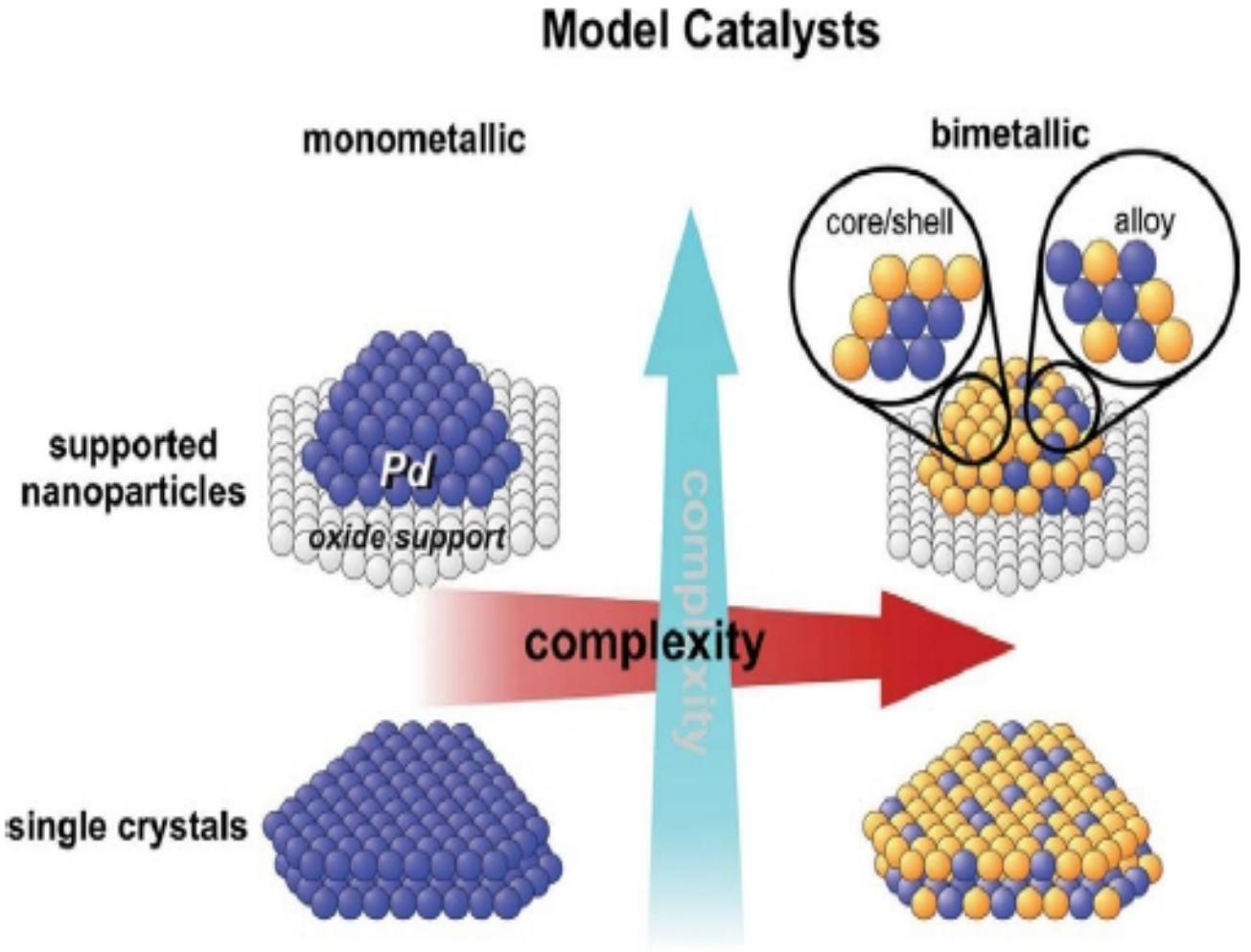
# *DFT studies on catalysis and surface science*

The aim is to:

