Operando Computational Catalysis: Structure, Mechanism and Design of Cobalt Fischer-Tropsch catalysts

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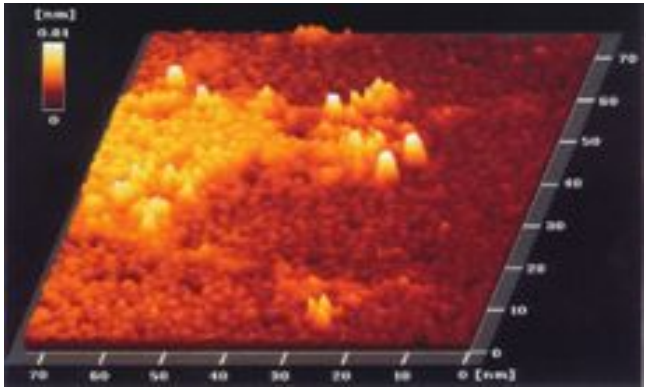
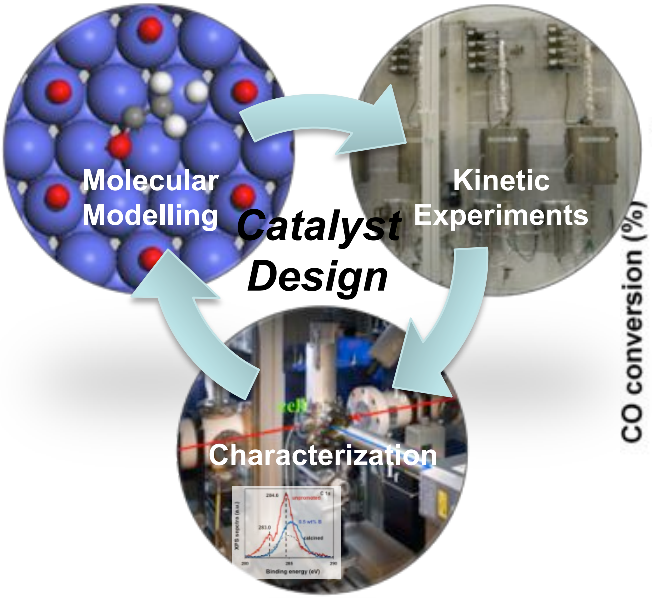
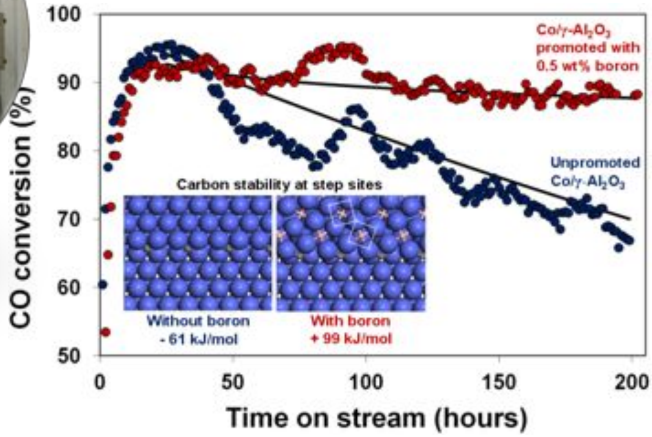



