

# CO and NO-induced disintegration of Rh, Pd, and Pt nanoparticles on TiO<sub>2</sub>(110): *ab initio* thermodynamics study

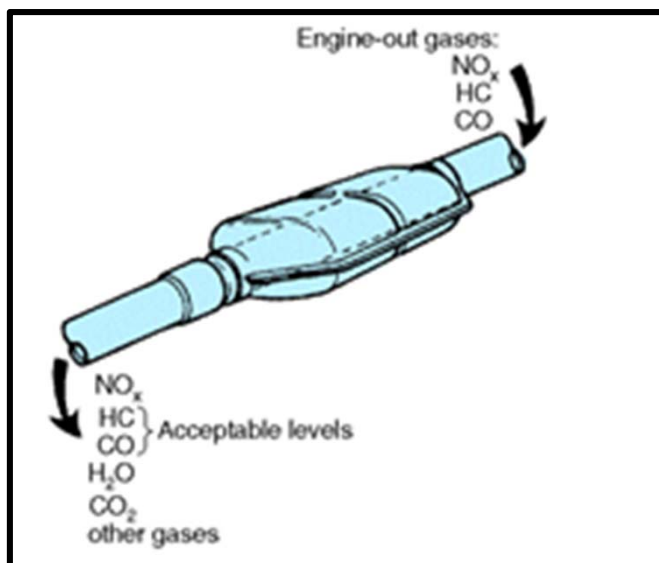
Bryan R. Goldsmith, Evan. D. Sanderson, Runhai Ouyang, Wei-Xue Li

University of California, Santa Barbara  
Dalian Institute of Chemical Physics

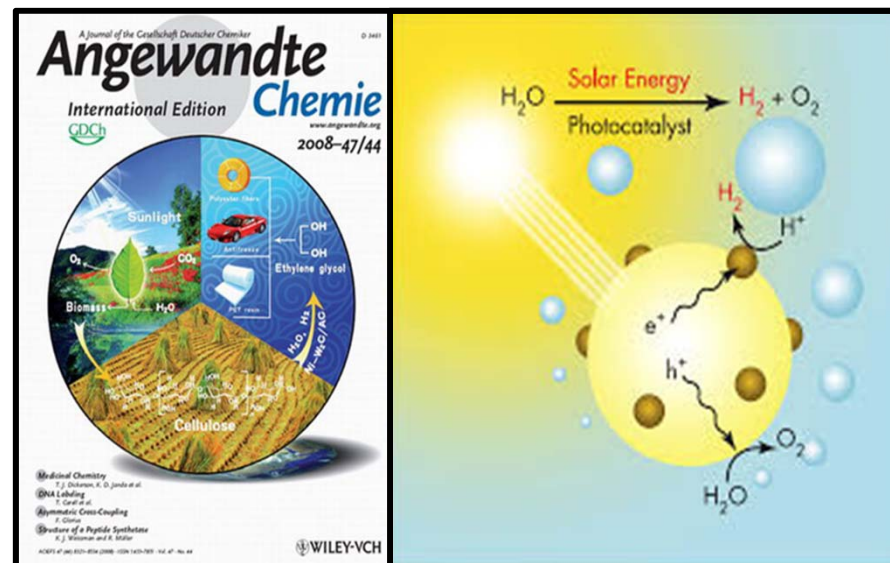
Increasing catalyst durability  
and recyclability is important



