CO As an Active Spectator Species in Hydrocarbon Conversions Related to Fischer-Tropsch Synthesis

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ECOSS XXXIV, 29 August, Aarhus

5 years

syngaschem BV
synthesis gas chemistry
fundamental research projects

Research partner of
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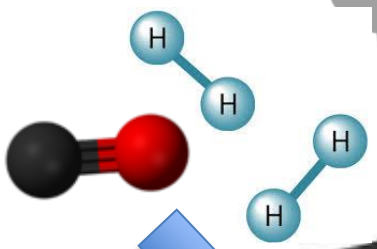
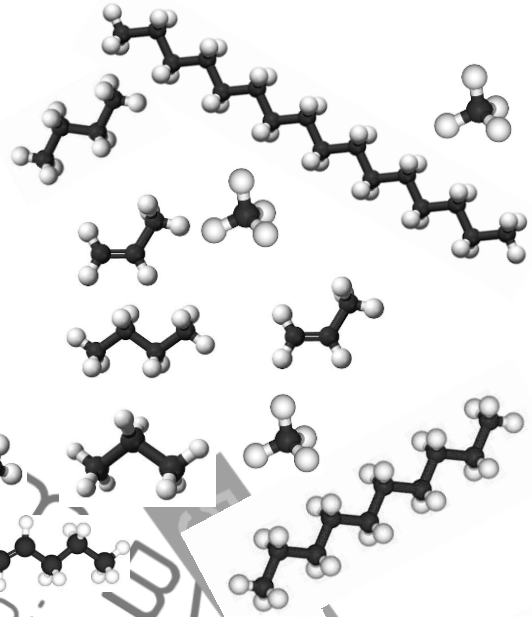
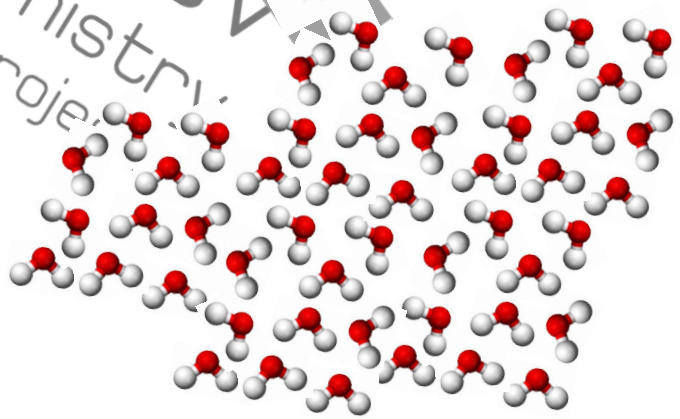
Fischer-Tropsch synthesis

$$CO + 2\,H_2 \xrightarrow[\text{10-50 bar; 180-350°C}]{\underline{\text{Co}}\text{, Fe (Ru) catalyst}} C_nH_{2n(+2)} + H_2O$$

fluidized bed; slurry phase







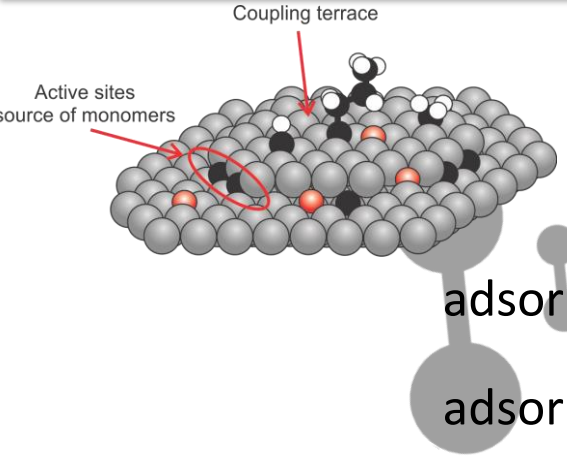
Important role in future energy

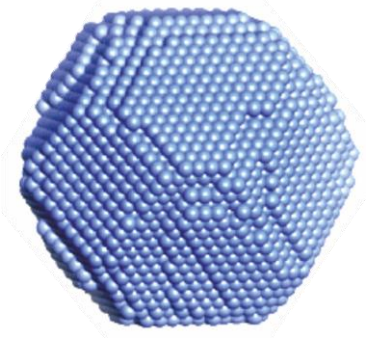
Synthesis gas: (gas, coal)

biomass, $CO_2 + H_2O$ + e-..

Produces valuable chemicals and/or clean-burning synthetic fuels

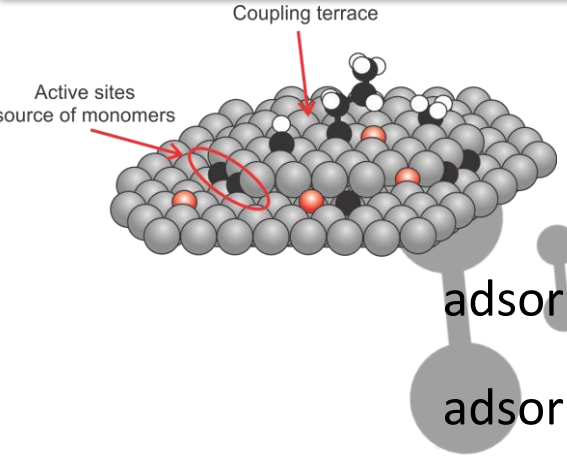
FTS surface chemistry on fcc Co

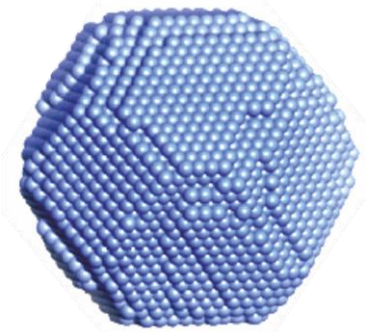




adsorption of CO	$CO\ (g) + * \leftrightarrow CO_{ad}$
adsorption of H_2	$H_2\ (g) + 2* \leftrightarrow 2\ H_{ad}$
monomer formation	$CO\ (+ x\ H) \leftrightarrow C(H_{x-y}) + O(H_y)$
oxygen removal	$O(H) + x\ H \leftrightarrow H_2O\ (g)$
chain initiation	$CH_x + CH_y \leftrightarrow C_2H_{(x+y)}$
chain growth	$C_xH_y + CH_z \leftrightarrow C_{x+1}H_{(y+z)}$
chain termination	$C_xH_y + z\ H \leftrightarrow C_xH_{(y+z)}\ (g)$

FTS surface chemistry on fcc Co





adsorption of CO $CO\ (g) + * \leftrightarrow CO_{ad}$

adsorption of H_2 $H_2\ (g) + 2* \leftrightarrow 2\ H_{ad}$

r ***How do chains grow on the catalyst surface??*** (H_y)

c

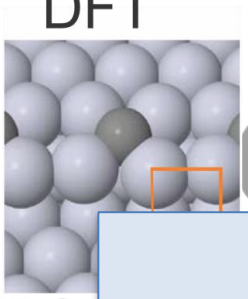
chain initiation $CH_x + CH_y \leftrightarrow C_2H_{(x+y)}$

chain growth $C_xH_y + CH_z \leftrightarrow C_{x+1}H_{(y+z)}$

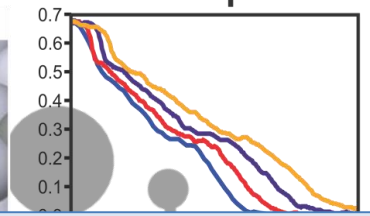
chain termination $C_xH_y + z\ H \leftrightarrow C_xH_{(y+z)}\ (g)$

The toolbox: UHV surface science

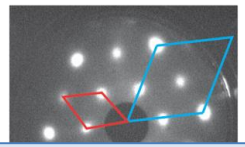
DFT



Kelvin probe

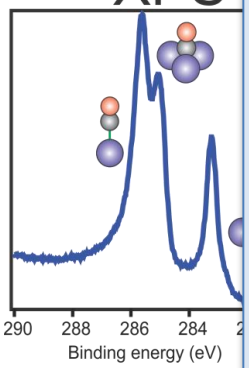


LEED



Co(0001) used throughout this presentation

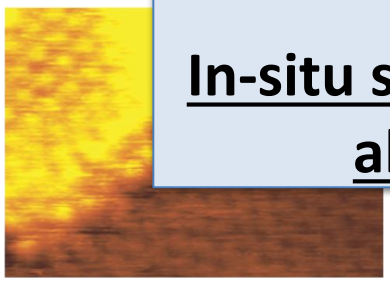
XPS

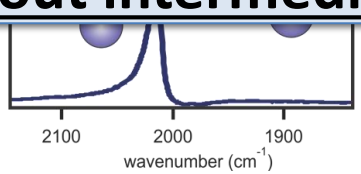


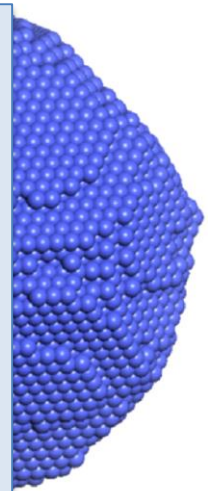
Applied catalysis:

- **Chain length distribution: many different intermediates present**
- **Concentration growth intermediates low**
- **Products build up**

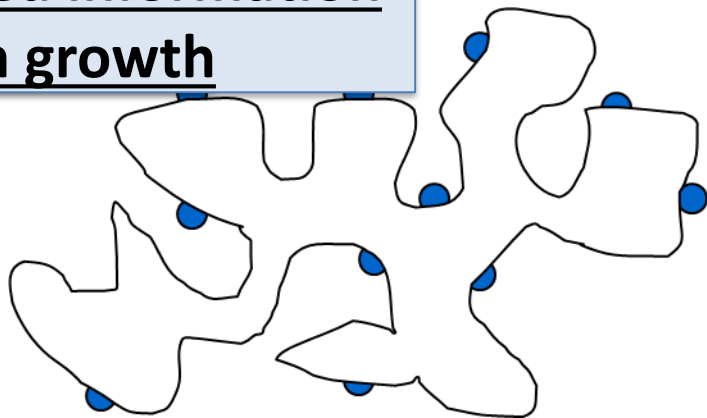
<u>In-situ spectroscopy provides limited information about intermediates of chain growth</u>







