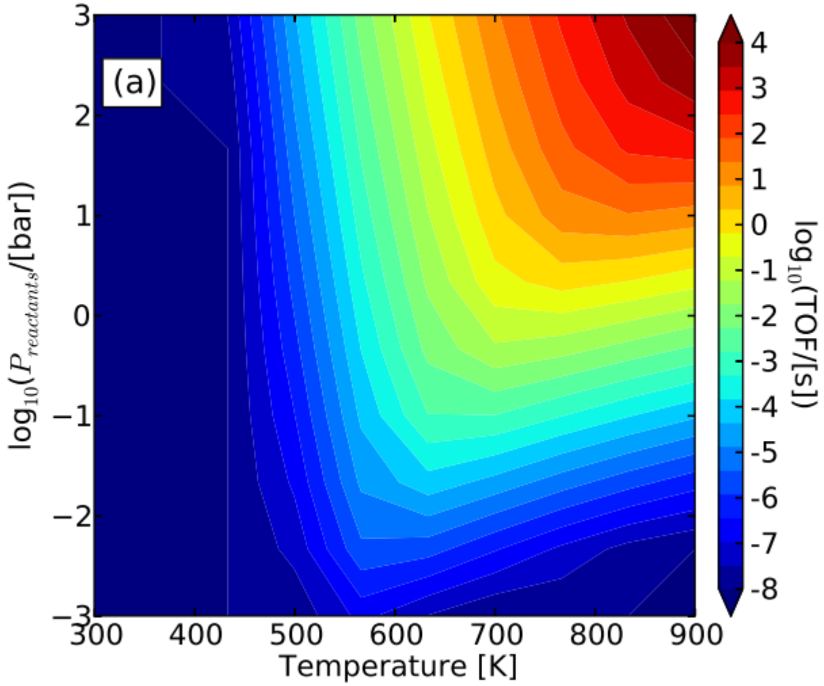
- Effect of Co Promotion
- Towards a predictor of HDS activity

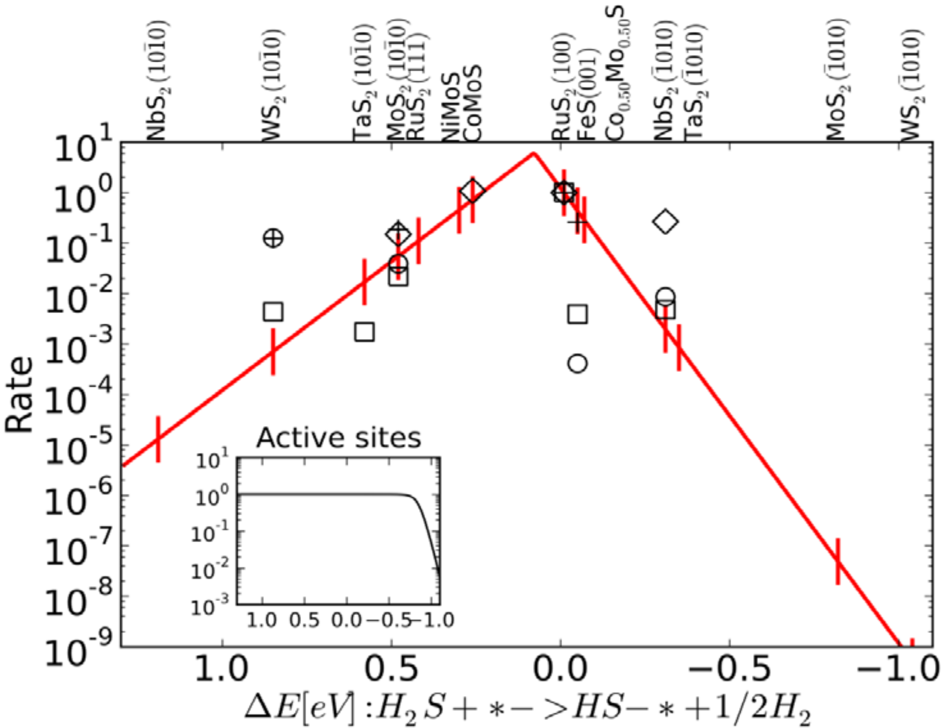




Summary

- Thermodynamics
- (Micro)kinetic modeling
- Data bases of DFT values
- (Linear) correlations to fill the gaps





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DTU

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CAMd
Center for Atomic-scale Materials Design

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