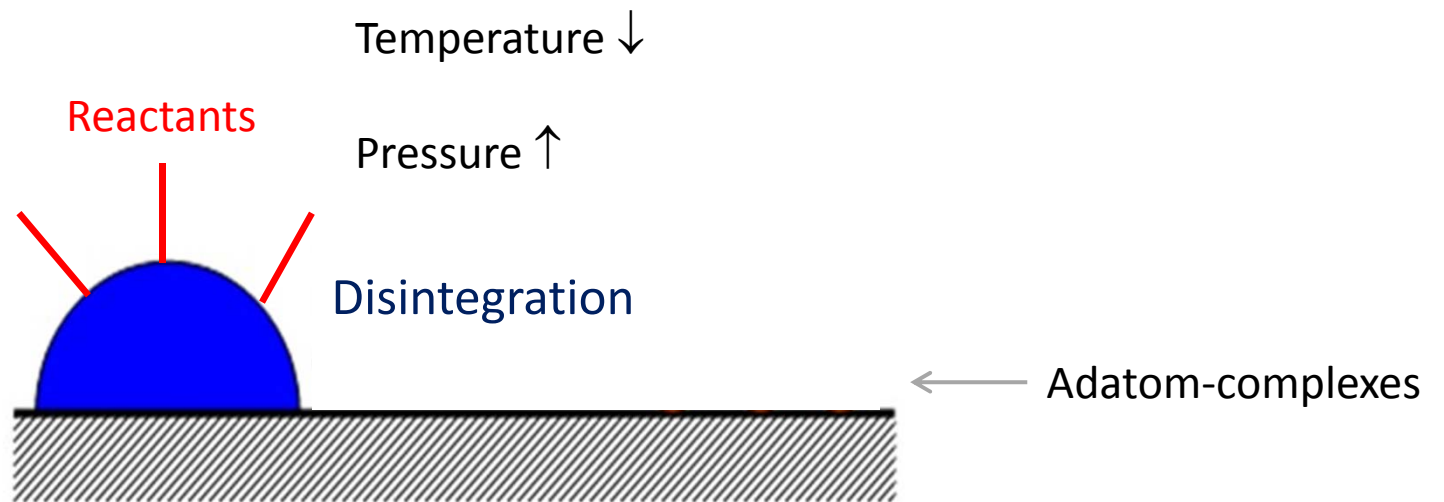
Pollution control



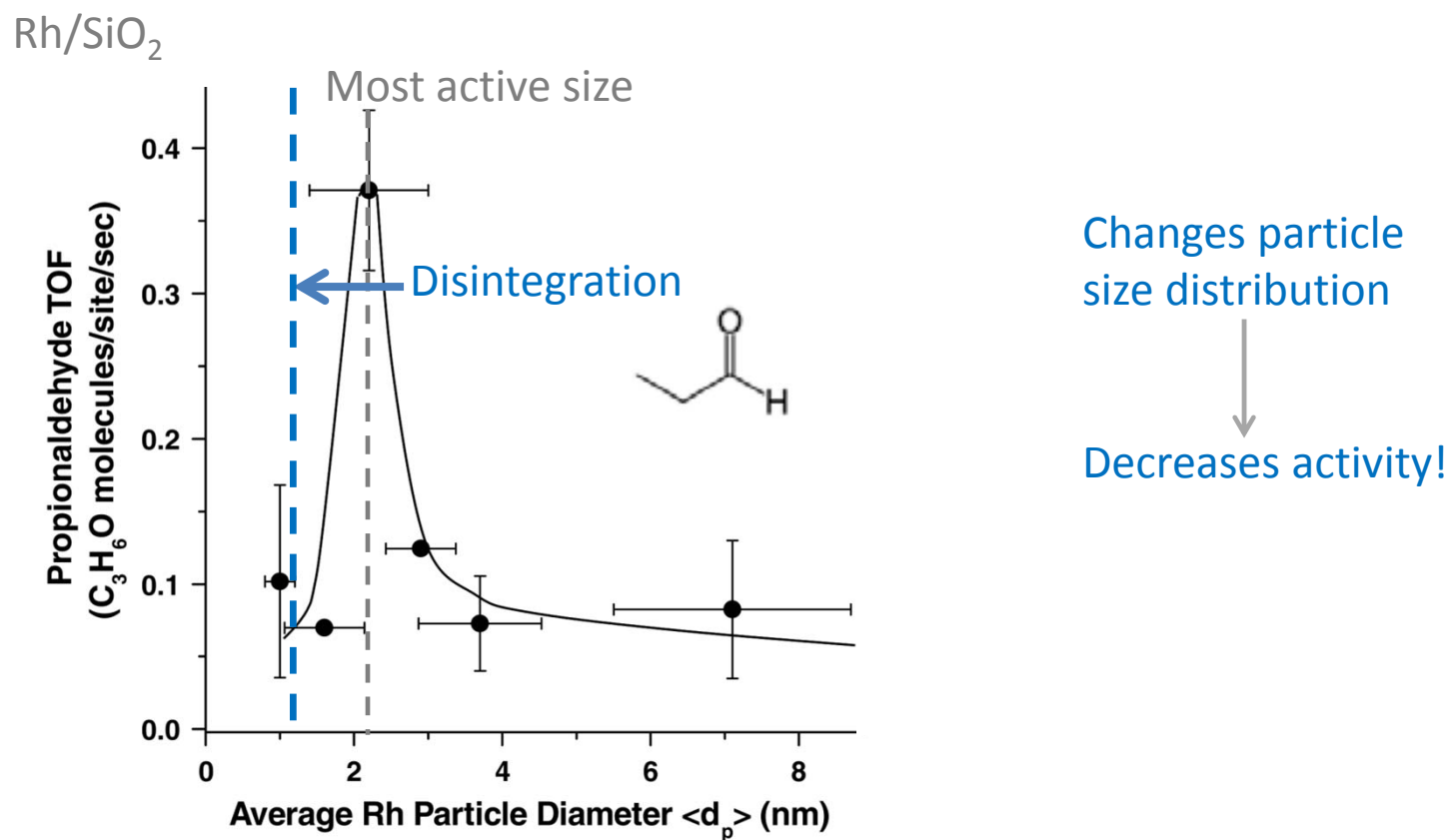
Alternative energy



# Nanoparticle disintegration is a common phenomena

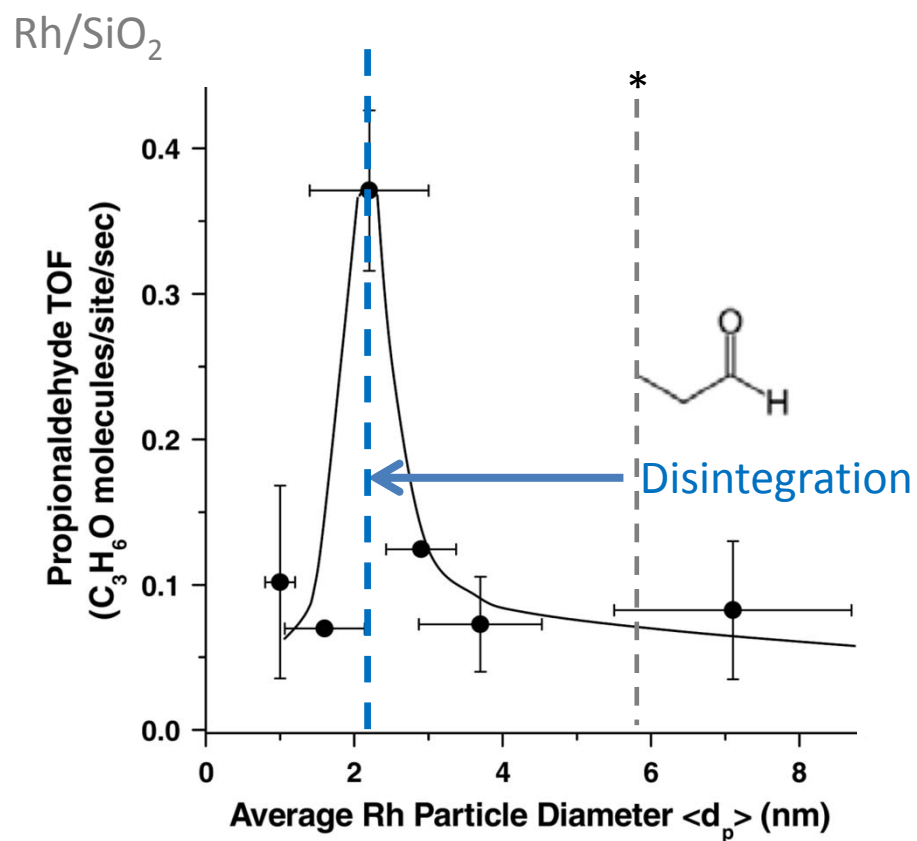


# Nanoparticle disintegration can cause catalyst deactivation

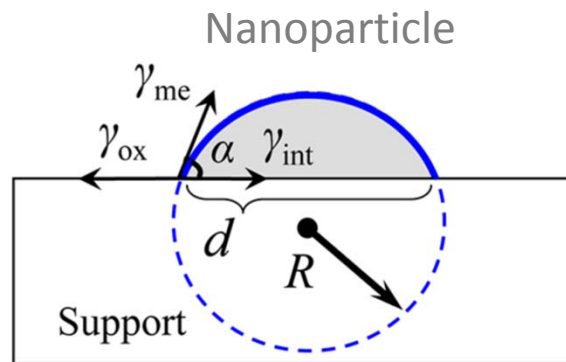


McClure, S. M.; Lundwall, M. J.; Goodman, D. W. *Proc. Natl. Acad. Sci.* 2011, 108, 931

Or, Nanoparticle disintegration  
can *redisperse agglomerated particles*



# Energetics of supported nanoparticles

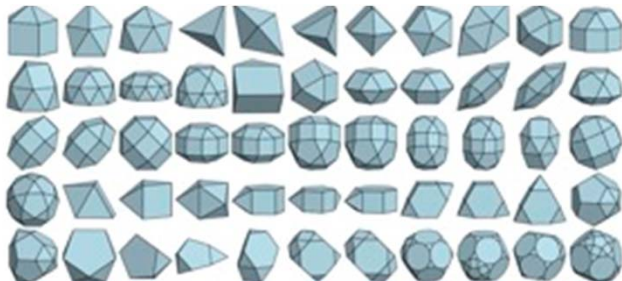


Average energy of particle per atom

$$\Delta E_{NP} = \frac{3\Omega\gamma_{me}}{R}$$

What about the effect of reactants?