Molecular Modelling

Kinetic Experiments

Catalyst Design

Characterization



Gas-to-Liquids

Process

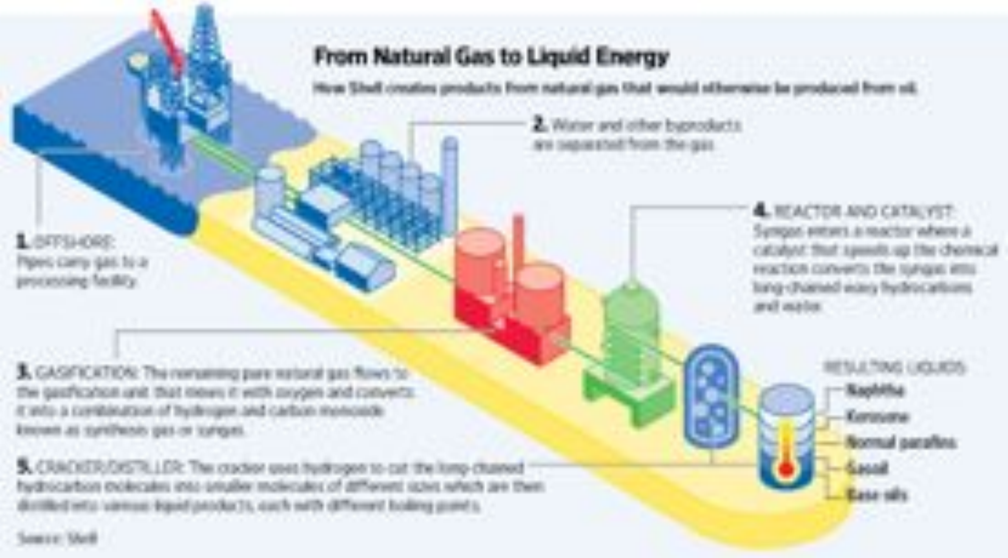
Gasification

$CH_4 + ½ O_2 \rightarrow CO + 2 H_2$

Fischer-Tropsch synthesis

$CO + 2 H_2 \rightarrow -CH_2- + H_2O$

Air separation, product upgrading



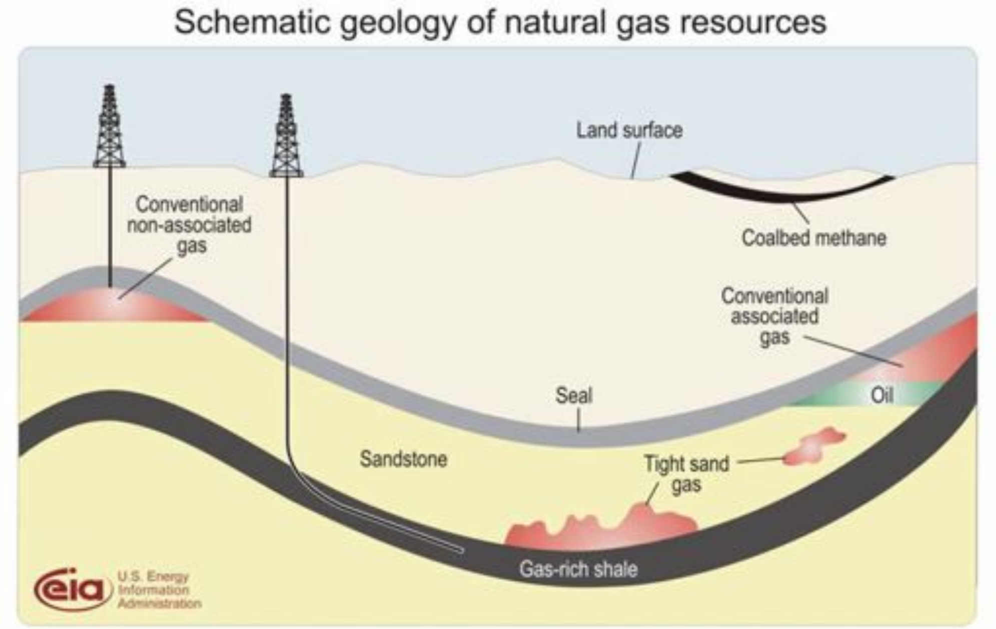
Source: Shell

Qatar: 14% of known gas reserves

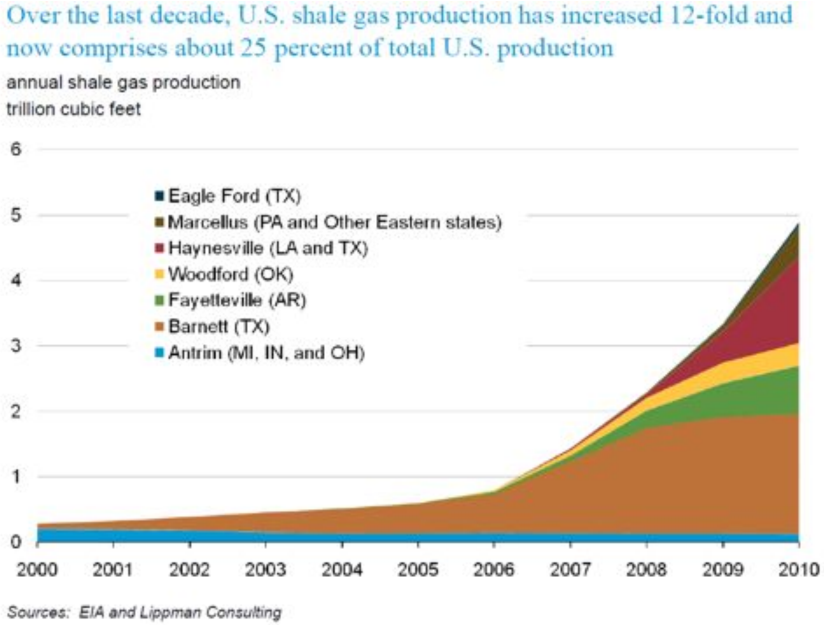
~50,000 US$/capita from oil and gas

Shell Pearl: 250,000 bbl/day

Shale Gas - a Game Changer

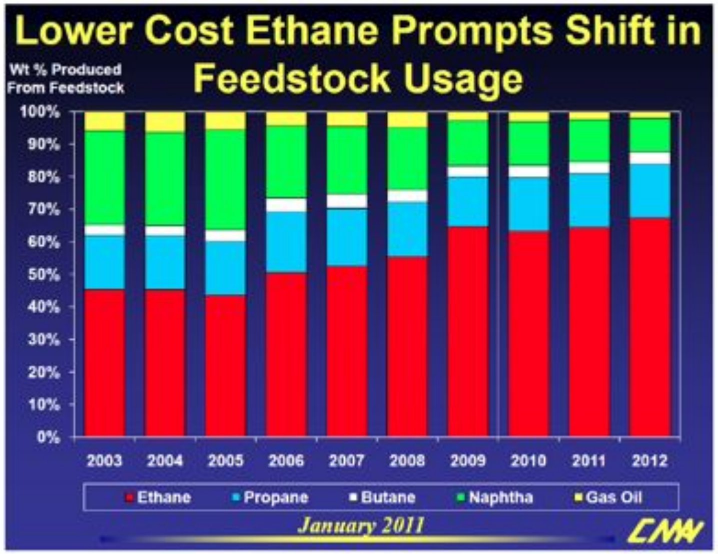


Schematic geology of natural gas resources



Over the last decade, U.S. shale gas production has increased 12-fold and now comprises about 25 percent of total U.S. production

Sources: EIA and Lippman Consulting



Lower Cost Ethane Prompts Shift in Feedstock Usage

Dramatic change in natural gas supply -> price collapsed

