

Catalytic dehydrogenation of propane on Pt catalysts: the positive effect of hydrogen co-feeding

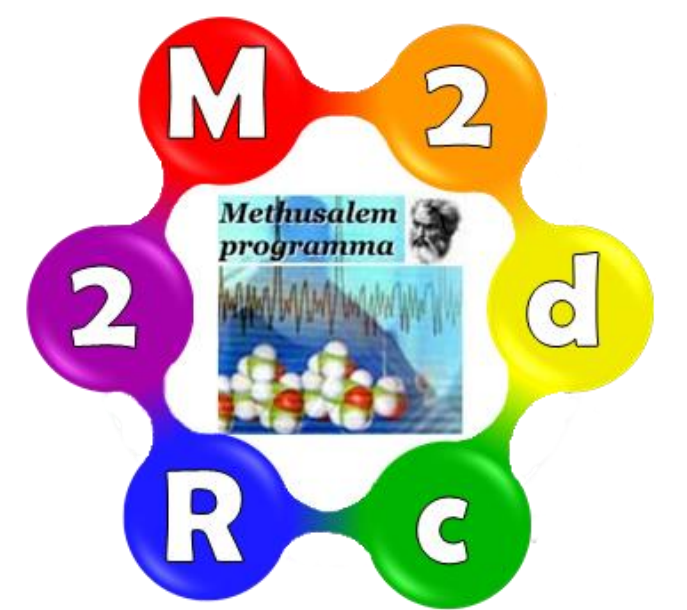
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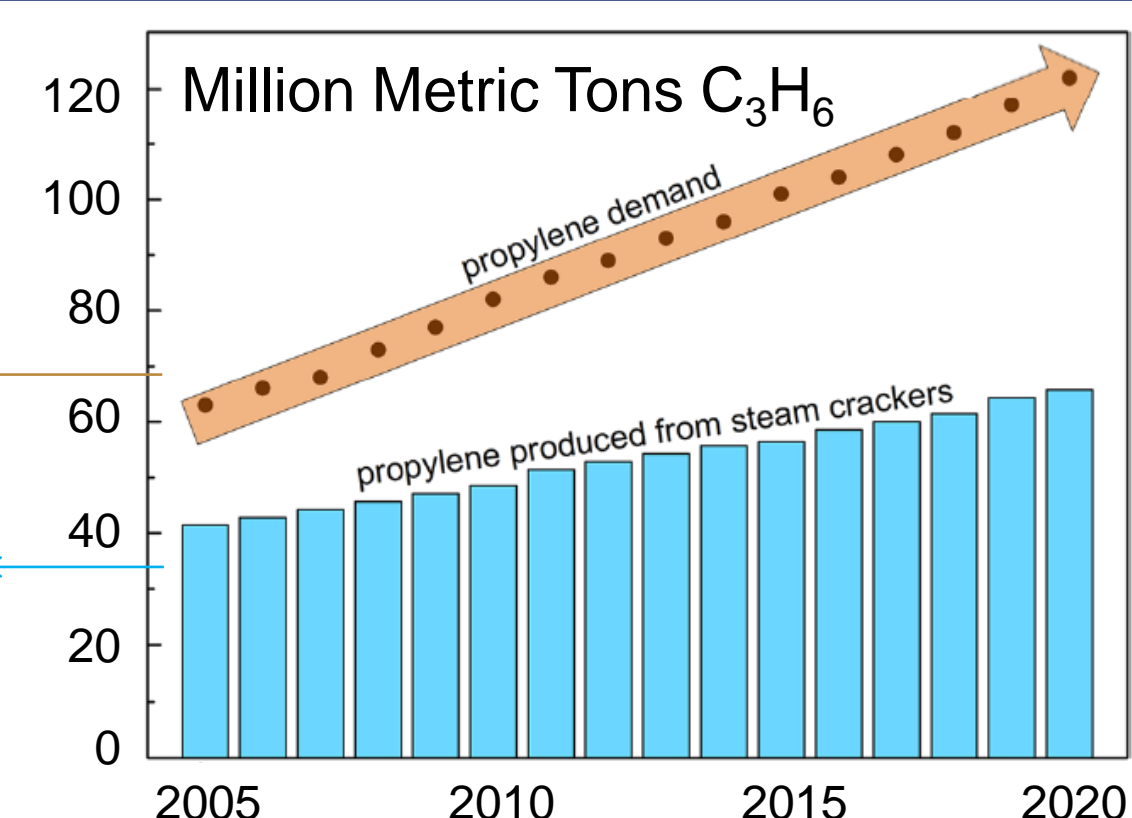