Metal nanoparticles have different exposed facets



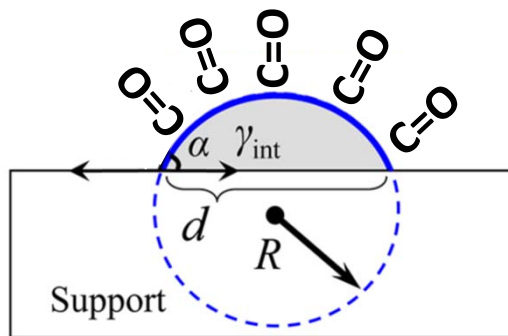
$$\gamma_{me} = \sum_i f_i \times \gamma_i$$

Surface energy of metal particle

Area ratio of facet i

Surface energy of facet i

# Reactant adsorption lowers particle surface energy



In presence of gases

Average energy of particle per atom

$$\Delta \bar{E}_{\text{NP}} = \frac{3\Omega \bar{\gamma}_{\text{me}}}{R}$$

$$\bar{\gamma}_{\text{me}} = \sum_i f_i [\gamma_i + \Delta \gamma_i (T, P)]$$

Change in surface energy  
due to reactant adsorption

## Disintegration can be modeled by the Gibbs Free Energy

$$\Delta G_{\text{disintegration}} < 0$$



$$\Delta G_{\text{disintegration}}(R, T, p) = G_{\text{adatom-complex}} - G_{\text{reactant}} - G_{\text{nanoparticle}}$$

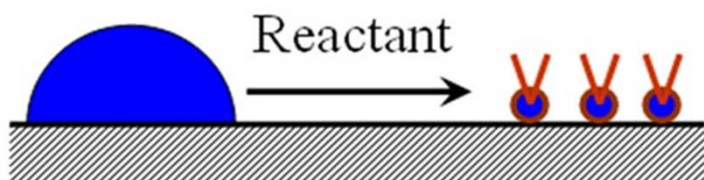


Free energy of disintegration  
via adatom complex formation



# Disintegration can be modeled by the Gibbs Free Energy

$$\Delta G_{\text{disintegration}} < 0$$



$$\Delta G_{\text{disintegration}}(R, T, p) = E_f - \frac{3\Omega\bar{\gamma}_{\text{me}}}{R} - n \left[ \mu_x^0(T, p_0) + k_B T \ln \frac{p_x}{p_0} \right] - TS$$

Standard gas phase chemical potential

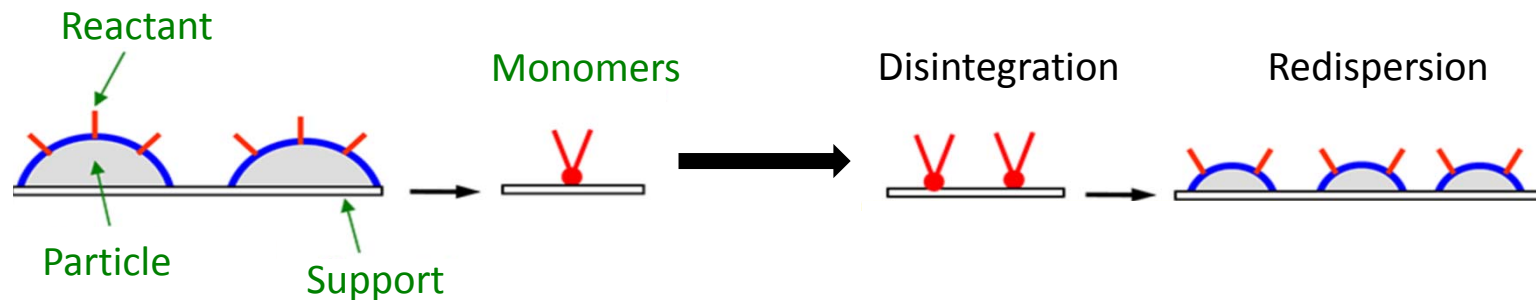
Configurational entropy of complexes

Formation energy of adatom complex

Nanoparticle energy

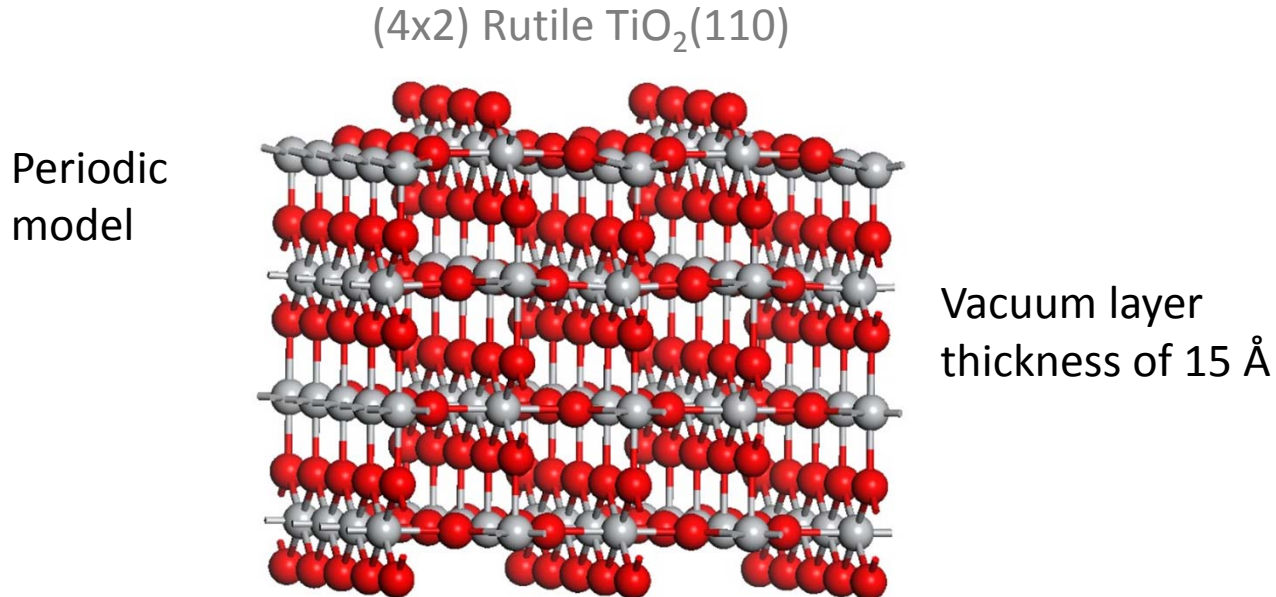
# Towards controlling nanoparticle disintegration

- Between supported Rh, Pd and Pt catalysts, which one is more susceptible to the disintegration?
- Among NO and CO, which one is more efficient for catalyst redispersion?
- How sensitive do these results depend on the particle size, temperature and pressure?



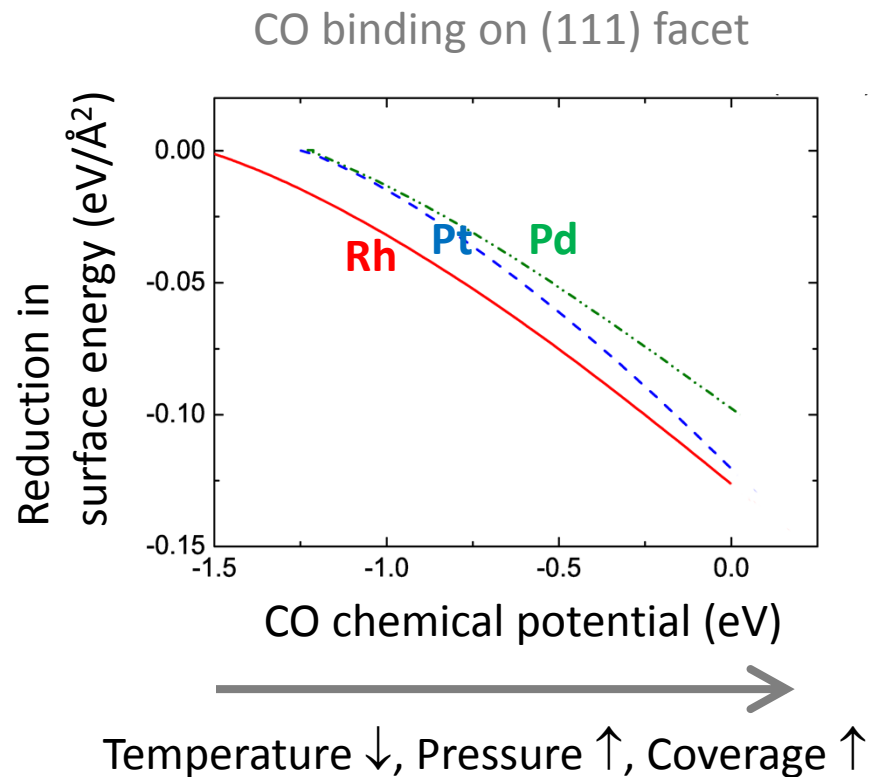
# Density Functional Theory modeling using VASP