P. van Helden

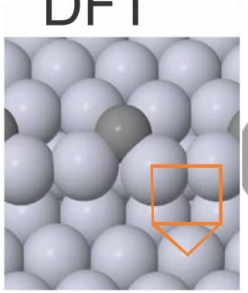


Reduce complexity to gain molecular level insight

syngaschem BV
synthesis gas chemistry
fundamental research projects
5 years

The toolbox: UHV surface science

DFT



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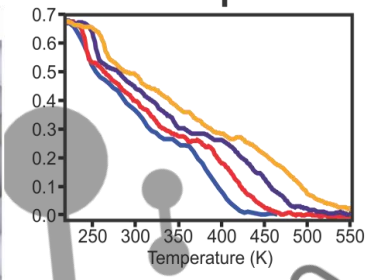

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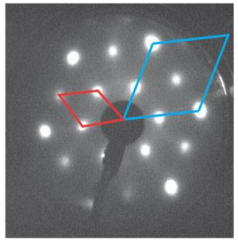

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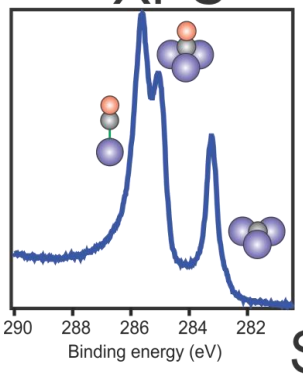
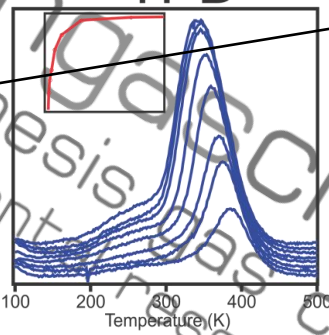
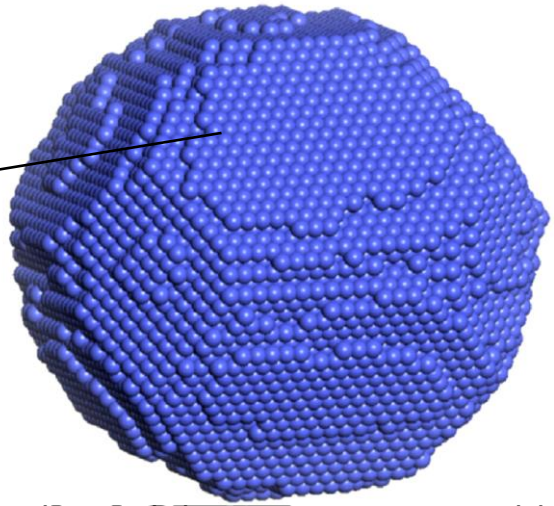


Co(0001)

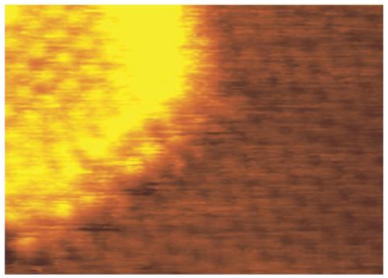
TPD



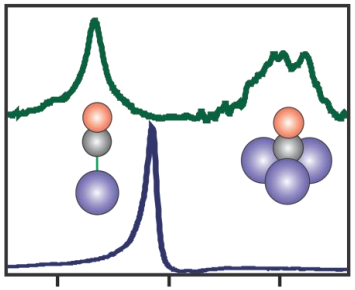


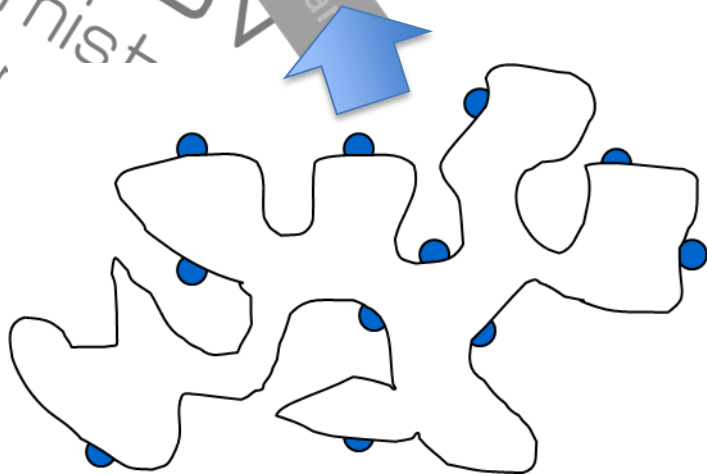
Particle model courtesy P. van Helden

STM



RAIRS





Reduce complexity to gain molecular level insight

Identifying feasible growth intermediates

Feasible intermediates for FTS chain growth: stable, termination (as alkane or alkene) must be difficult (slow)

Identifying feasible growth intermediates

Feasible intermediates for FTS chain growth: stable, termination (as alkane or alkene) must be difficult (slow)

Question: which C_xH_y species is most stable

on the Co catalyst surface??

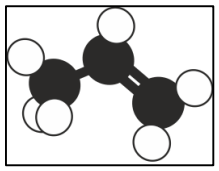
- **adsorb a sticky hydrocarbon at low temperature**

(ethene, propene and longer 1-alkenes)