Justification

→ Propylene traditionally a co-product of naphtha steam cracking or FCC

→ Due the US shale gas boom, more ethane cracking which has a very low selectivity towards propylene

C_3H_6 demand
 C_3H_6 production from steam cracking



→ Predicted propylene capacity increase leads to on-purpose production technologies e.g. catalytic propane dehydrogenation (PDH)

→ Pt-based catalysts are intensively researched for PDH

Grant et al. Top Catal 1545-1553 (2016)

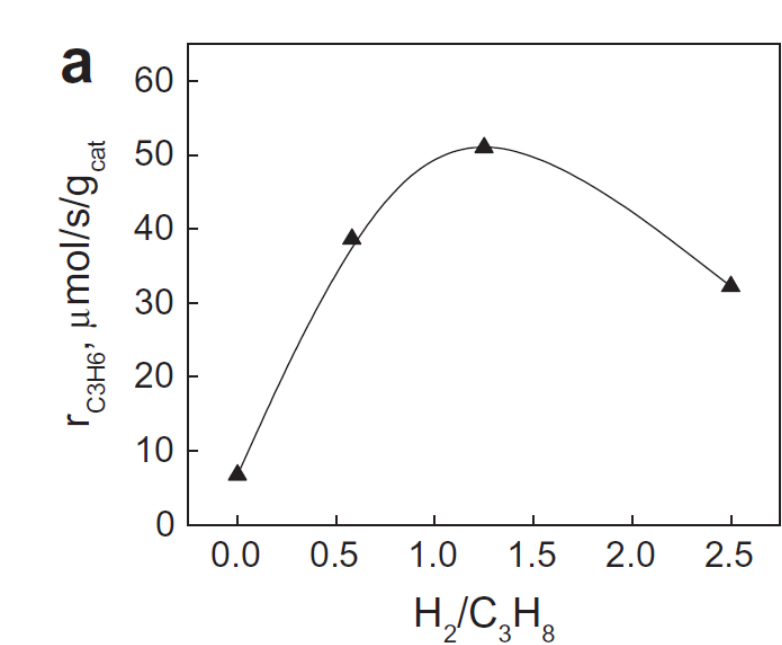
Hydrogen co-feeding

Pt catalysts

- ✓ Sufficient C_3H_6 selectivity (~80%)
- ✗ Low activity for dehydrogenation
- ✗ Fast catalyst deactivation