- Projector Augmented Wave method
- RPBE Functional
- Plane wave kinetic energy cutoff = 400 eV
- Forces converged to 0.03 eV/Å



# Modeling reduction in surface energy due to reactant adsorption

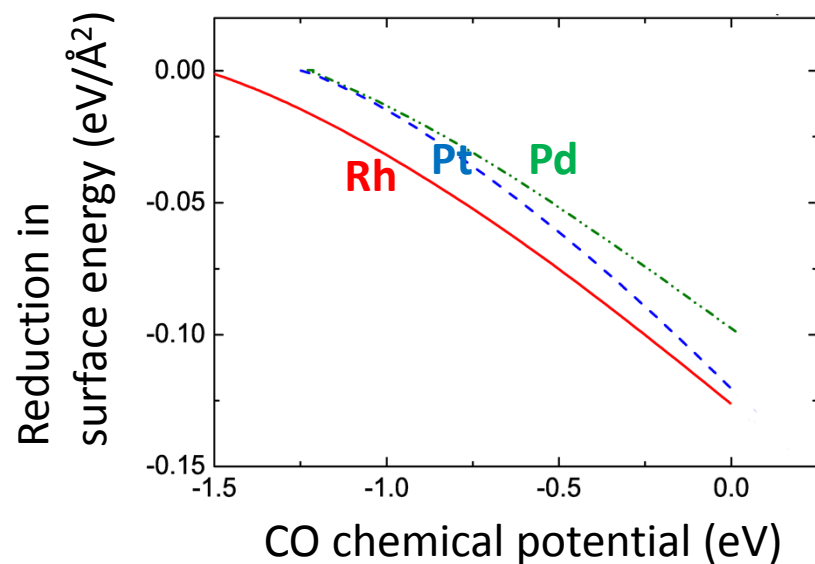
$$\bar{\gamma}_{me}(T, P) = \sum_i f_i [\gamma_i + \Delta\gamma_i(T, P)] \approx \gamma_{me}^{111} + \Delta\gamma_{me}^{111}(T, P)$$



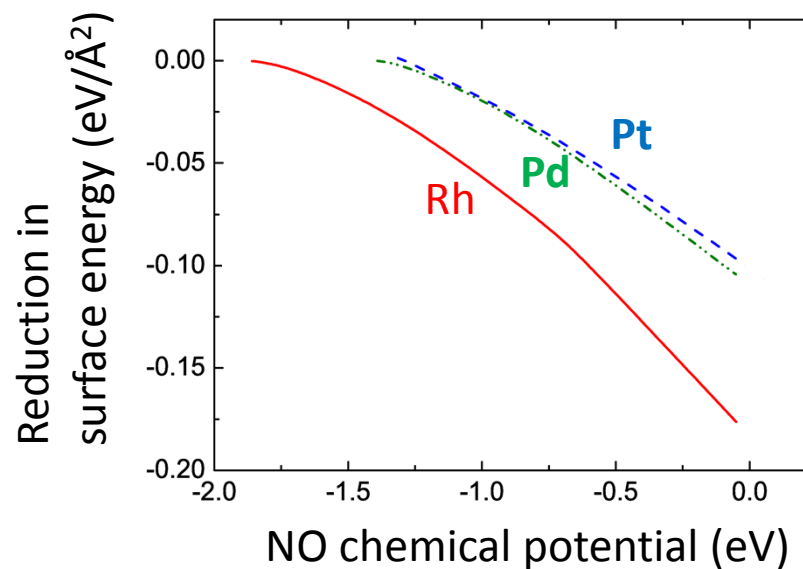
# CO and NO bind strongest to Rh metal compared to Pd and Pt metals

$$\bar{\gamma}_{me}(T, P) = \sum_i f_i [\gamma_i + \Delta\gamma_i(T, P)] \approx \gamma_{me}^{111} + \Delta\gamma_{me}^{111}(T, P)$$