- explain and understand
- predict
- bridge the material and pressure gaps

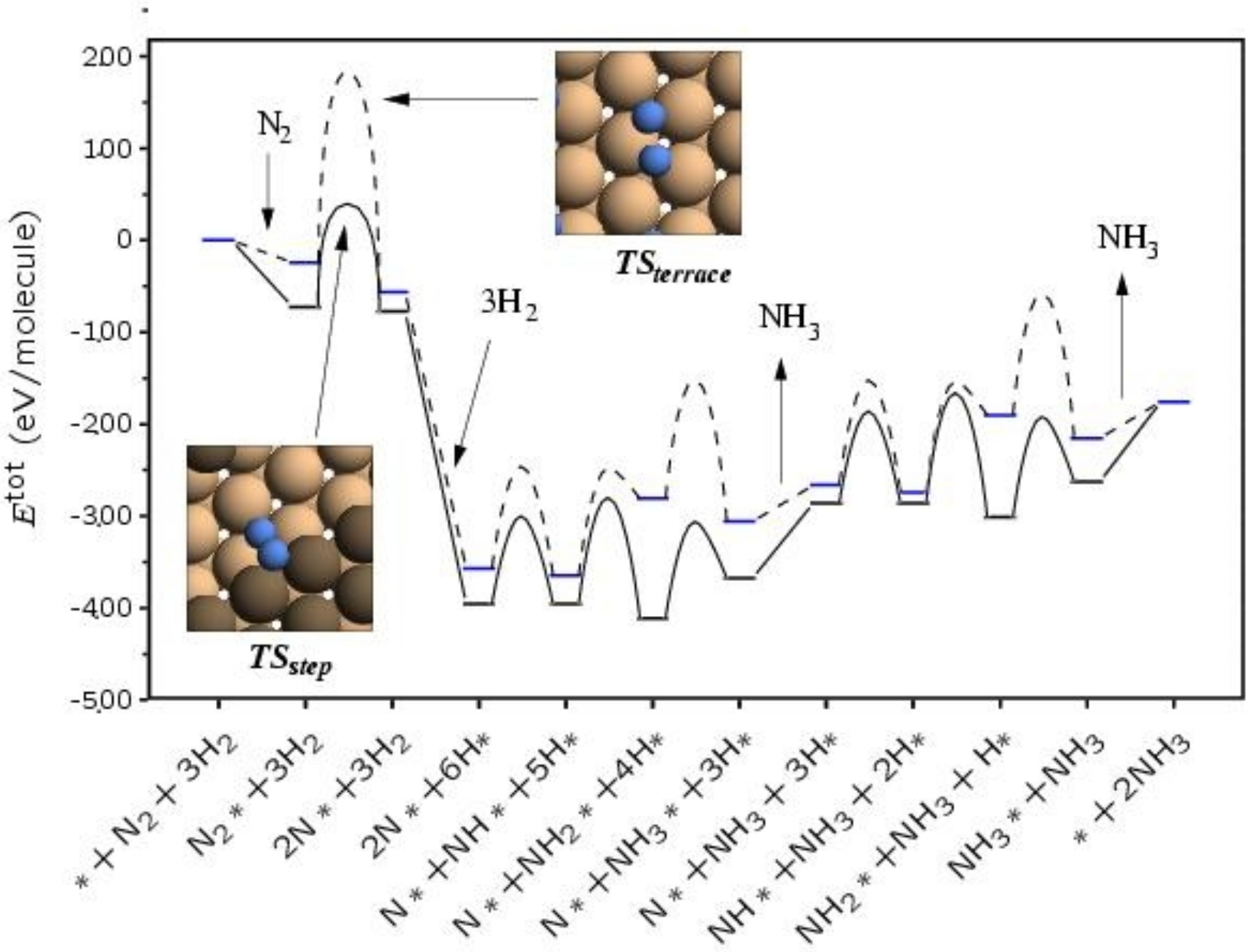
# Complexity of models




G. Rupprechter and C. Weilach Nanotoday, 2, 20 (2007)

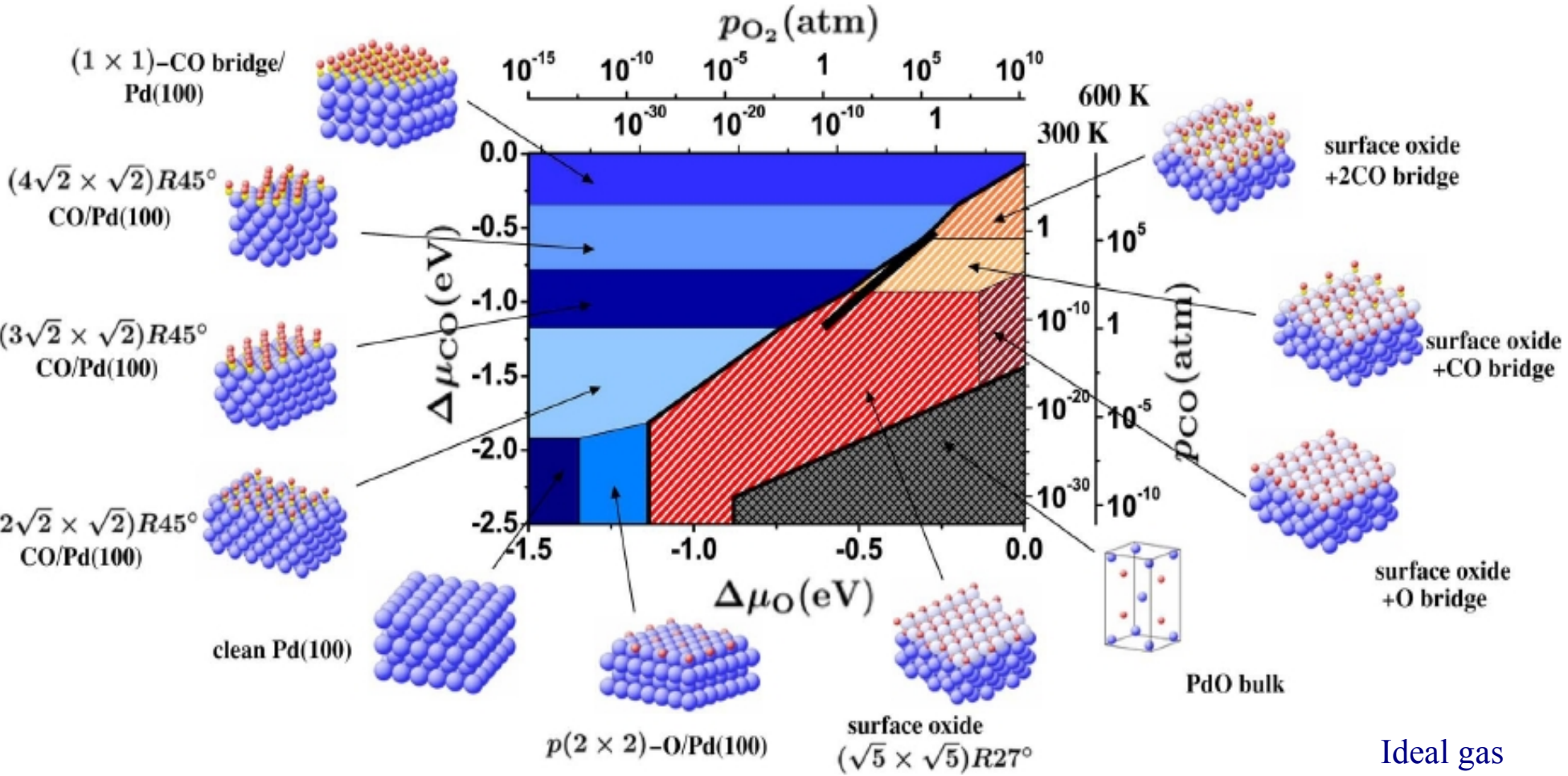
# Ammonia synthesis over Ru

Logadottir, Nørskov, J. Catal. **220**, 273-279 (2003)



# Bridging the gap: Surface "phase diagram" of the Pd(100) in constrained thermodynamic equilibrium with an $O_2$ and CO gas phase