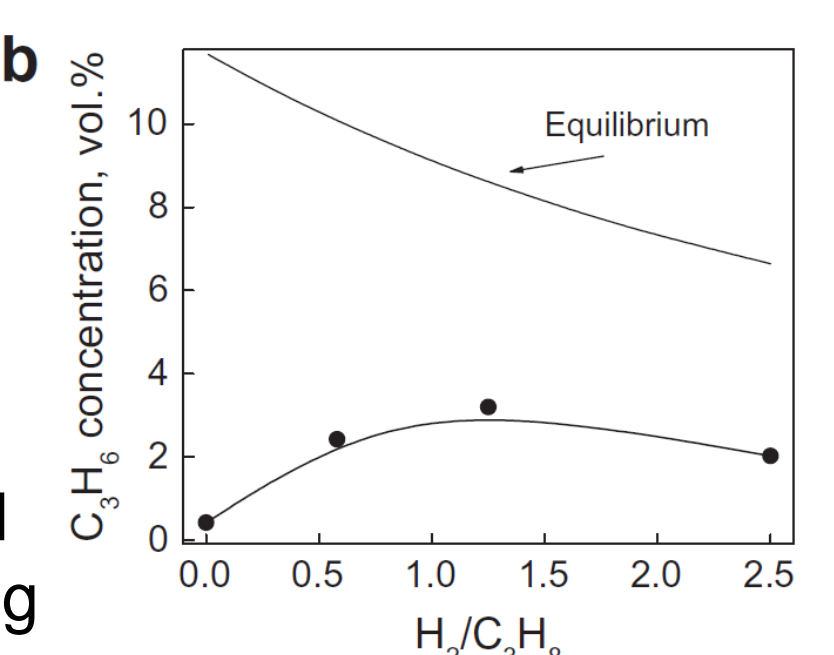
Positive effect of H_2 co-feeding on the catalyst activity