- **Identify nature of surface intermediates during heating**

→ derive which C_xH_y species is the most stable of all

C_xH_y identification by HR-XPS

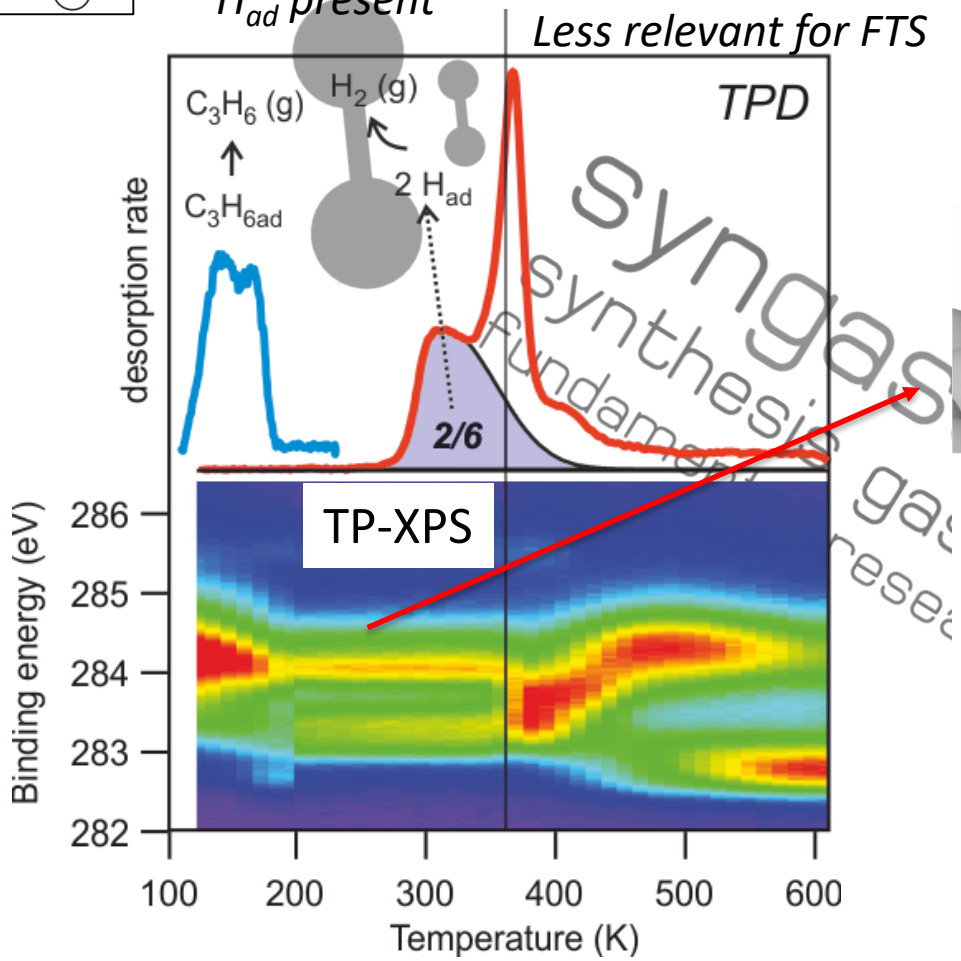


Propene decomposition

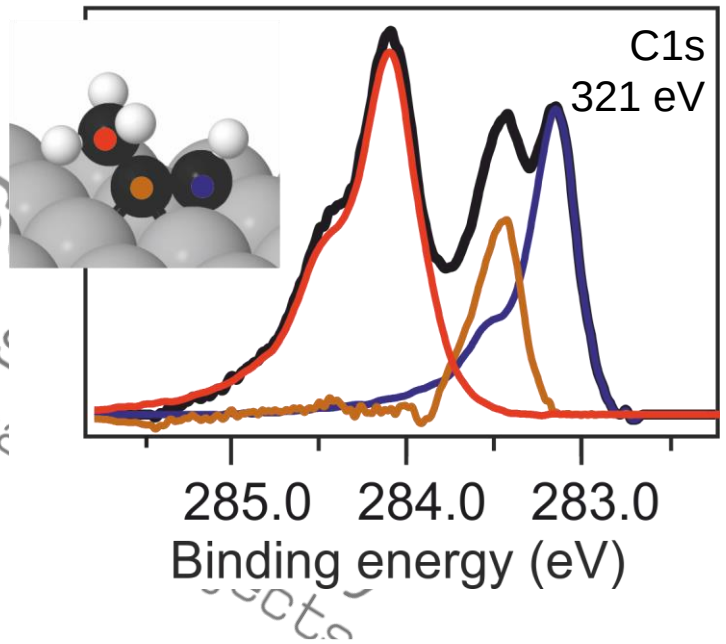
H_{ad} present

H-lean due to UHV: Less relevant for FTS

Intermediate @300 K



TPD: C_3H_4 stoichiometry

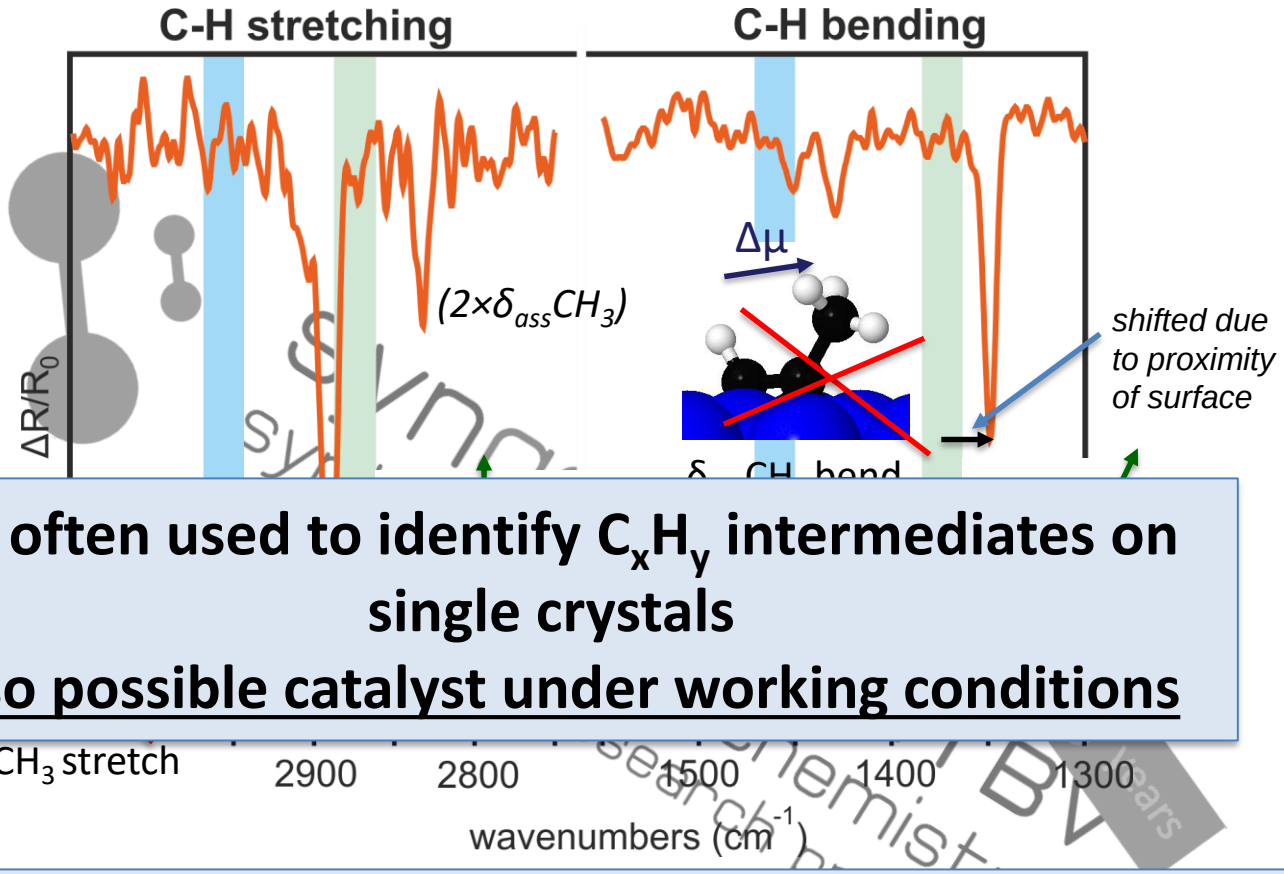


XPS: propyne

*C.J. Weststrate I.M. Ciobîcă, J. van de Loosdrecht, J.W. Niemantsverdriet, J. Phys. Chem. C **120** (2016), 29210*

ID of propyne by RAIRS

animations derived from DFT, courtesy I.M. Ciobîcă



IR: often used to identify C_xH_y intermediates on single crystals

Also possible catalyst under working conditions

"ONLY vibrational modes which give rise to an oscillating dipole perpendicular to the surface are IR active and give rise to an observable absorption band"

Methyl in propyne points up, only symmetric CH_3 modes detected

C.J. Weststrate I.M. Ciobîcă, J. van de Loosdrecht, J.W. Niemantsverdriet, J. Phys. Chem. C ***120*** *(2016),* 29210

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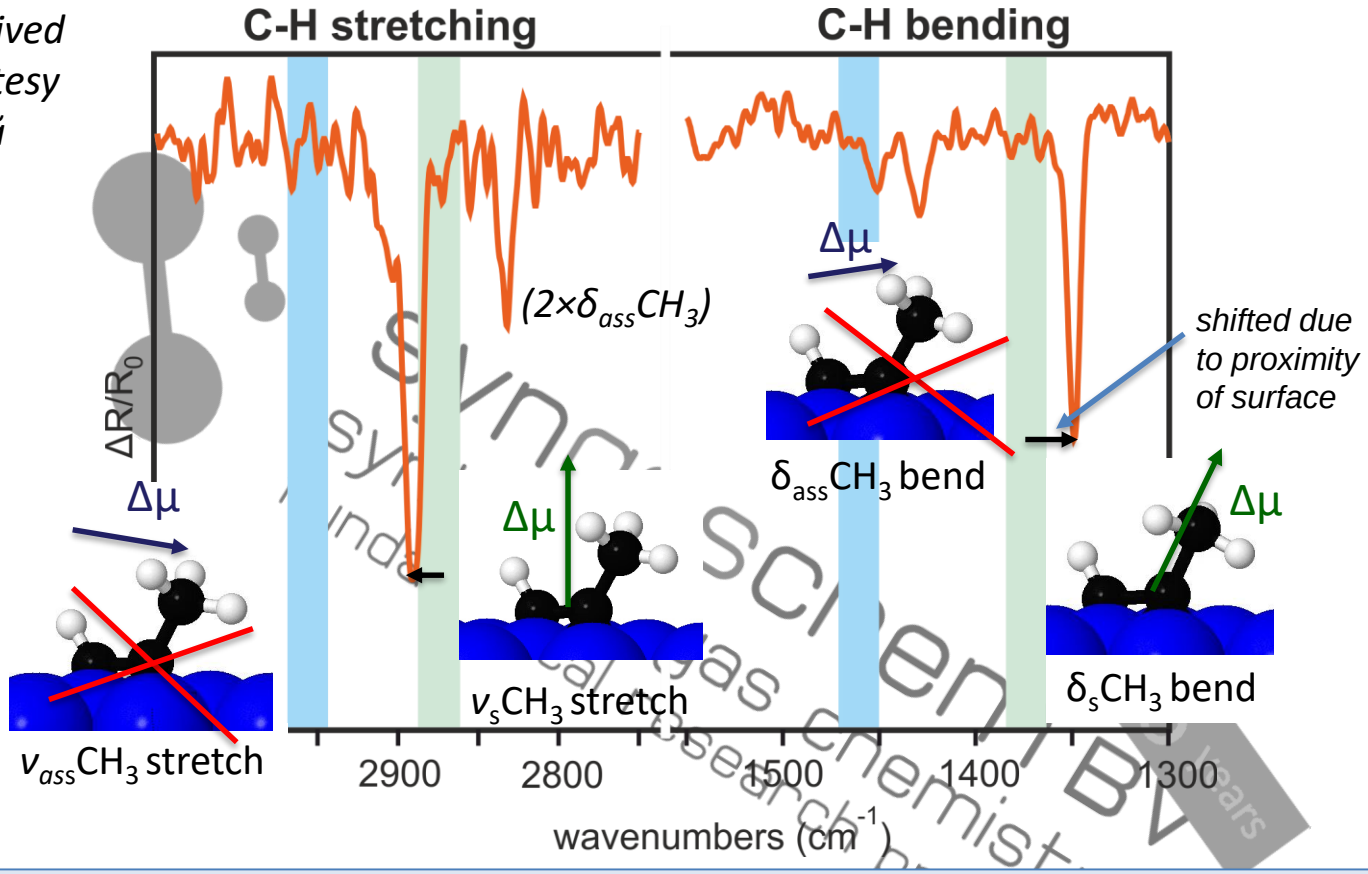
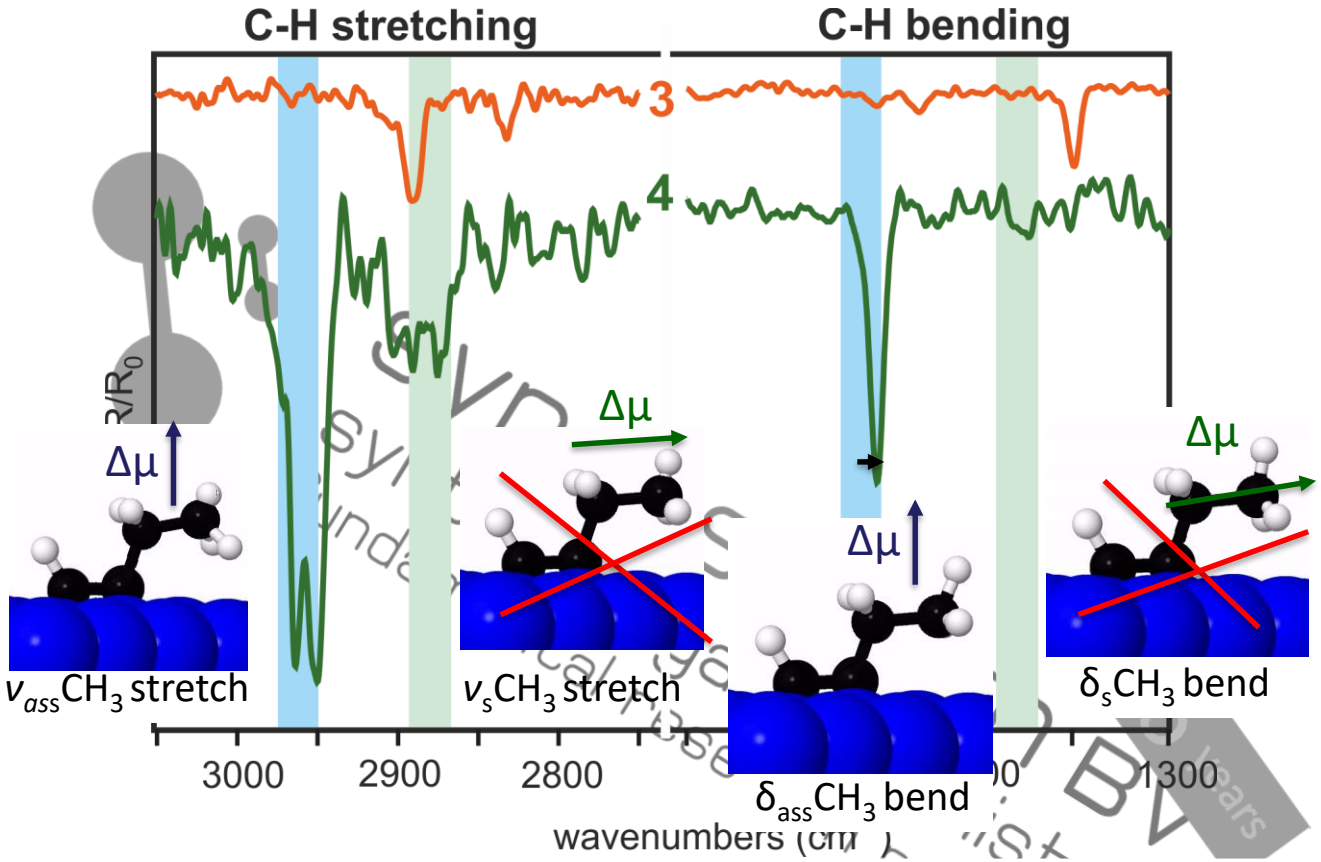