J. Rogal et al. PRB 75, 205433 (2007)

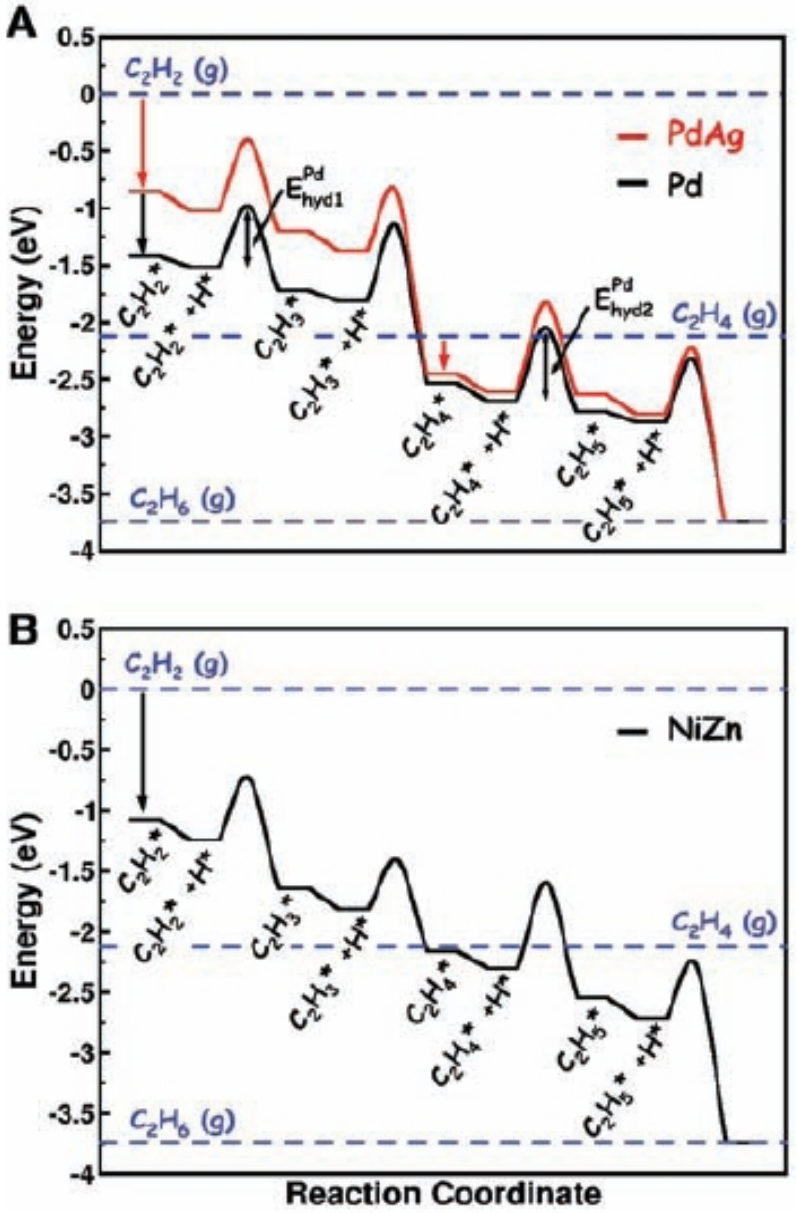


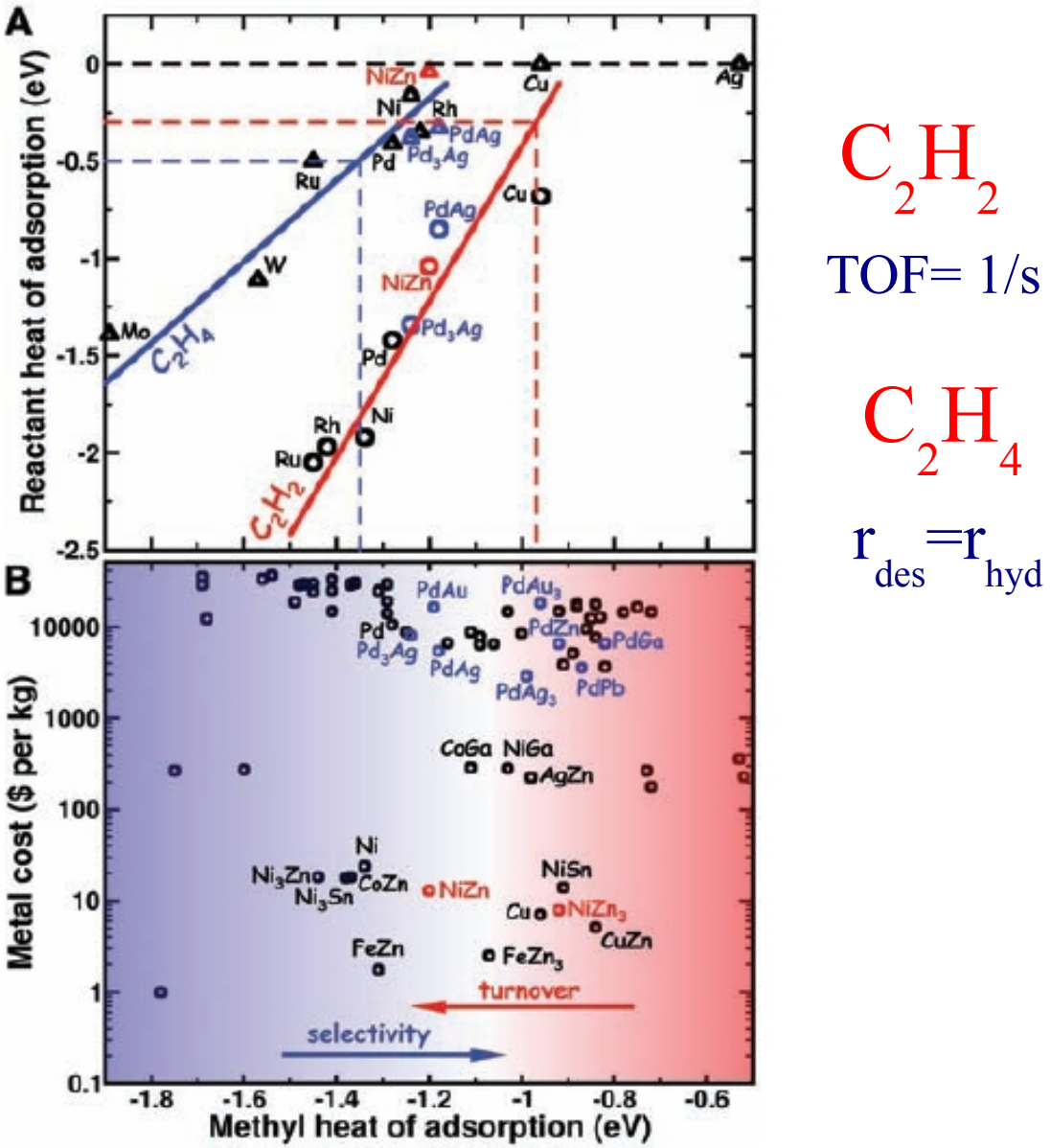

Ideal gas

$$\Delta G^{ads}(\Delta\mu_O, \Delta\mu_{CO}) = \gamma_{Pd(100)} - \gamma_{O,CO@Pd(100)}$$

$$= \frac{1}{A}\left\{G^{surf}_{O,CO@Pd(100)} - G^{surf}_{Pd(100)} - \Delta N_{Pd}\mu^{bulk}_{Pd} - N_O\mu_o - N_{CO}\mu_{CO}\right\}$$