Experimental results

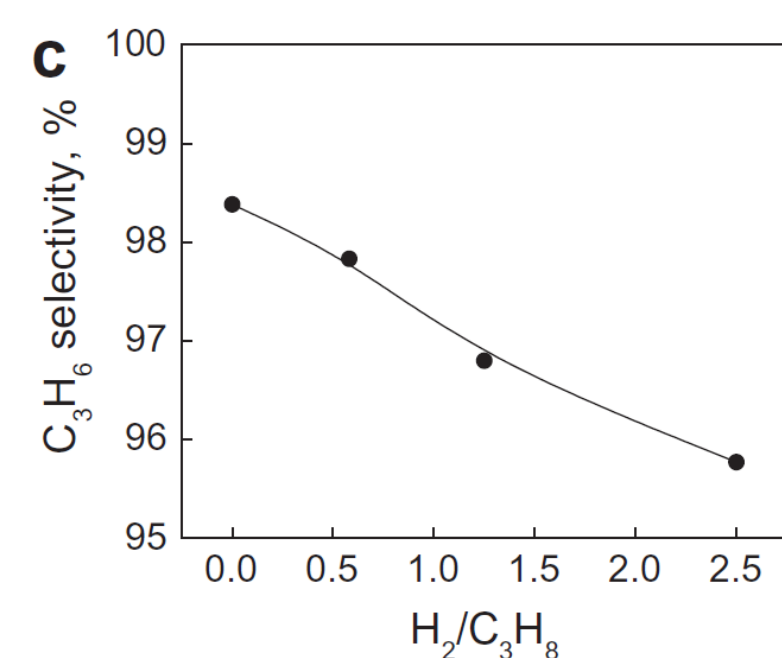


← Co-feeding of hydrogen enhances dehydrogenation activity

← Closer to equilibrium at high H_2/C_3H_8 ratios



← Selectivity is only weakly influenced by hydrogen co-feeding



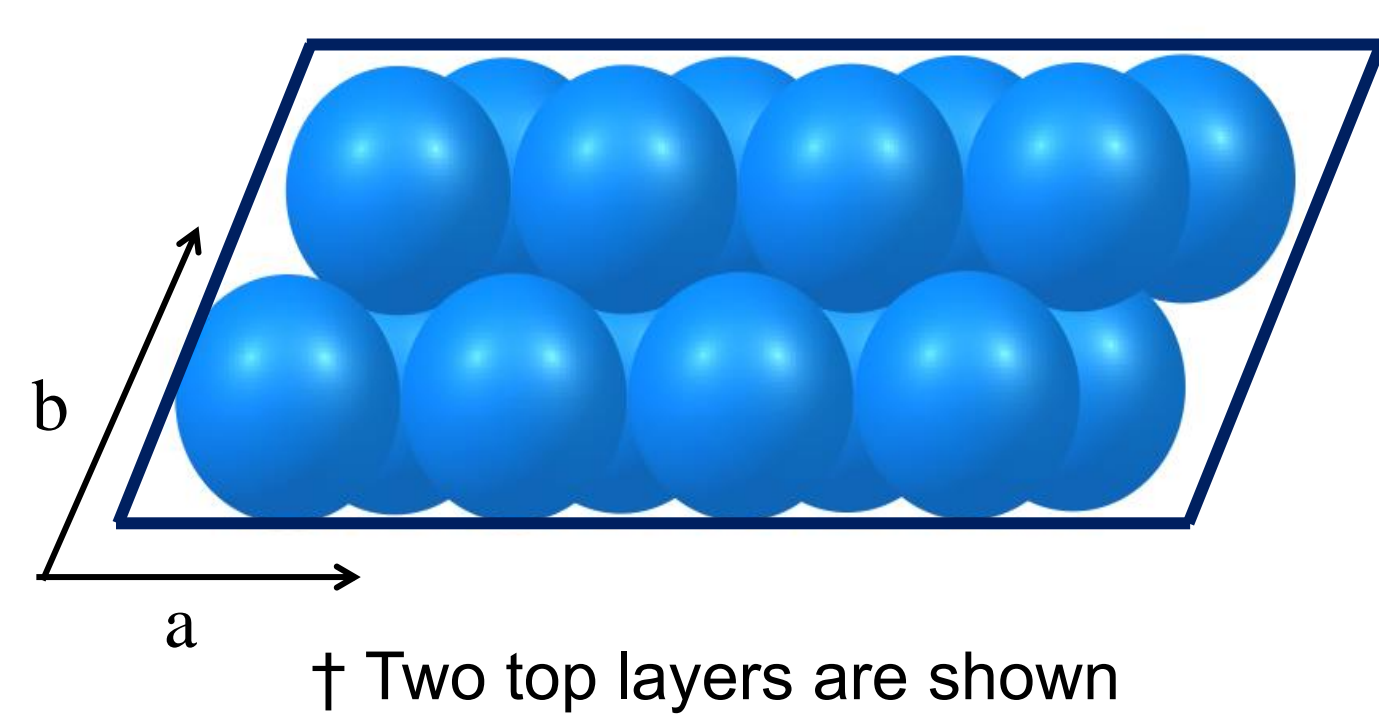
GOAL: Explain the 'positive hydrogen effect' using DFT kinetics for an extended reaction network

Siddiqi et al. J. Catal 200-206 (2010), Sun et al. J. Catal 192-199 (2010)