"ONLY vibrational modes which give rise to an oscillating dipole <u>perpendicular to the surface</u> are IR active and <u>give rise to an observable absorption</u> band"

Methyl in propyne points up, only <u>symmetric</u> CH_3 modes detected

*C.J. Weststrate I.M. Ciobîcă, J. van de Loosdrecht, J.W. Niemantsverdriet, J. Phys. Chem. C **120** (2016), 29210*

1-Butene decomposition product @300 K

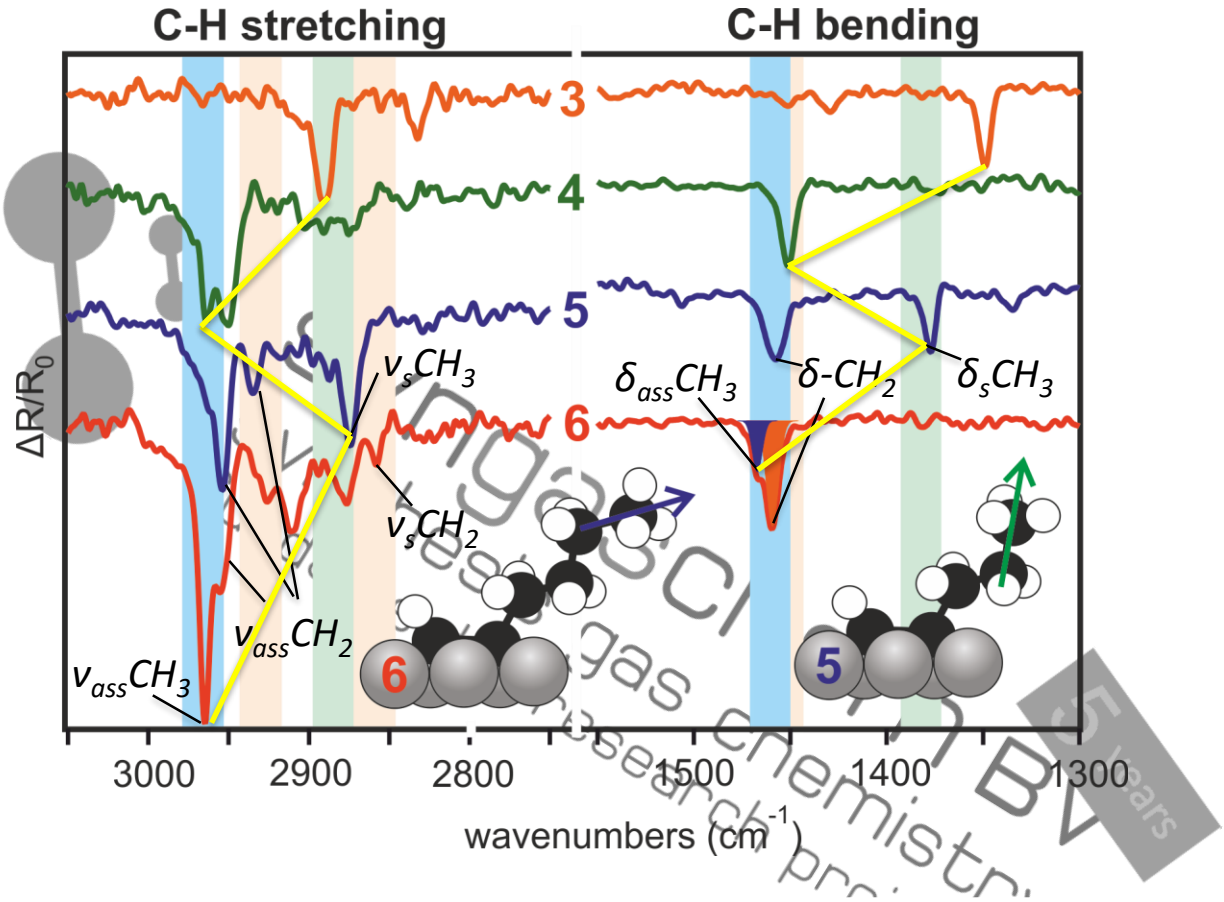


Butyne: C-CH_3 bond oriented parallel to the surface:

Only assymmetric CH_3 vibrations visible

C.J. Weststrate et al. submitted

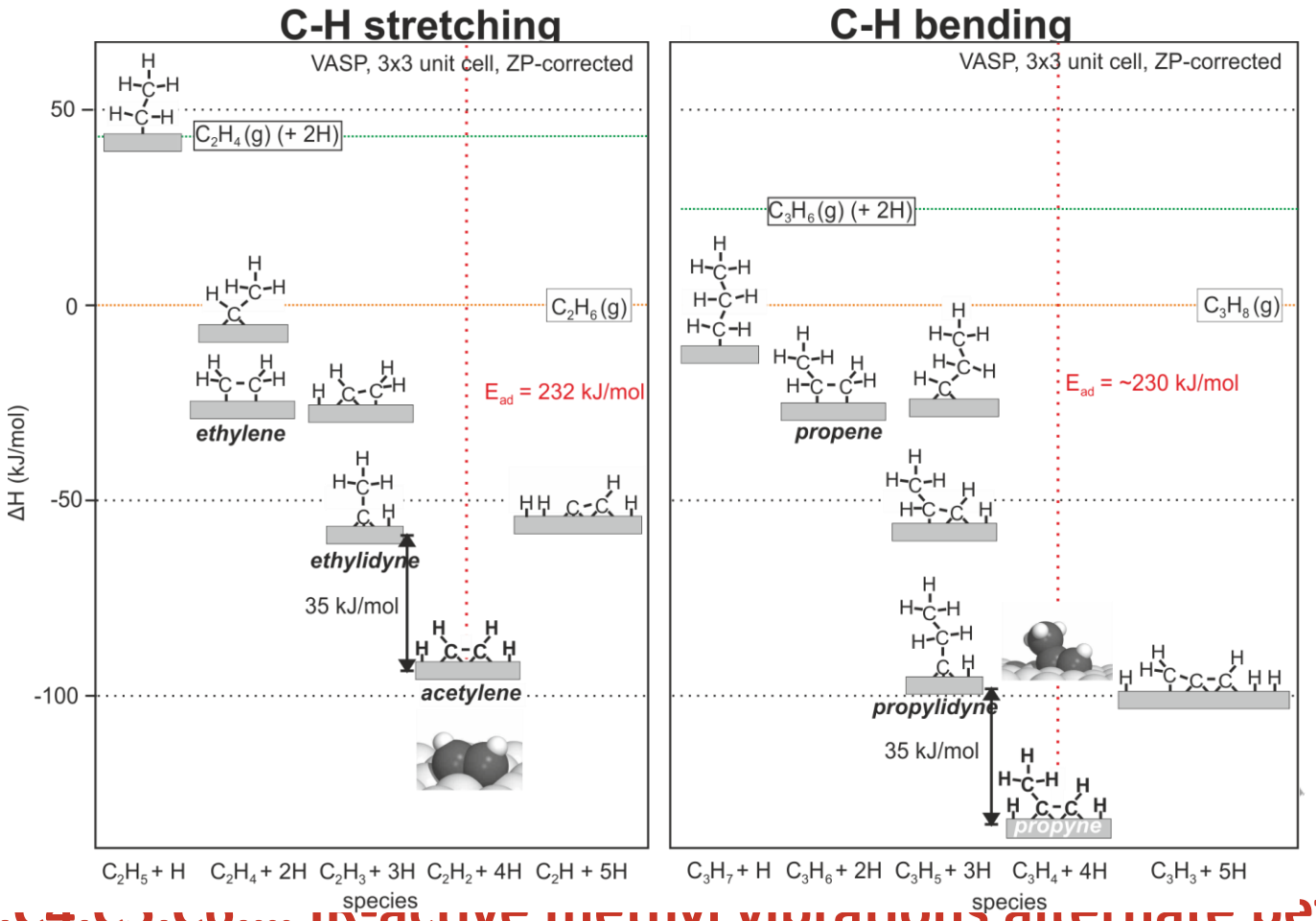
IR of 1-alkenes, heated to 300 K



C3,C4,C5,C6,… IR-active methyl vibrations alternate between symmetric and assymetric due to adsorbate geometry