# Identification of Non-precious Metal alloy Catalysts for selective hydrogenation of acetylene ($C_2H_2$)




$C_2H_2$

TOF= 1/s

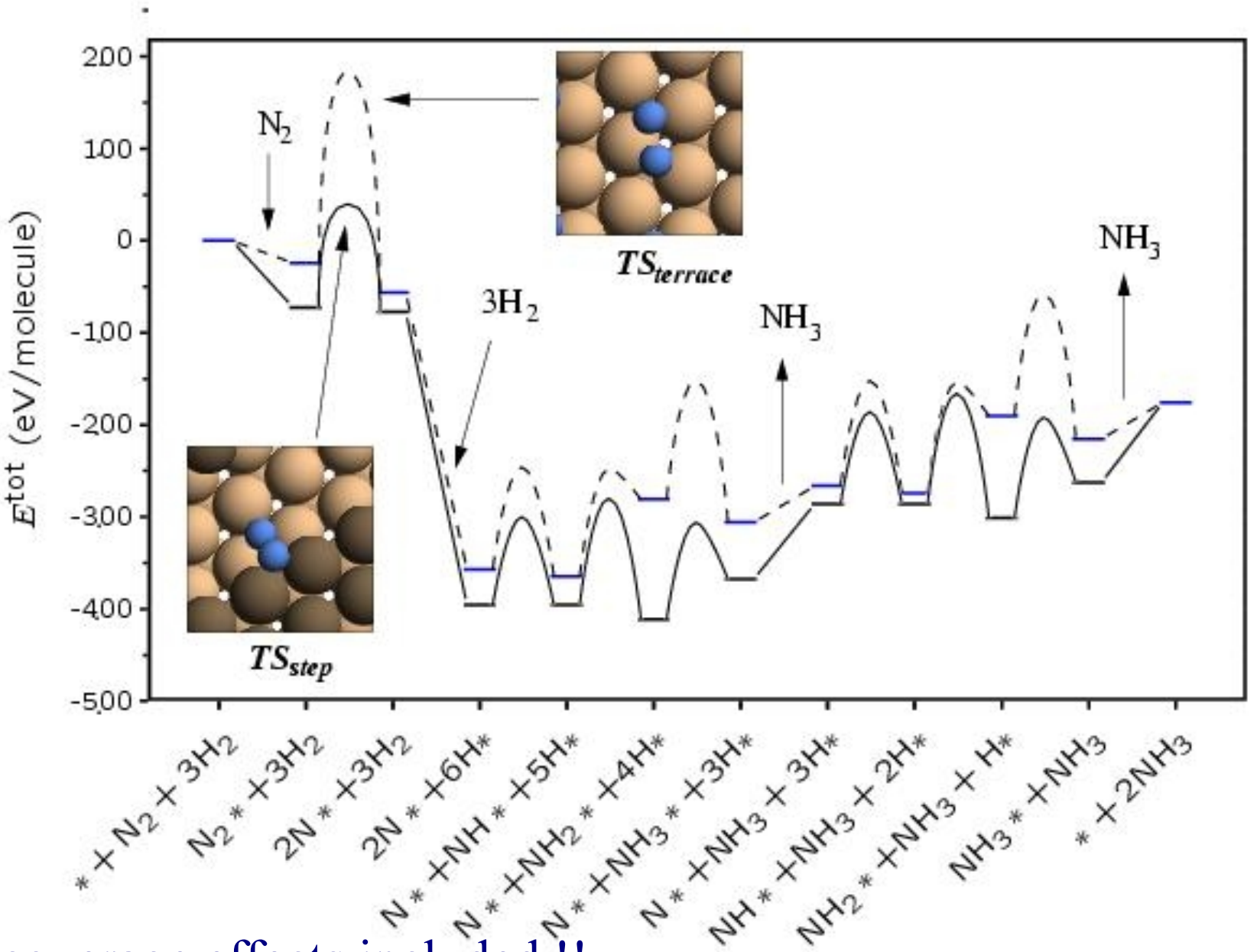
$C_2H_4$

$r_{des} = r_{hyd}$

F. Studt et al. Science 320, 1320 (2008)

# Ammonia synthesis over Ru

Logadottir, Nørskov, J. Catal. **220**, 273-279 (2003)




No coverage effects included !!