CO binding on (111) facet



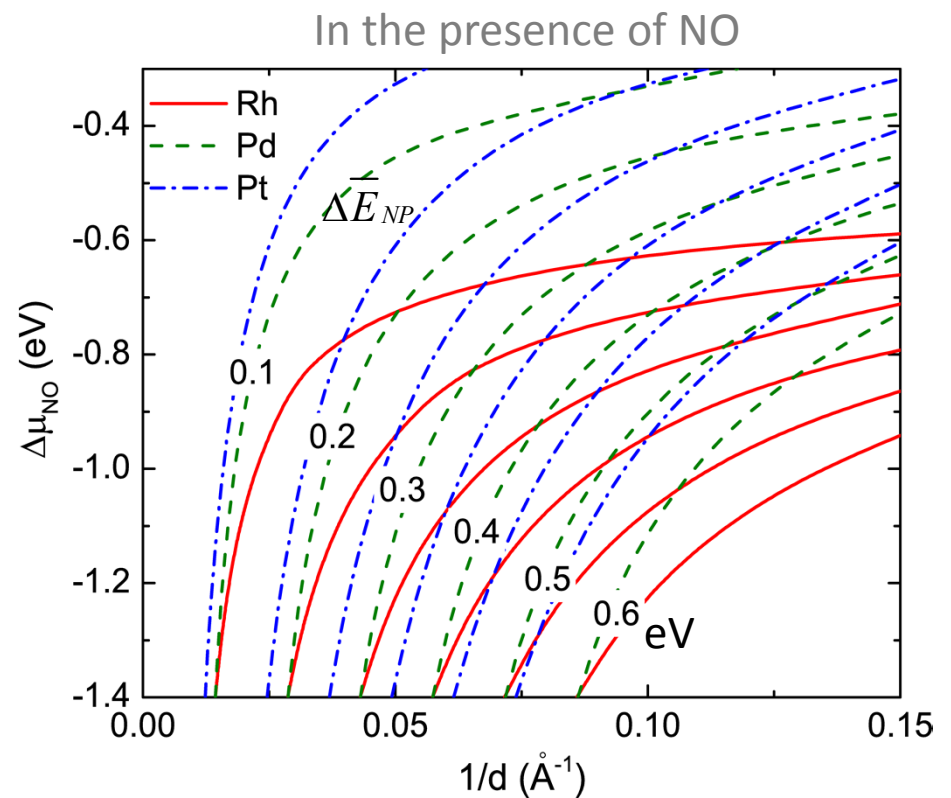
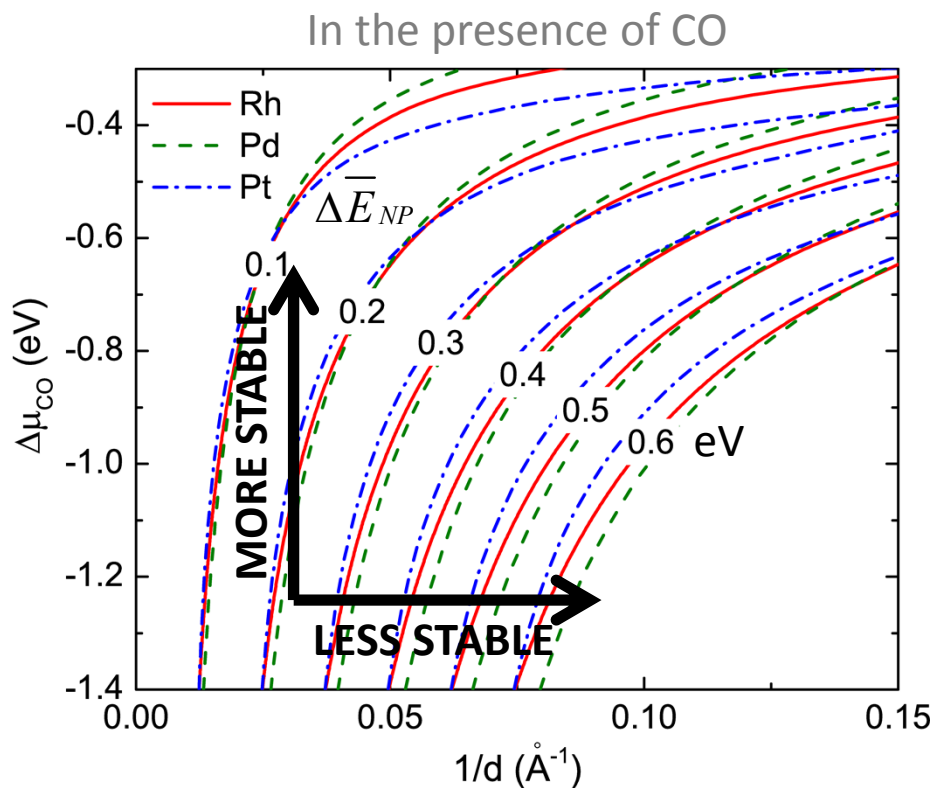
NO binding on (111) facet



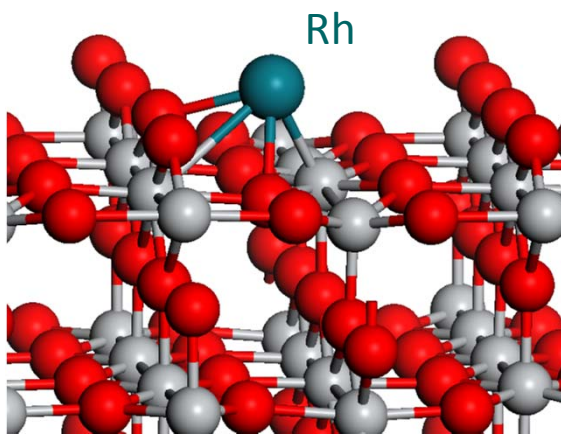
Temperature ↓, Pressure ↑, Coverage ↑

# Effects of chemical potential and particle size on particle energy

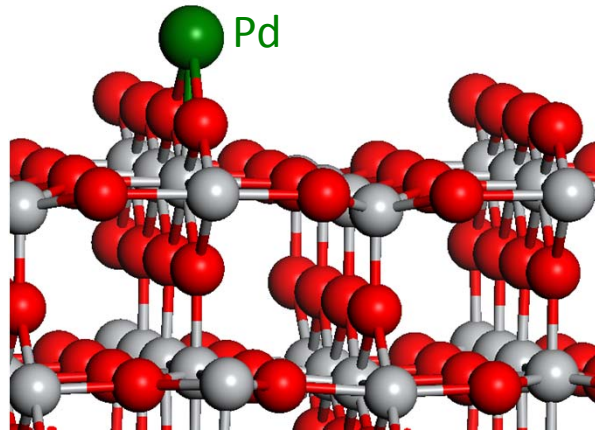
$$\Delta \bar{E}_{NP} = \frac{3\Omega\bar{\gamma}_{(111)}}{R} \quad \text{contours}$$



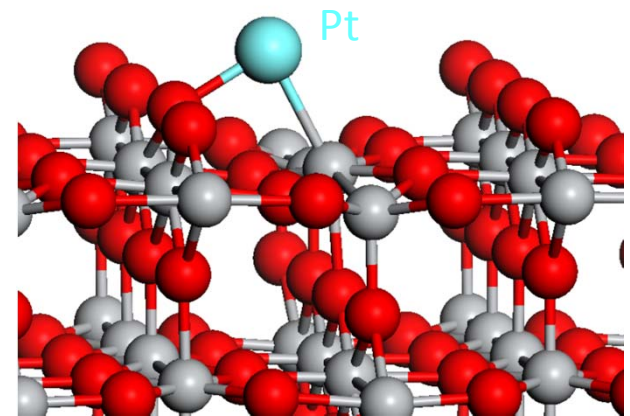
## Adatom formation energies are large and endothermic



Formation energy = 2.88 eV



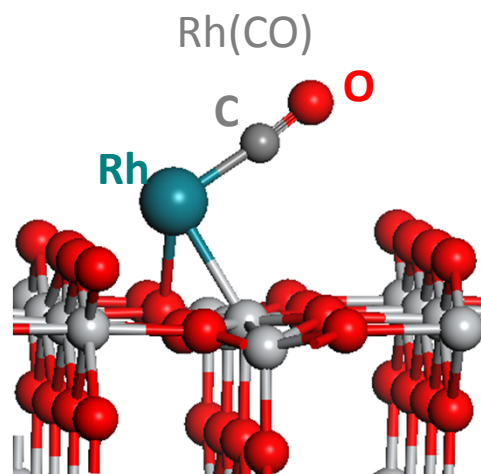
2.01 eV



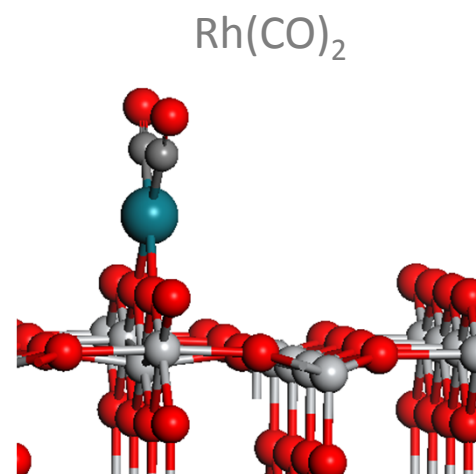
3.12 eV

$$\text{Formation energy} = E_{\text{adatom/support}} - E_{\text{support}} - E_{\text{bulk}}$$