C.J. Weststrate et al. in preparation

IR of 1-alkenes, heated to 300 K



C.J. Weststrate I.M. Ciobîcă, J. van de Loosdrecht, J.W. Niemantsverdriet , J. Phys. Chem. C ***120*** *(2016),* 29210

C3,C4,C5,C6,... IR-active methyl vibrations alternate between

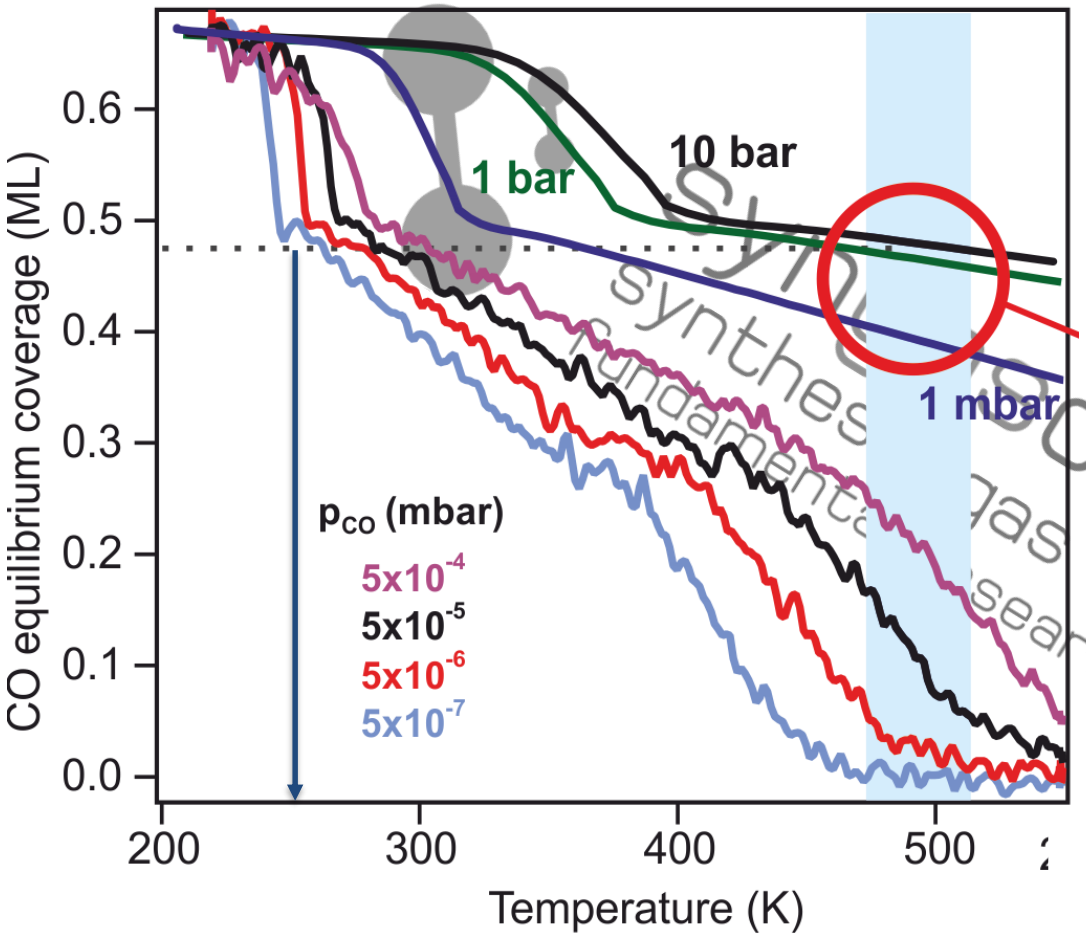
symmetric a e geometry

Alkynes (R-C≡C-H) most stable
$C_{2+}H_y$ species on Co(0001)

C.J. Weststrate et al. in preparation

FTS: happens on a crowded surface*

C.J. Weststrate, J. van de Loosdrecht, J.W. Niemantsverdriet, J. Catal. ***342*** *(2016), 1*



Work function → CO coverage at p_{CO} ≤5x10^{-4} mbar and T
→ extrapolate to FTS p and T

CO coverage ~0.5 ML @FTS
Weakly dependent on p_{CO}

J. Schweicher, A. Bundhoo, N. Kruse, JACS* ***134* *(2012), 16135*

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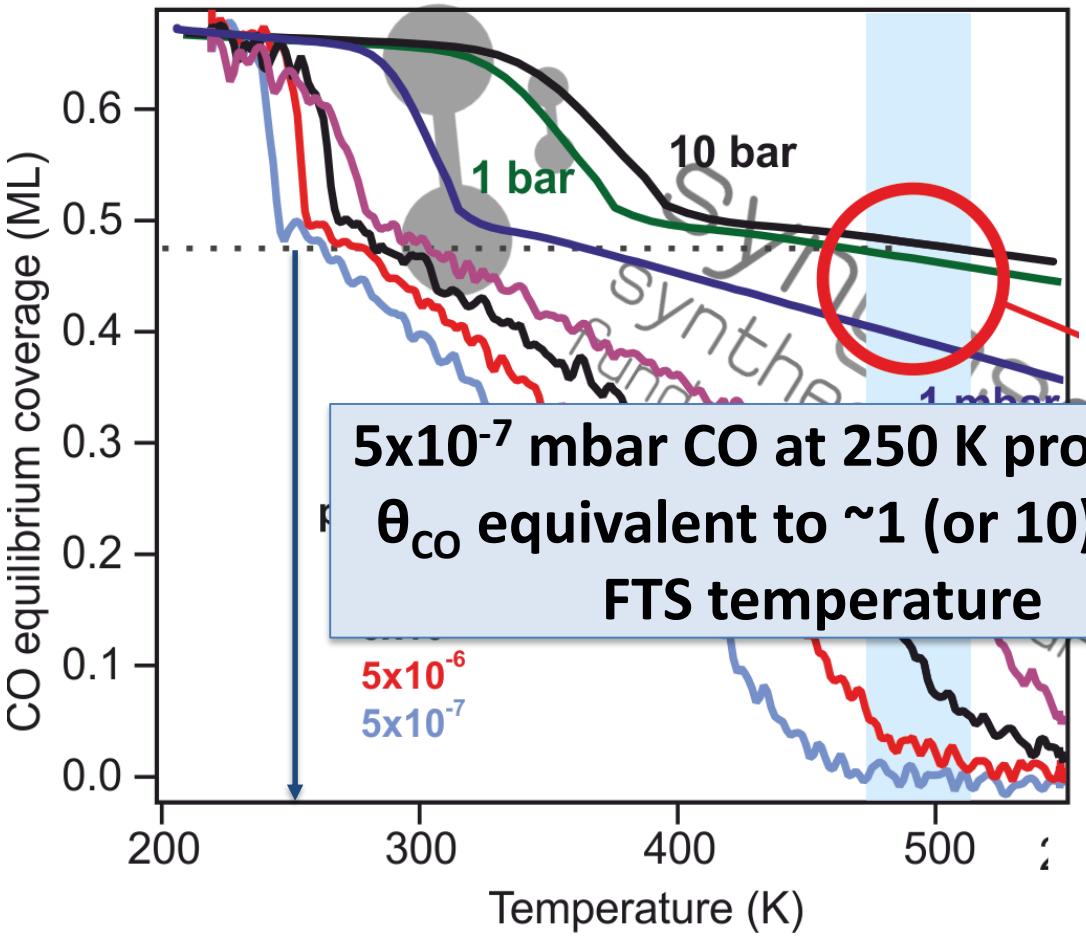


Work function → CO coverage at p_{CO} ≤5x10^{-4} mbar and T
→ extrapolate to FTS p and T