# Reaction mechanism

## Reaction mechanism

$$N_2 + 2* \rightarrow 2N*$$ ← Rate-limiting step

At equilibrium

$$\begin{cases} N* + H* \leftrightarrow NH* + * \\ NH* + H \leftrightarrow NH_2* + * \\ NH_2* + H* \leftrightarrow NH_3* + * \\ NH_3* \leftrightarrow NH_3 + * \\ H_2 + 2* \leftrightarrow 2H* \end{cases}$$

# Kinetic model

Reaction rate per site: $r_{tot}(T, p_{N_2}, p_{H_2}, p_{NH_3}) = (1-\gamma) r^f$

$$r^f = \sum_i P_i k_i p_{N_2} \qquad \gamma = \frac{p_{NH_3}^2}{K_g p_{N_2} p_{H_2}^3}$$

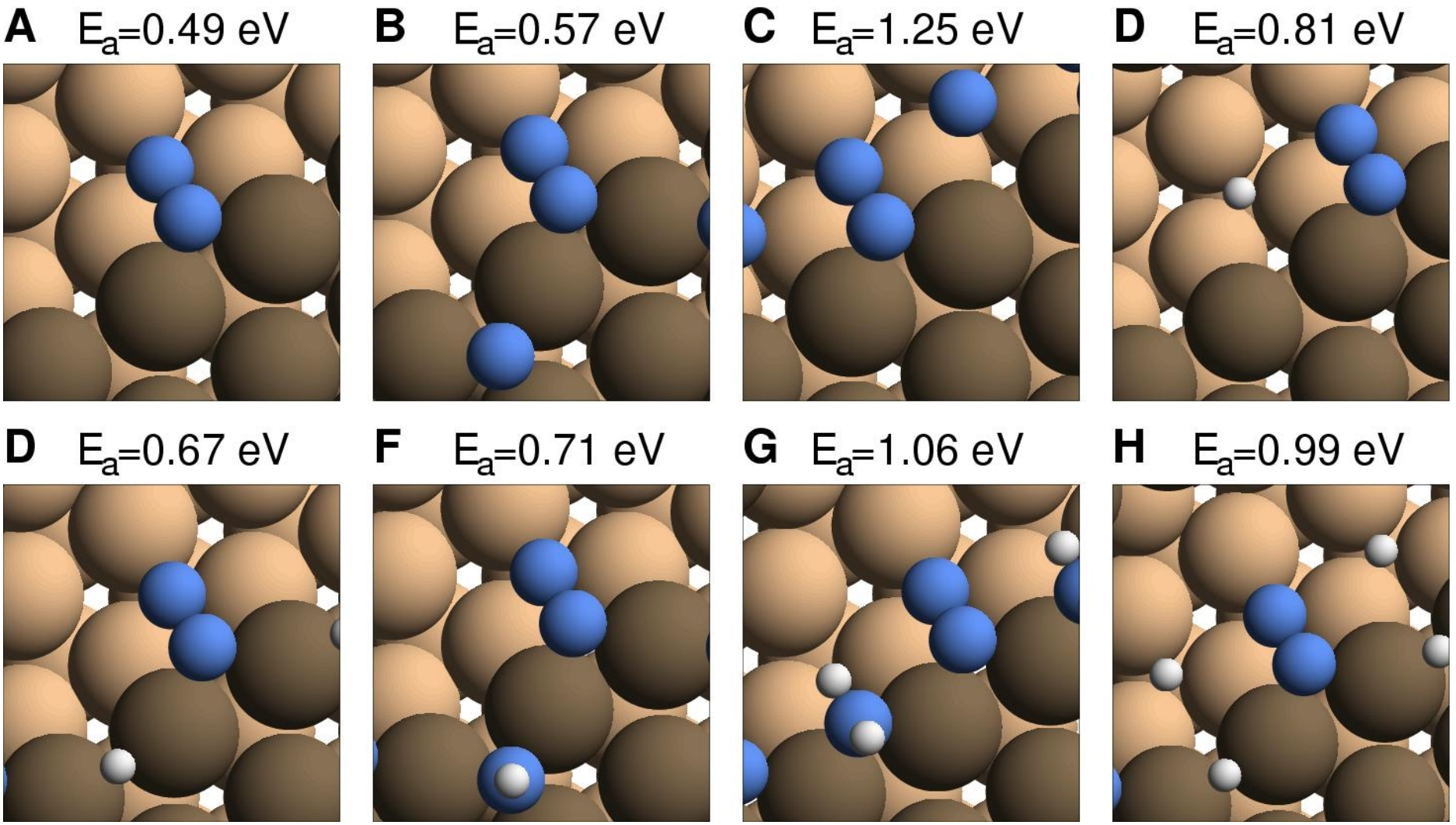
Harmonic transition state theory: $k_i = \nu \exp(-E_a / k_B T)$