# Reactant binding stabilizes formation of adatoms



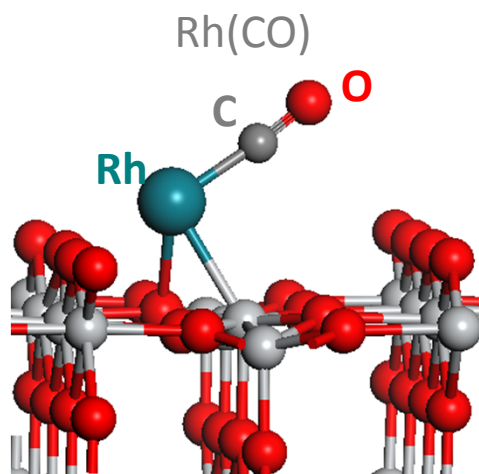
Formation energy = 0.75 eV



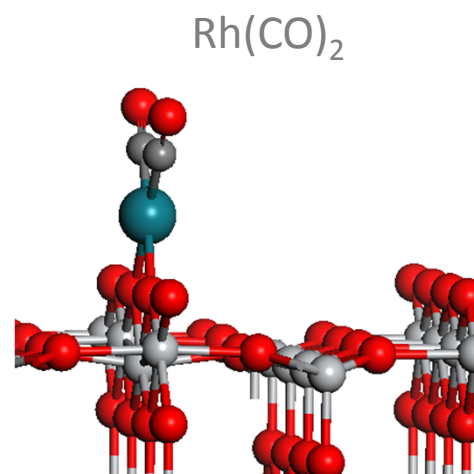
-1.35 eV



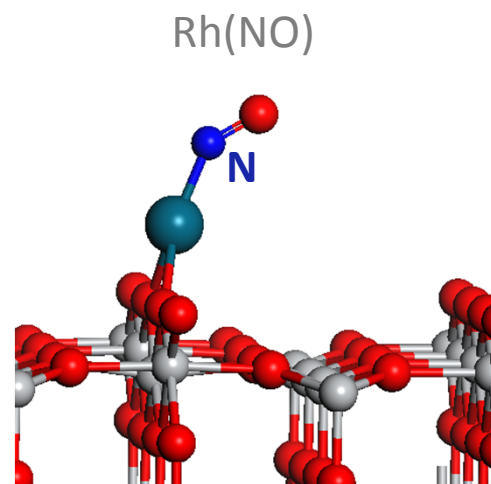
**$\text{Rh}(\text{CO})_2$  and  $\text{Rh}(\text{NO})_2$  have more favorable formation energies than  $\text{Rh}(\text{CO})$  and  $\text{Rh}(\text{NO})$**



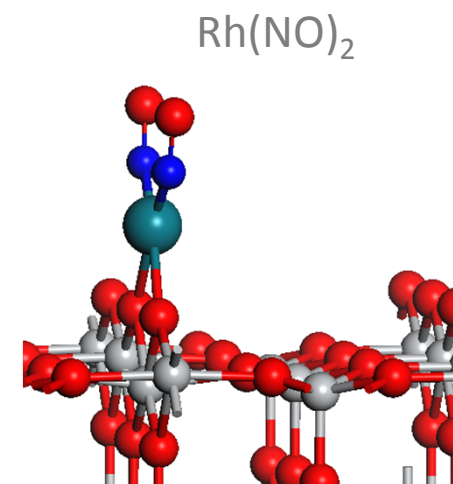
Formation energy = 0.75 eV



-1.35 eV



-0.02 eV



-1.58 eV

## The interaction of CO and NO with Rh adatom is greater than for Pd and Pt adatoms

Formation energy	Rh	Pd	Pt
Metal(CO)	0.75	0.26	0.09
Metal(CO) <sub>2</sub>	-1.35	-0.54	-0.69
Metal(NO)	-0.02	-0.05	-0.10
Metal(NO) <sub>2</sub>	-1.58	-0.67	-0.68

Energies are in eV.

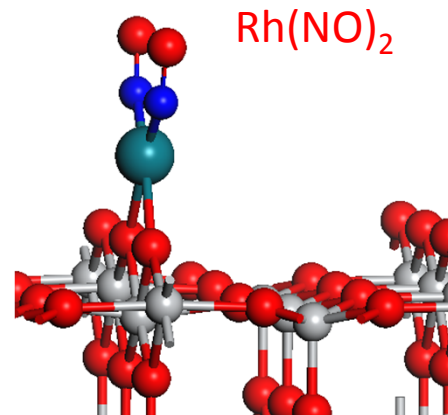
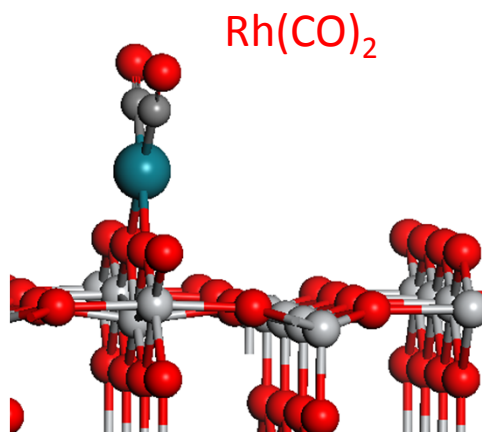
Exothermic formation energy promotes particle disintegration

## The interaction of CO and NO with Rh adatom is greater than for Pd and Pt adatoms

Formation energy	Rh	Pd	Pt
Metal(CO)	0.75	0.26	0.09
Metal(CO) <sub>2</sub>	-1.35	-0.54	-0.69
Metal(NO)	-0.02	-0.05	-0.10
Metal(NO) <sub>2</sub>	-1.58	-0.67	-0.68

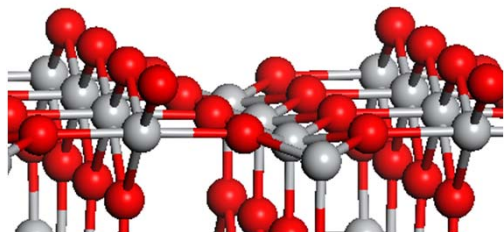
Exothermic formation energy promotes particle disintegration

Energies are in eV.

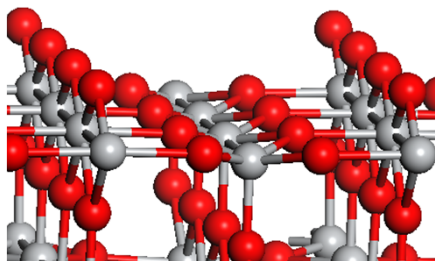
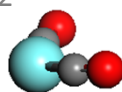


## Gas phase metal complexes not considered in disintegration analysis

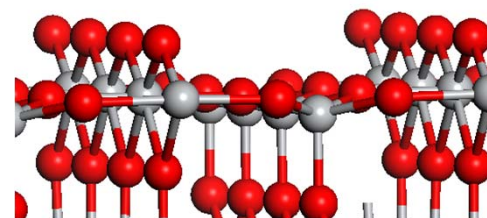
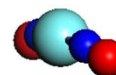
$\text{Pd}(\text{CO})_2$