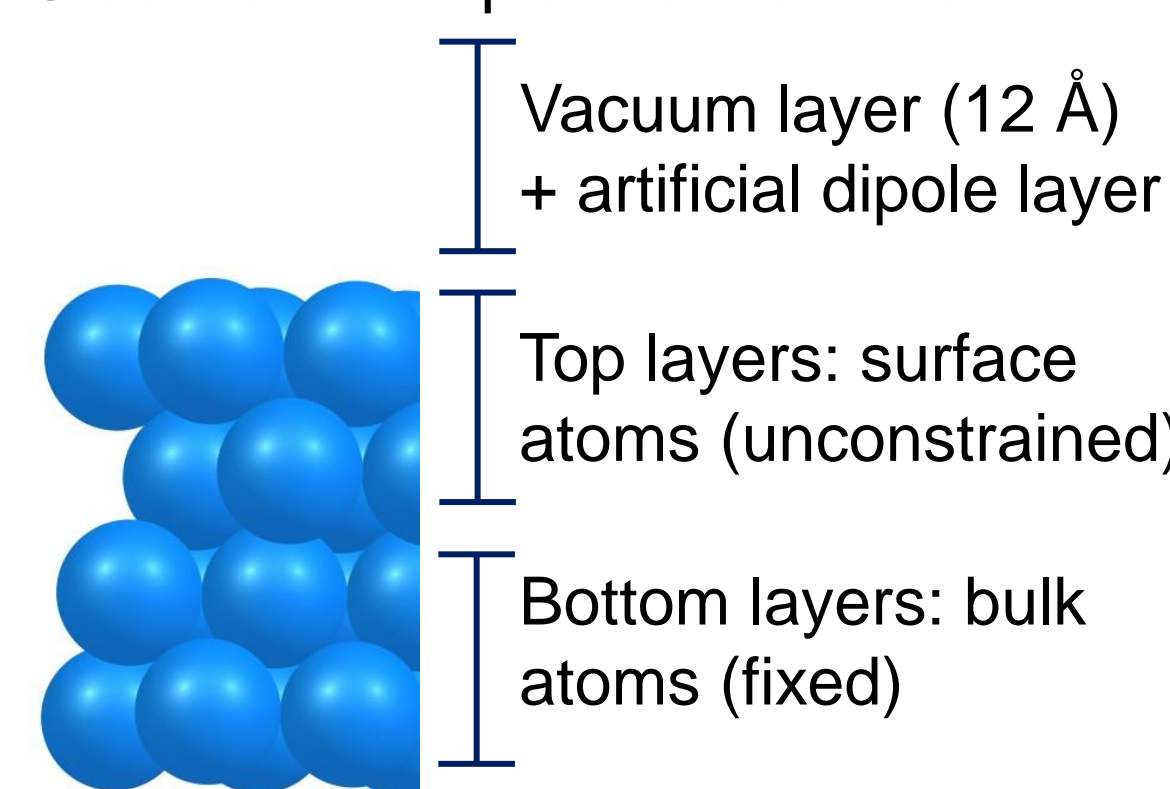
Computational methodology

Catalyst model

Top view 4×2 Pt(111) unit cell †



Side view 4×2 platinum unit cell

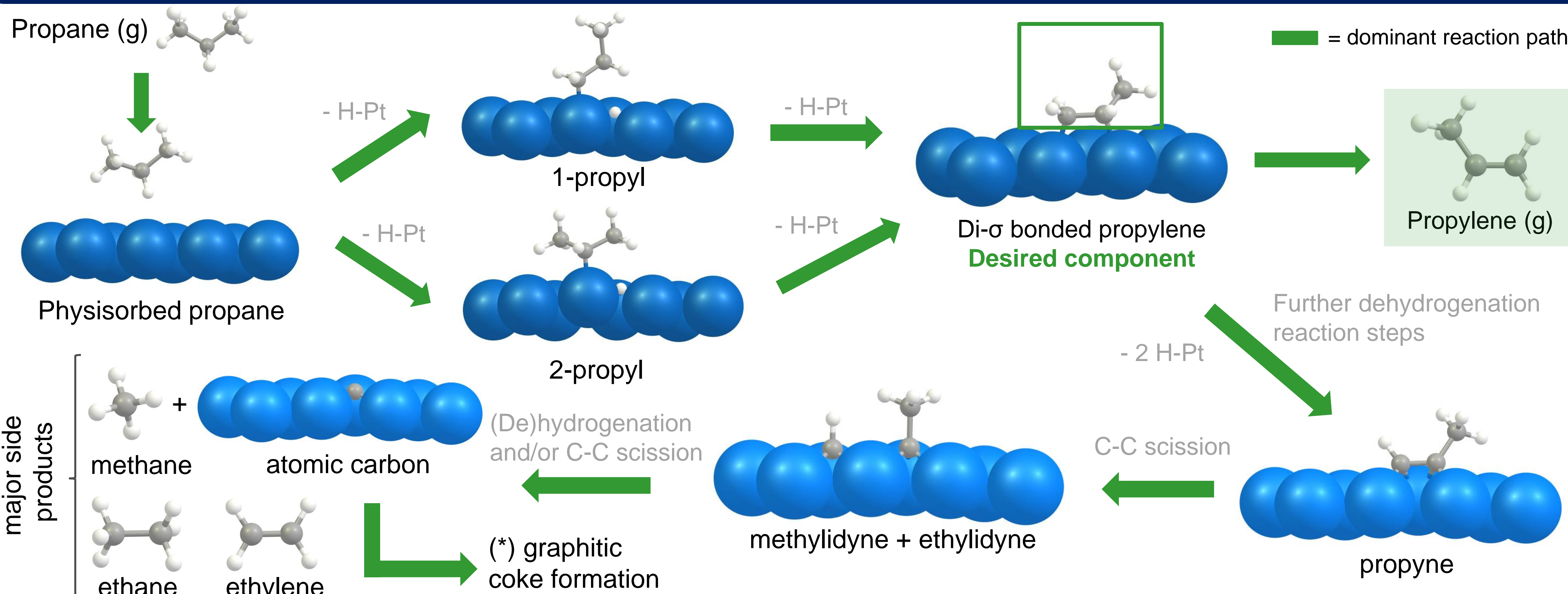


Calculation techniques

- Density functional theory (DFT) calculations using VASP (periodic slab)
- optPBE vdW-DF functional: account for long range interactions
- Determination of transition states: Nudged Elastic Band (NEB) method combined with dimer method



Reaction path analysis on Pt(111)



Results on Pt(111)

- Reaction path towards propylene occurs via both 1-propyl and 2-propyl species ↔ In literature only focus on 1-propyl species (Yang et al. 2012 and Valcárcel et al. 2006)
- Reaction barriers for C-C scission and isomerization reactions are larger than for dehydrogenation reactions ($E_a \sim 180$ kJ/mol)
- C-C scission of propyne does occur ($E_a \sim 110$ kJ/mol) leading to formation of methylidyne (CH) and ethylidyne (CH_3C) → Precursors responsible for side product formation (CH_4 and coke)

Coke formation (*)