$P_i$ is the probability to have a certain local environment

Total rate through the reactor:

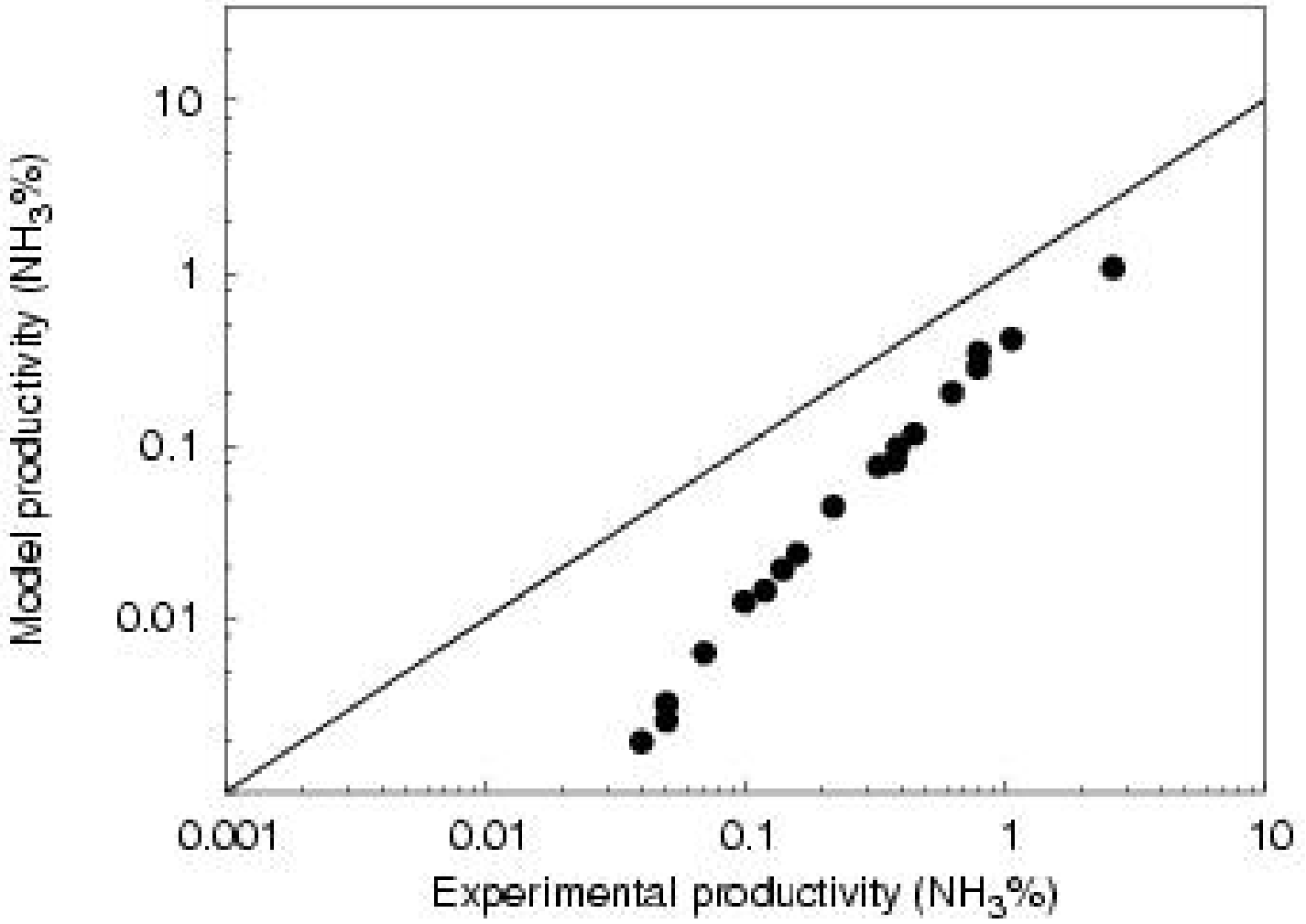
$$r_{PFR}^{total} = \sum_{j=0}^{N} r(T, p_{N2}^j, p_{H2}^j, p_{NH3}^j) \times \frac{\rho \mathrm{m}}{\mathrm{N}}$$