CO coverage ~0.5 ML @FTS
Weakly dependent on p_{CO}

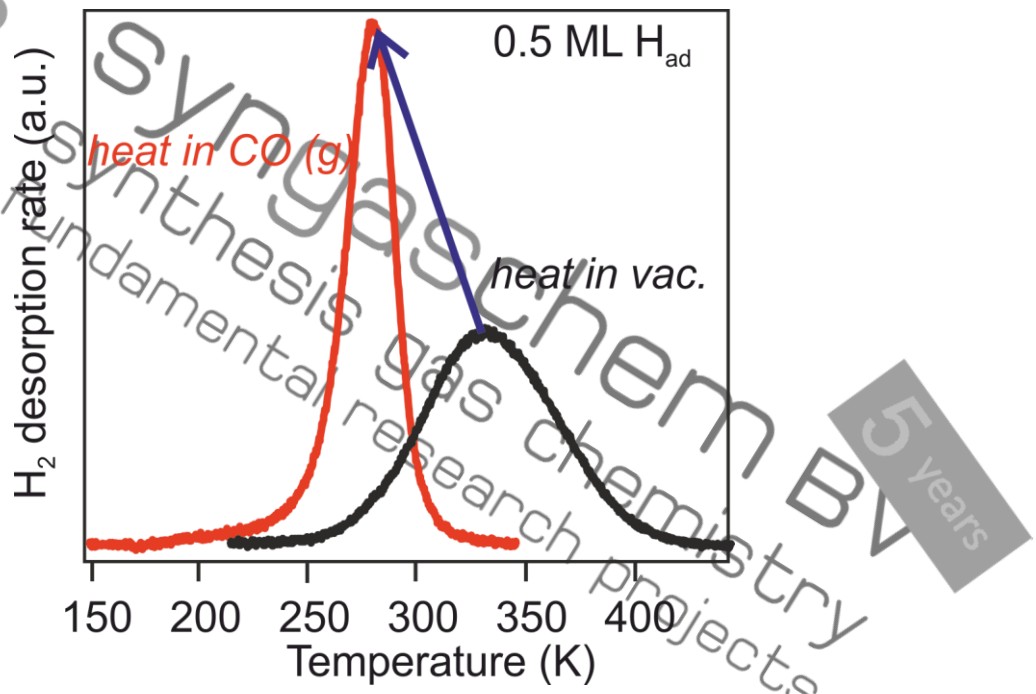
5x10^{-7} mbar CO at 250 K produces a θ_{CO} equivalent to ~1 (or 10) bar at FTS temperature

syngaschem BV 5 years
synthesis gas chemistry
fundamental research projects

J. Schweicher, A. Bundhoo, N. Kruse, JACS* ***134* *(2012), 16135*

CO affects surface hydrogen

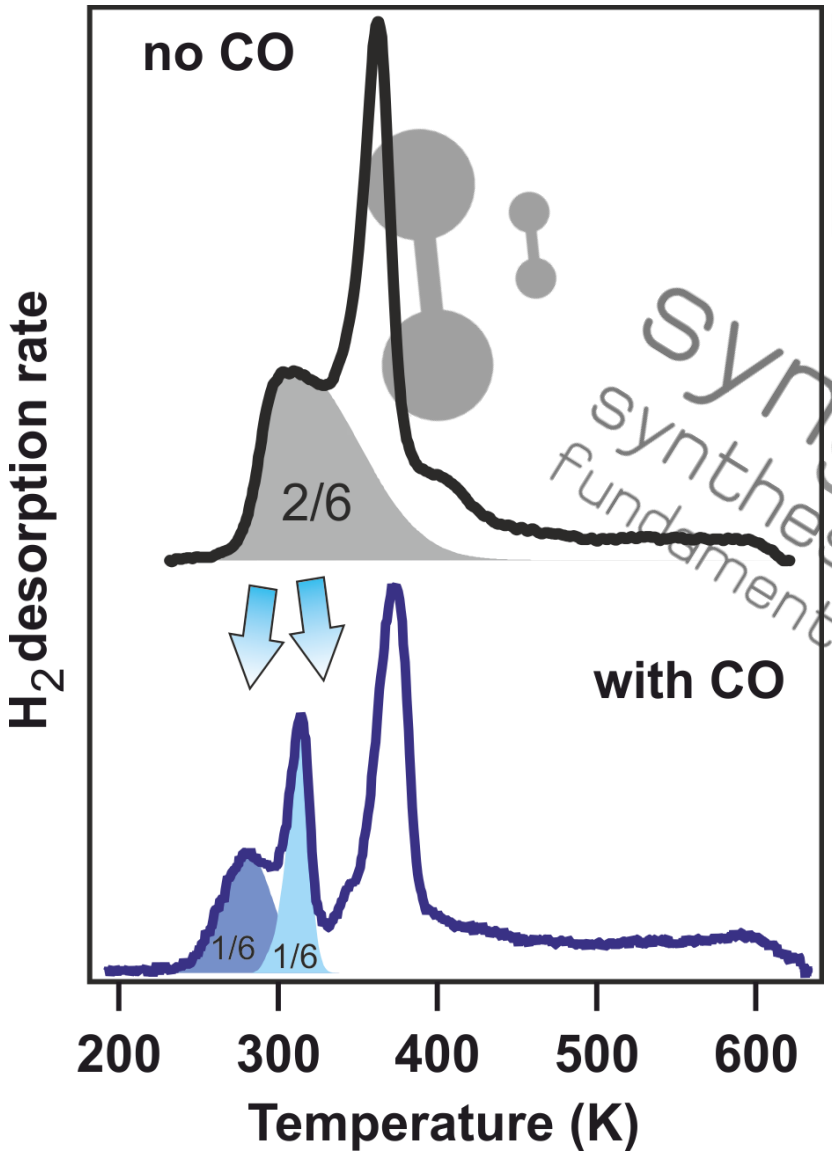
0.5 ML H_{ad}, heated in ~5x10^{-7} mbar CO (g)



CO destabilizes surface-bound hydrogen

C.J. Weststrate, J.W. Niemantsverdriet, Faraday Discuss. ***197*** *(2017), 101*

CO_{ad} affects C_xH_y surface chemistry



ΔT, 280 K

Step 1: propene$_{ad}$ → propyne$_{ad}$ + 2 H$_{ad}$

Step 2: heat in 5x10^{-7} mbar CO

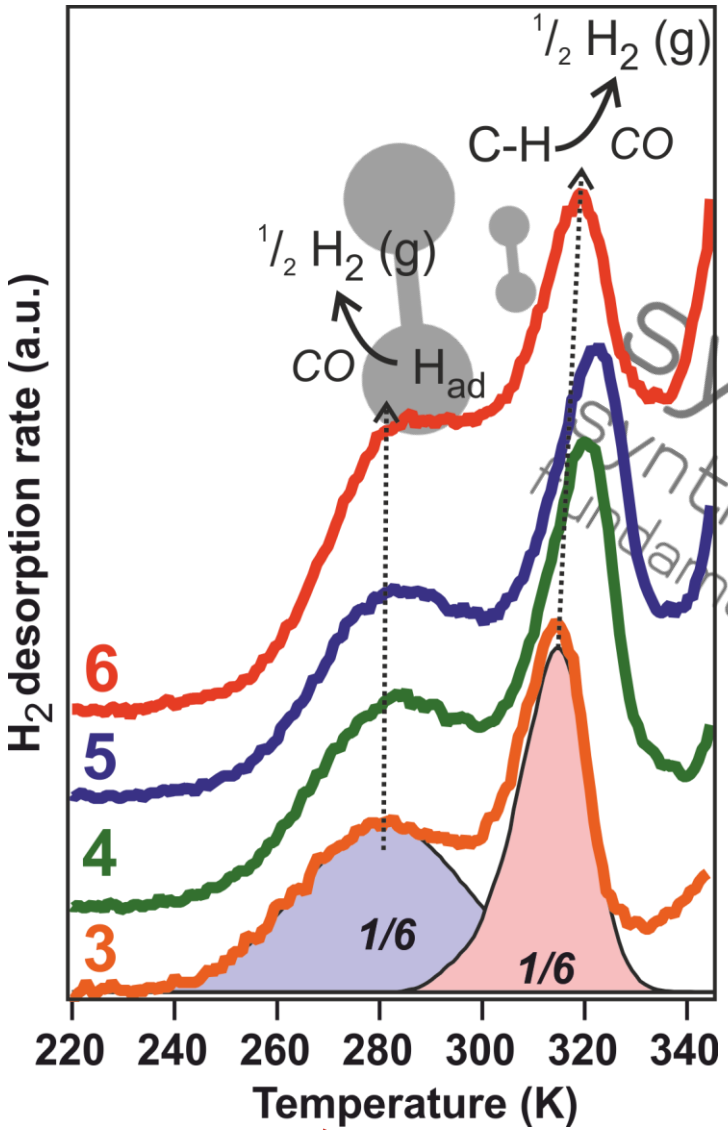
Effect of CO most prominent <350 K

'splitting' of H_2 peak due to

$H_{ad} + H_{ad} \rightarrow H_2$ (g)