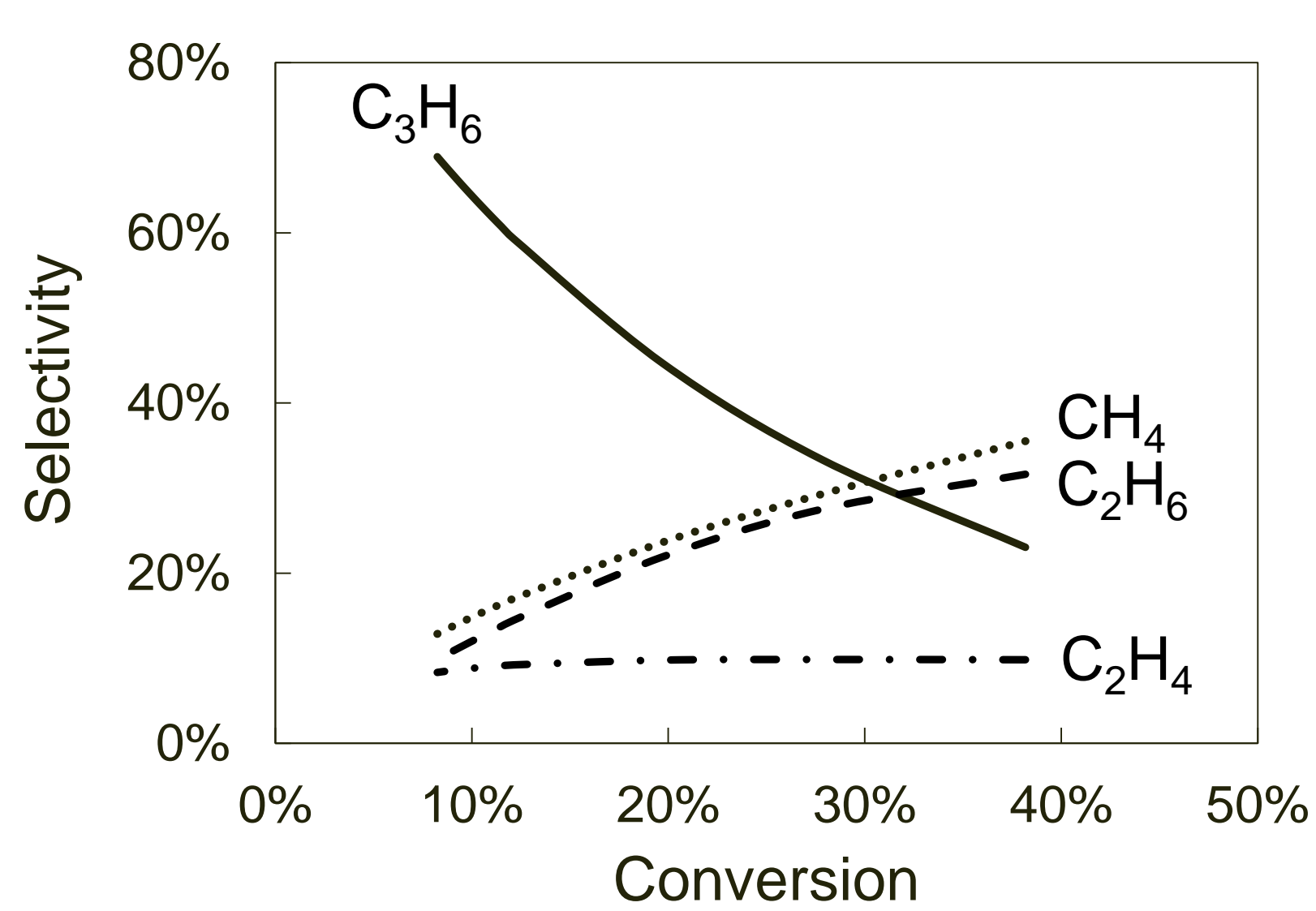
- Too complex to include in ab initio network
- Experimental evidence of graphitic coke formation on support
- Rate coefficient $k = 2.67 \cdot 10^3 s^{-1}$ (873 K), based on $32 \text{ mol}_C/\text{mol}_{Pt, \text{surface}}$ after 5' TOS

Siddiqi et al. (2010)

Base case simulation

- S and H: Statistical thermodynamics based on harmonic oscillator approach
- Rate coefficients k: Transition state theory
- CSTR reactor model: $F_{i0} - F_i + V \cdot r_i = 0$
- Surface species: $\frac{d\theta_i}{dt} = R_i = 0$ (PSSA)