# Different $N_2$ transition state geometries



# *Ab initio* prediction of the rate of the real catalyst

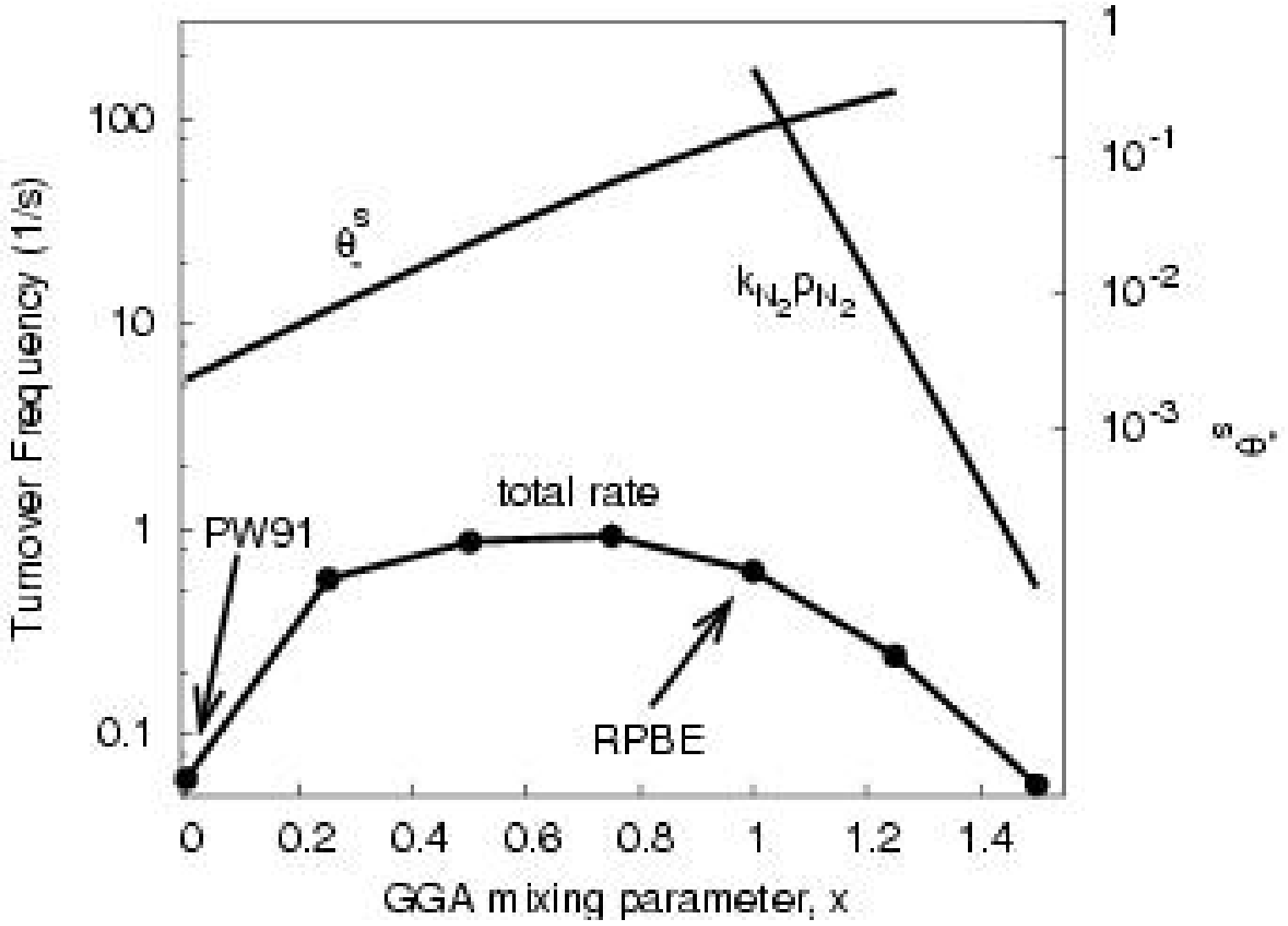
Experimental data: S Dahl & C. Christensen, Haldor Topsøe AS




Total pressure 100 bar, $H_2$:$N_2$=3:1

Honkala et al. Science **307**,555 (2005)

# Compensation effect




Honkala et al. Science **307**,555 (2005)