C.J. Weststrate et al. submitted

CO_{ad} affects C_xH_y surface chemistry



ΔT, 280 K

Step 1: 1-alkene$_{ad}$ → 1-alkyne$_{ad}$ + 2 H$_{ad}$

Step 2: heat in 5x10^{-7} mbar CO

2 H_{ad} per adsorbate at onset of heating, yet only 1 desorbs at expected T

Other H_{ad} does not desorb, but reacts with alkyne

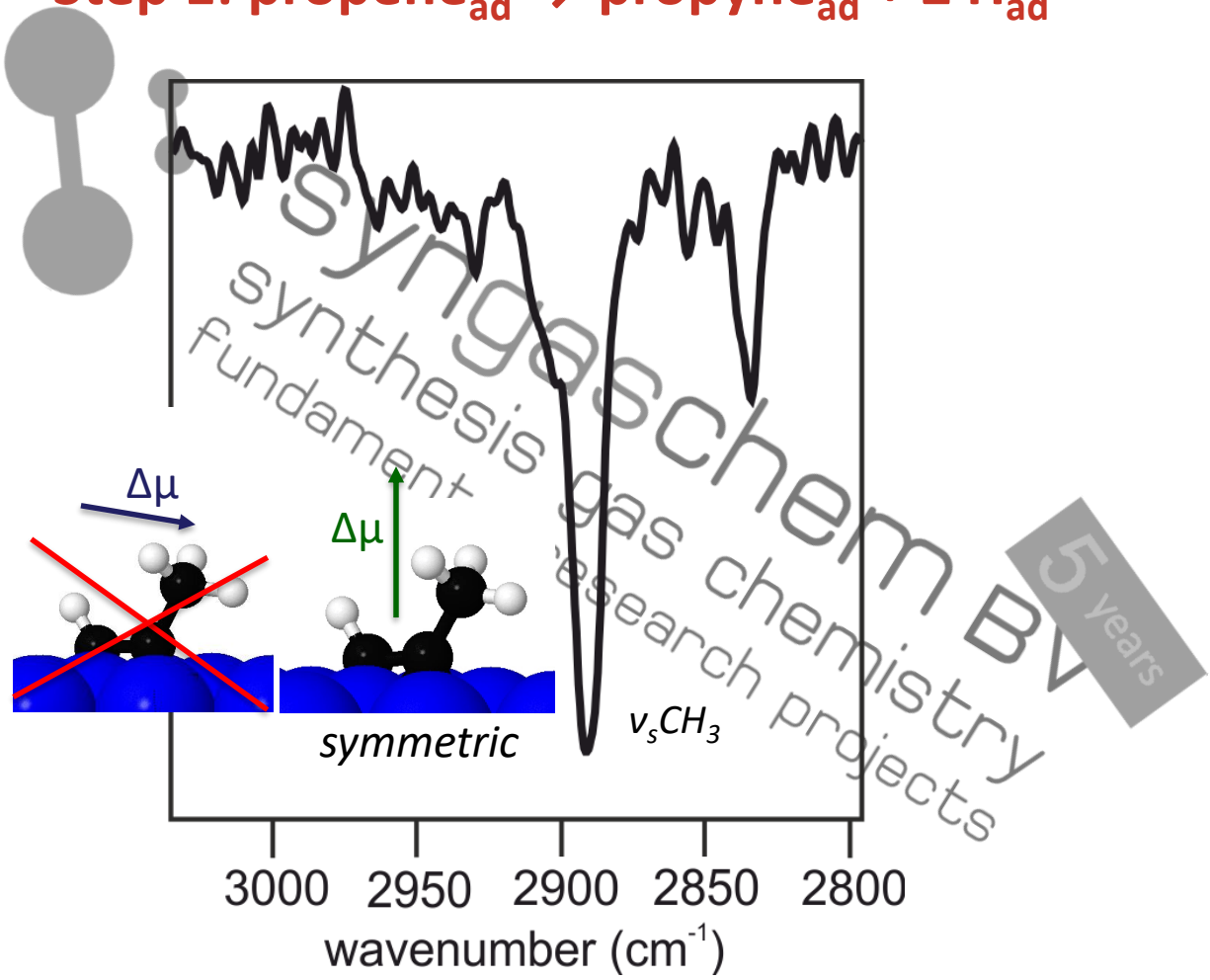
(product dehydrogenates again at 310 K, causing 2nd H_2 desorption peak)

C.J. Weststrate et al. submitted

CO_{ad} affects propyne

ΔT, 280 K

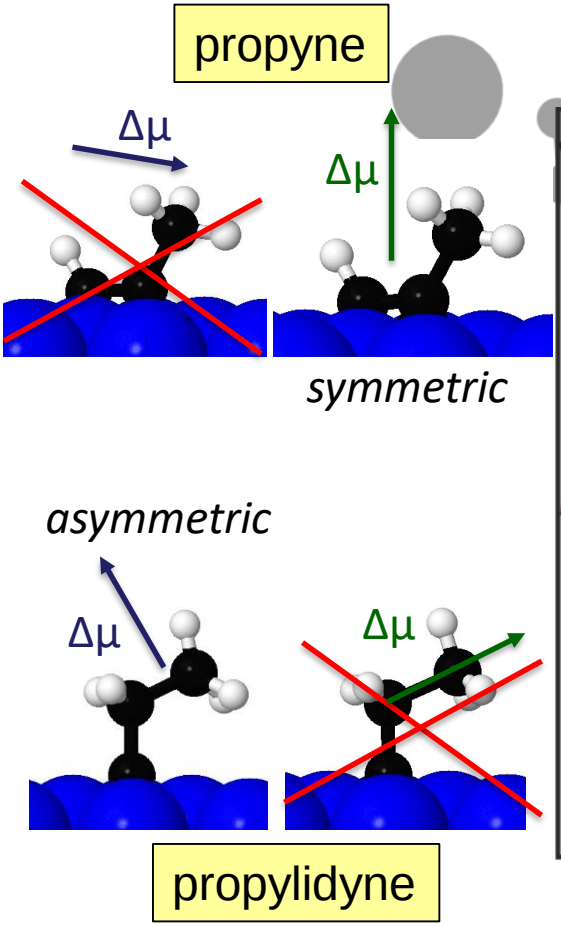
Step 1: $propene_{ad}$ → $propyne_{ad}$ + 2 H_{ad}

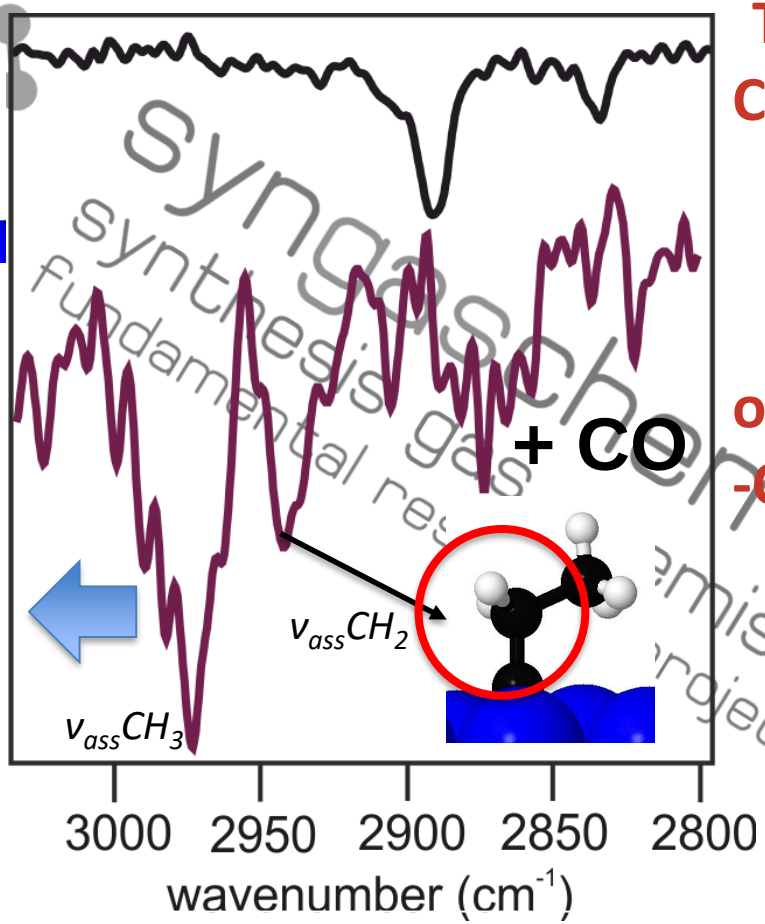


CO_{ad} affects propyne

Step 2: propyne$_{ad}$ + 2 H$_{ad}$ → C$_3$H$_5$ + H$_{ad}$

animations derived from DFT, courtesy I.M. Ciobîcă





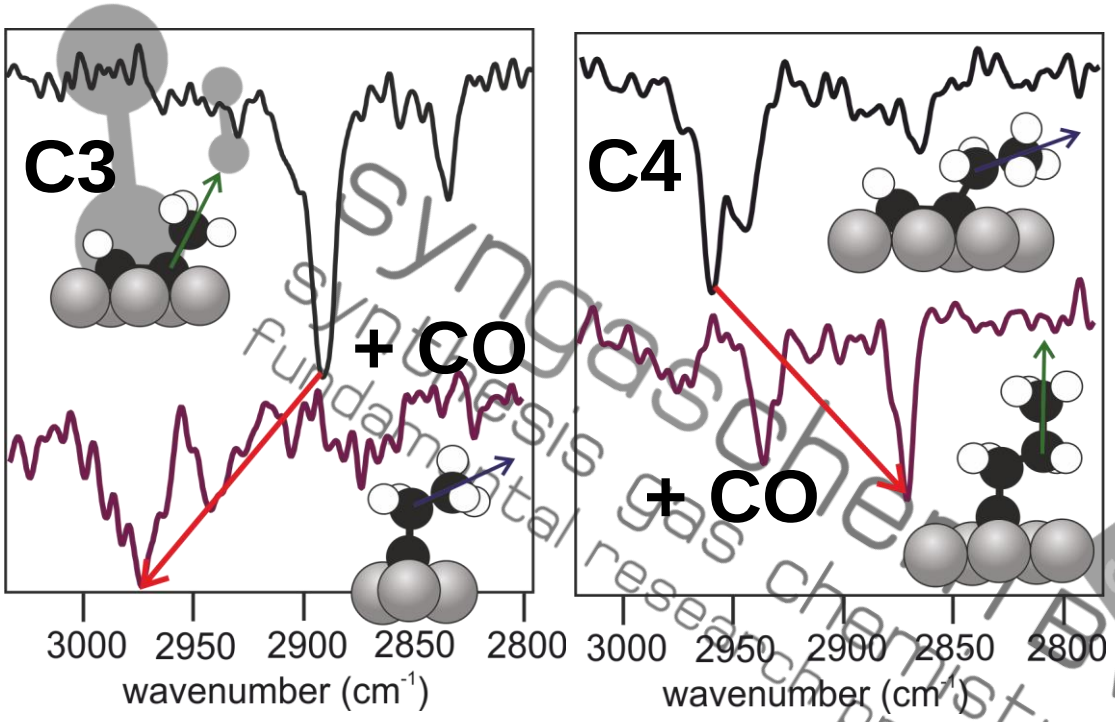
TPD:
C$_3$H$_5$ stoichiometry

RAIRS:
-change of CH$_3$ orientation
-CH$_2$ visible

Propylidyne formed
CO induces hydrogenation of propyne ≤250 K

C.J. Weststrate, I.M. Ciobîcă, A.M. Saib, D.J. Moodley, J.W. Niemantsverdriet, Catal. Today **228** (2014), 106