$\text{Pt}(\text{CO})_2$

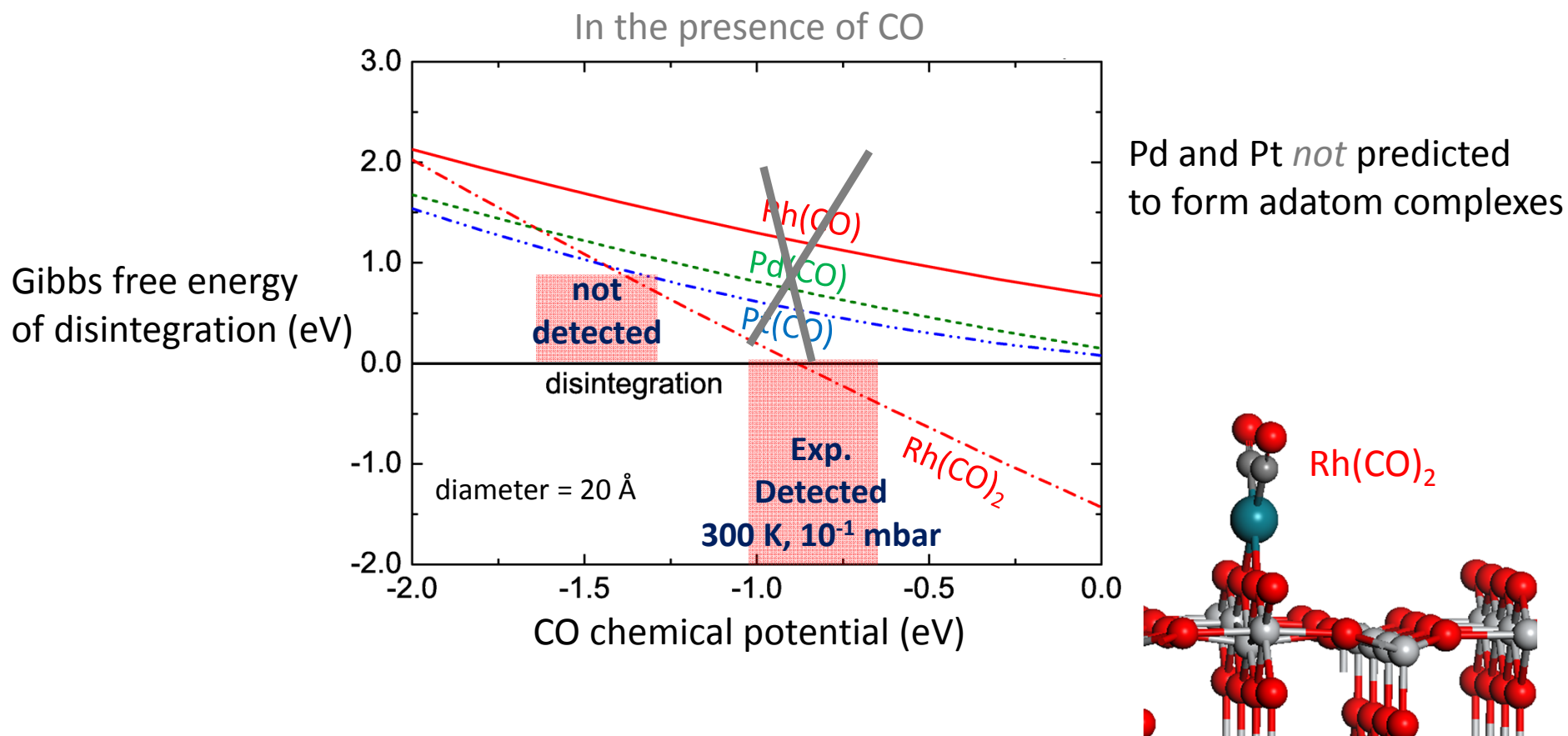


$\text{Pt}(\text{NO})_2$

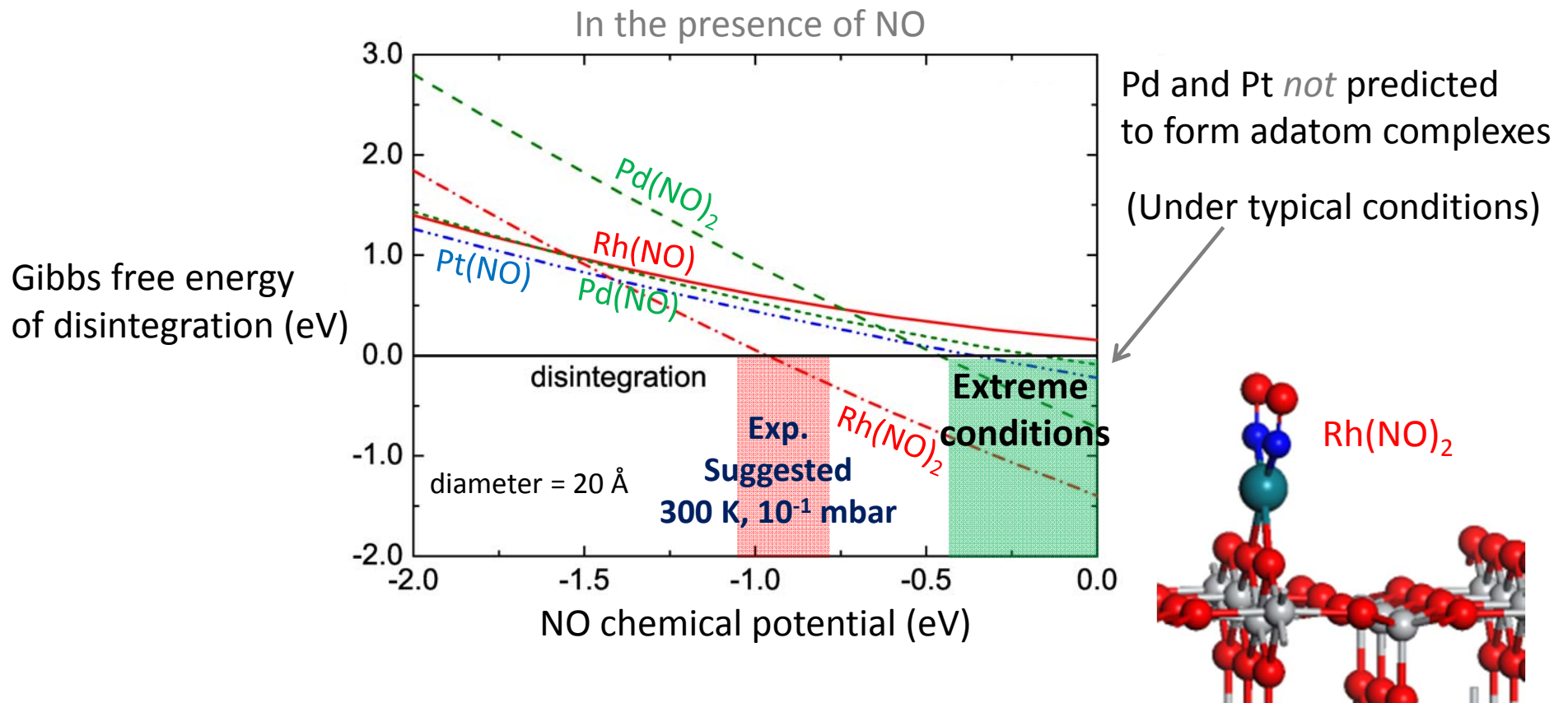


- Higher order complexes also preferred gas phase
- These complexes not observed in experiments bound to support
- May play a role in gas phase ripening