✓ Conversion-selectivity relation

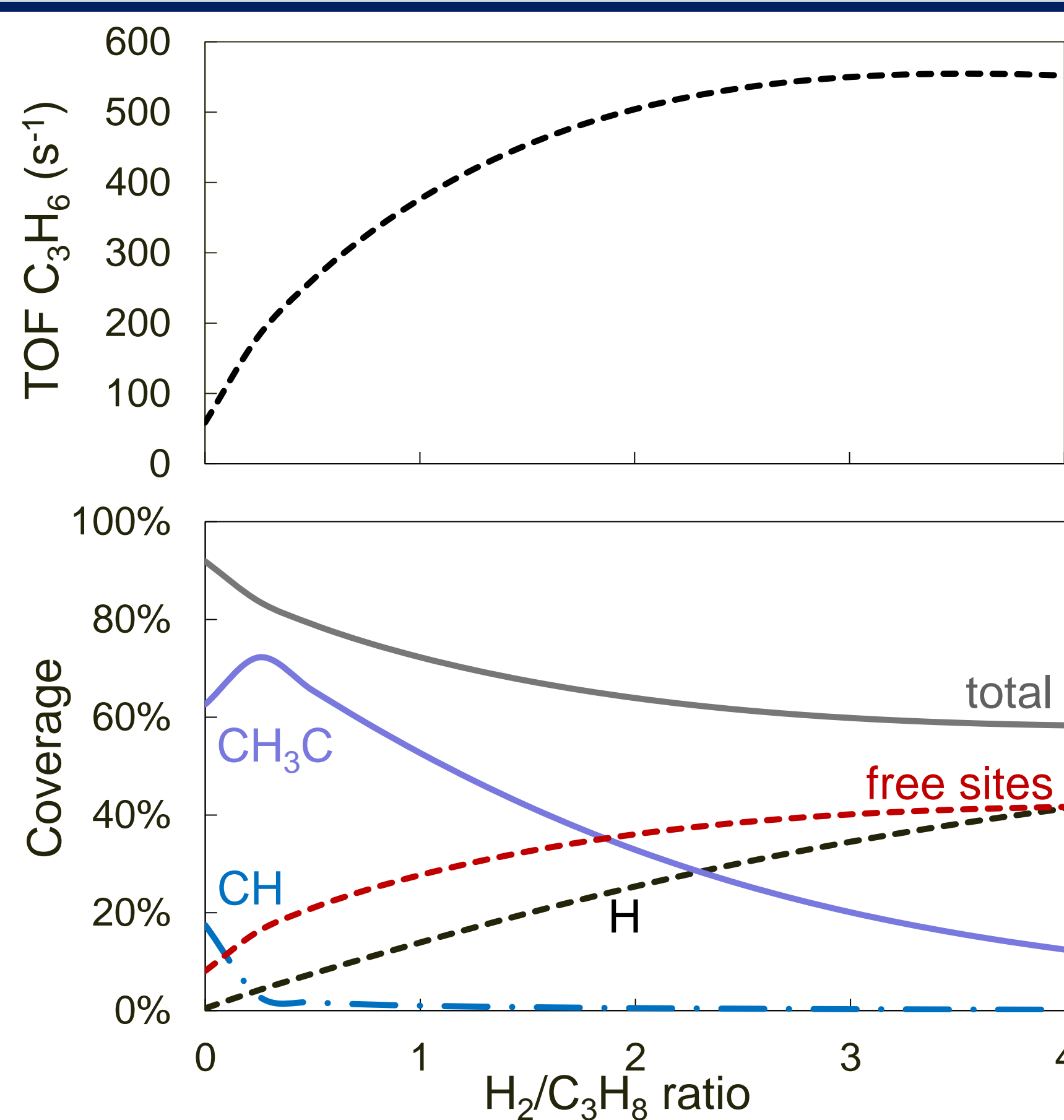


✓ Good agreement between simulation and experiment

	Experiment	Simulated
Conversion (%)	11.5	11.5
Selectivity C_3H_6 (%)	79.0	60.7
TOF (s^{-1})	1.0	418.7
Coke formation (5' TOS) ($\text{mol}_C/\text{mol}_{Pt, \text{surface}}$)	32.0	31.4

Siddiqi et al. (2010)

Variation of H_2/C_3H_8 feed ratio



✓ Simulations predict positive hydrogen effect

Insights into positive hydrogen effect

- TOF C_3H_6 same behavior as coverage of free sites
- $H_2/C_3H_8 = 0$: high coverage of deeply dehydrogenated species (ethylidyne CH_3C and methylidyne CH)
- $H_2/C_3H_8 > 0$: fast decrease of these species (due to hydrogenation reactions)
- More free sites → Higher activity
- Effect flattens out at high ratios due to equilibrium considerations

✓ Reduced blocking of active sites enhances catalytic activity when co-feeding H_2

Conclusions

- Co-feeding hydrogen has a positive effect on catalytic activity
- DFT calculations help to identify possible explanations
- Higher H_2/C_3H_8 feed ratios decrease deeply dehydrogenated coke precursors on the surface → More free sites

Future work

- Study the effect of promoting elements on activity/selectivity (e.g. Ga-alloying)
- Study the effect of catalyst nanoparticles (on support) on reaction characteristics