C_3-C_5: alkyne + H→ alkylidyne, due to CO



CO-induced alkyne hydrogenation to alkylidyne occurs for all chain lengths

C.J. Weststrate et al. submitted

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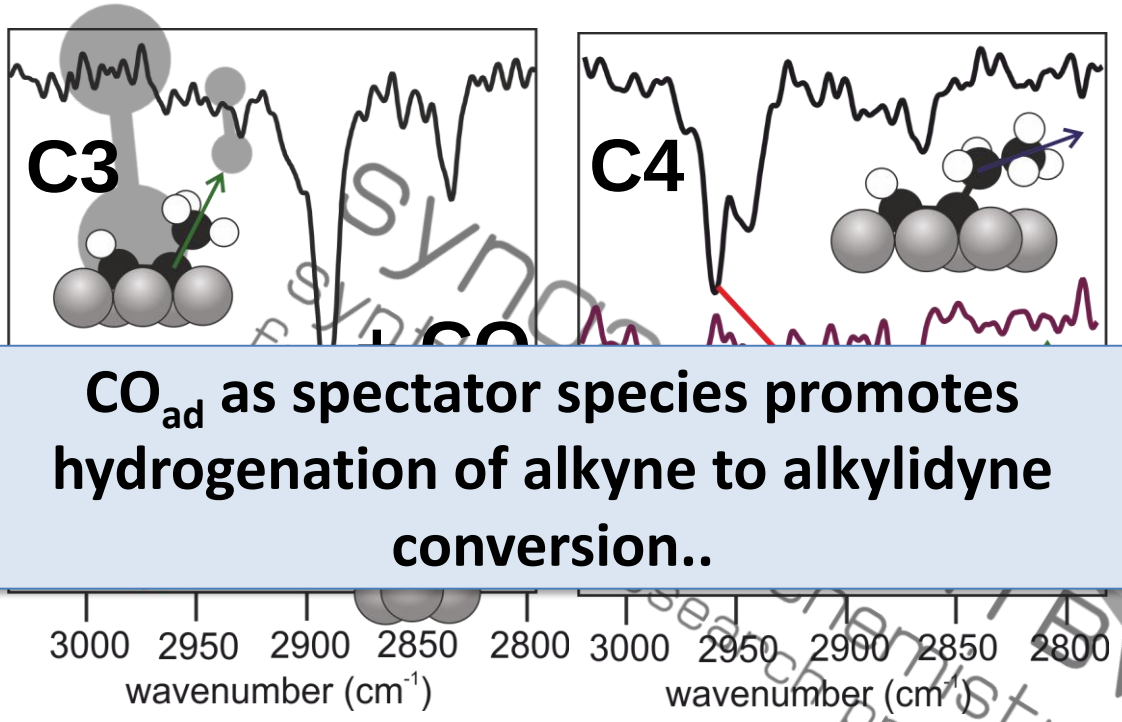


CO_{ad} as spectator species promotes hydrogenation of alkyne to alkylidyne conversion..

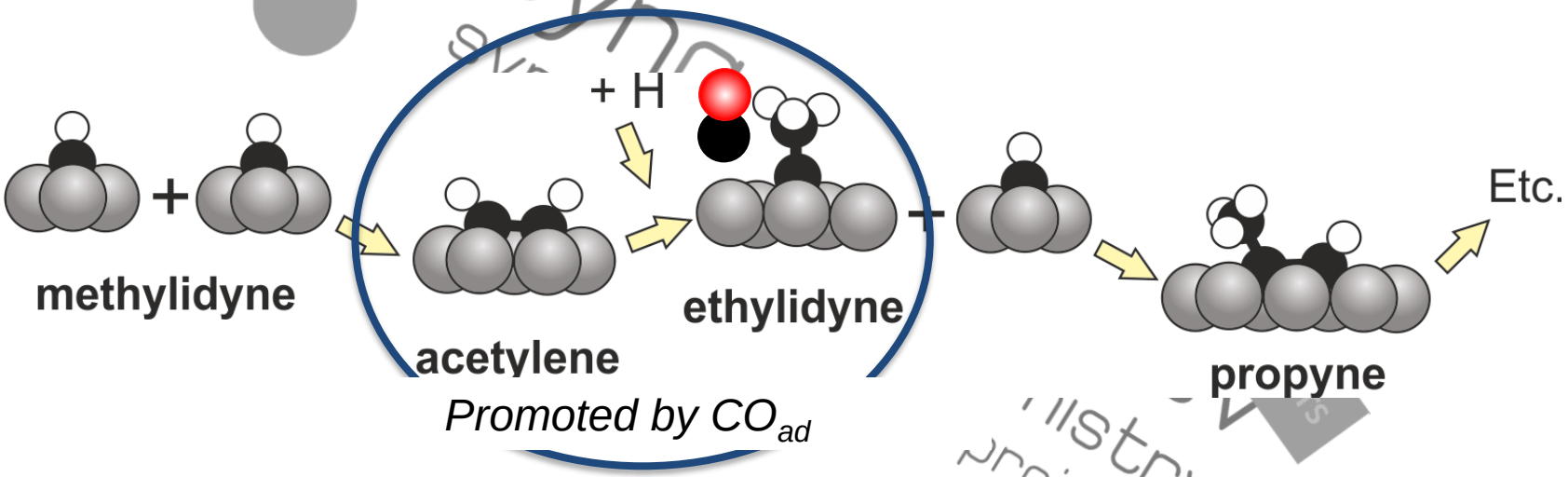
CO-induced alkyne hydrogenation to alkylidyne occurs for all chain lengths

C.J. Weststrate et al. submitted

Alkylidyne chain growth mechanism

Growth intermediates: resistant to termination, reactive for coupling

Chain growth: alkylidyne mechanism, on close-packed terraces



Elementary reaction steps: observed experimentally, occur readily on close-packed Co surface

CO_{ad} essential as spectator

C.J. Weststrate, P. van Helden, J.W. Niemantsverdriet, Catal. Today **275** (2016), 100-110

Alkylidyne chain growth mechanism

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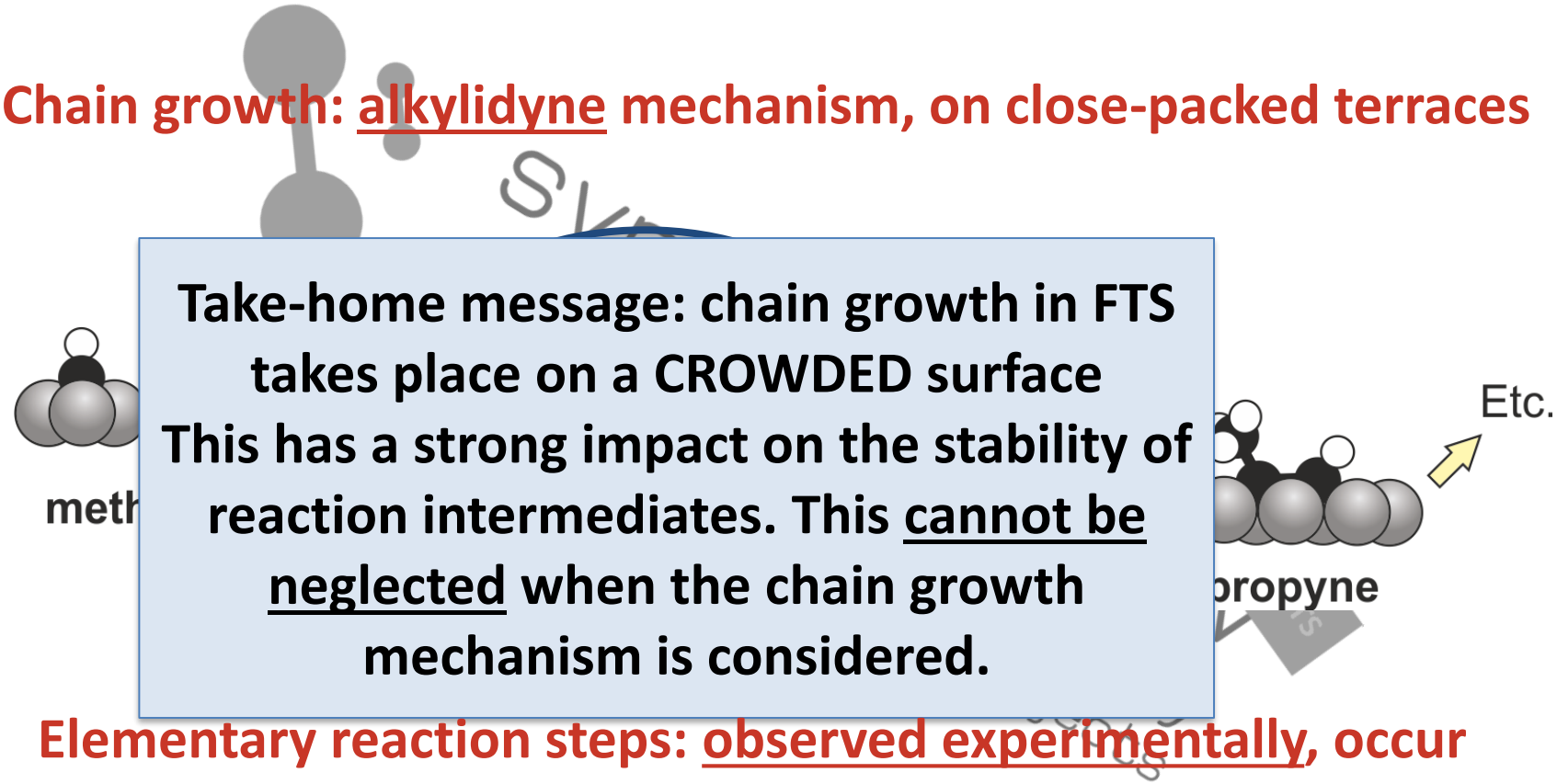

Take-home message: chain growth in FTS takes place on a CROWDED surface
This has a strong impact on the stability of reaction intermediates. This cannot be neglected when the chain growth mechanism is considered.

Elementary reaction steps: observed experimentally, occur readily on close-packed Co surface

CO_{ad} essential as spectator

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