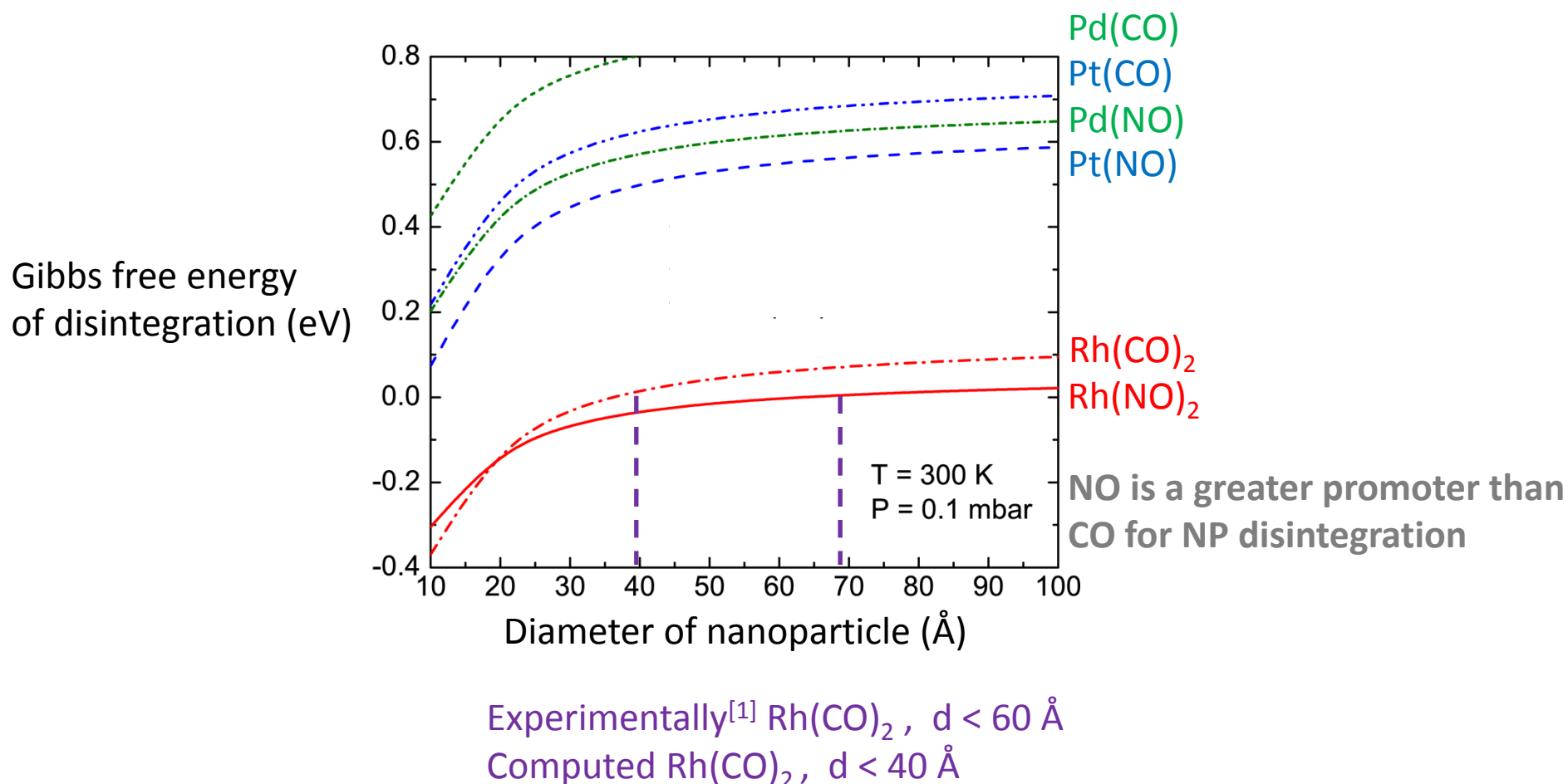
## In agreement with experiment, $\text{Rh}(\text{CO})_2$ predicted to form but not $\text{Rh}(\text{CO})$



Also in agreement with experiment,  
 $\text{Rh}(\text{NO})_2$  predicted to form but not  $\text{Rh}(\text{NO})$



# Rh/TiO<sub>2</sub>(110) more responsive to CO and NO-induced disintegration than Pd or Pt



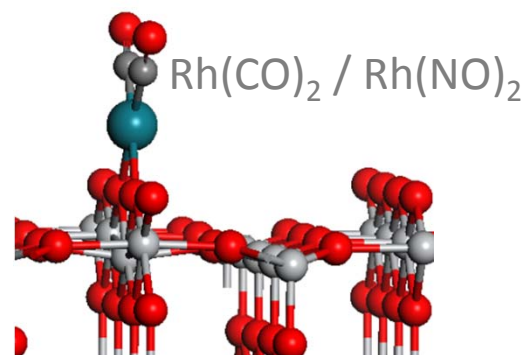
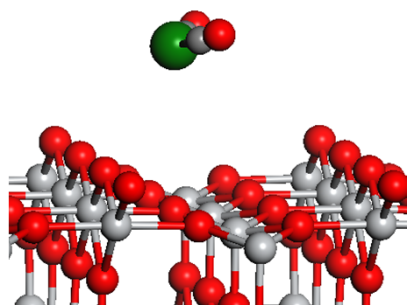
[1] Berkó, A.; Szökő, J.; Solymosi, F. *Surf. Sci.* 2004, 566, 337

# Disintegration can be predicted using *ab initio* thermodynamics

- Rh/TiO<sub>2</sub>(110) most susceptible to CO and NO-induced disintegration
- NO is a more efficient reactant for particle disintegration than CO

## Future work

Include gas phase disintegration, adatom translation, and particle size-dependent binding energies!



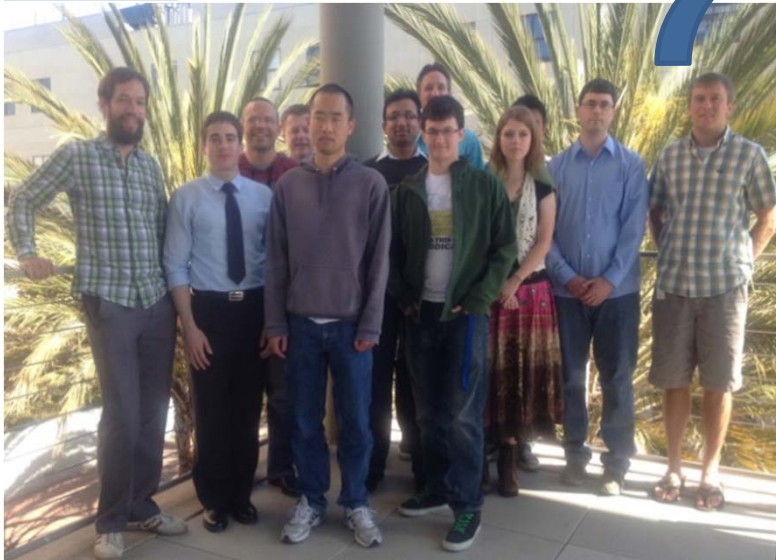


# Acknowledgements

Evan D. Sanderson  
Dr. Runhai Ouyang  
Prof. Wei-Xue Li  
Prof. Baron Peters



The Peters group



The Wei-Xue Li group