Dramatic shift from naphtha
-> ethane/propane cracking

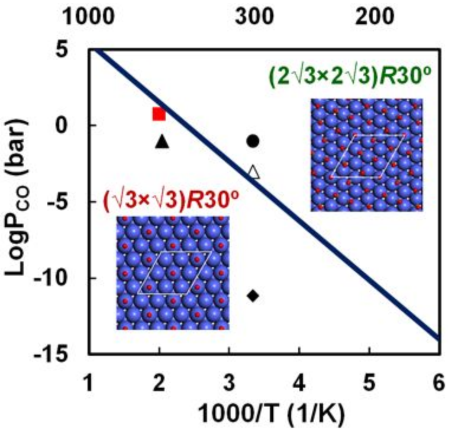
Towler, UOP, 2012

Outline

Cobalt catalysts

High activity, selectivity, low CO_2 production

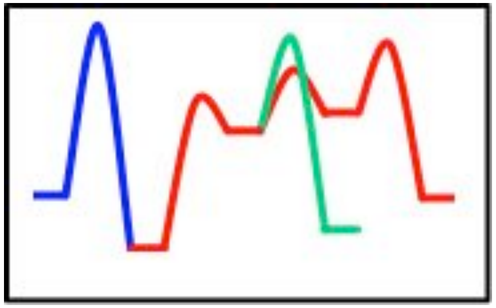
Structure, coverage, active sites, mechanism?



CO coverage on Co and Pt

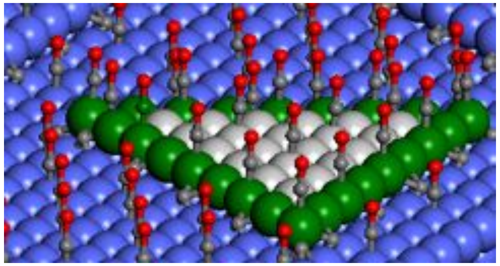
revPBE-VdW accurately describes CO on TM.

Phase transitions and changes in site preference



Effect of high CO coverage on kinetics

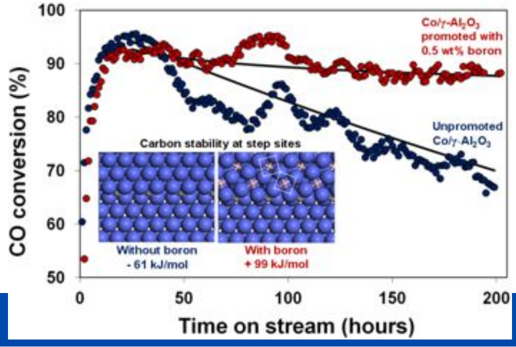
Accounting for coverage brings predicted kinetic parameters close to experiment



Dramatic surface reconstruction

Nature of experimentally observed islands/new sites

Origin of stability/formation



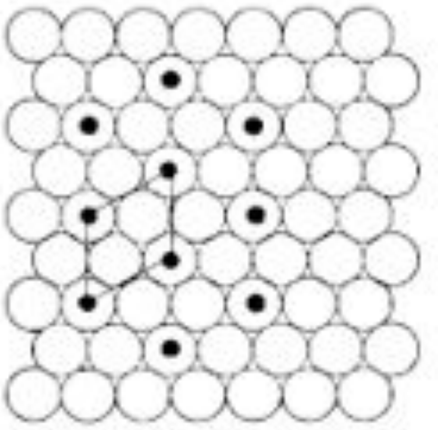
Modeling-guided Design: Stability

Co FT catalysts gradually deactivate

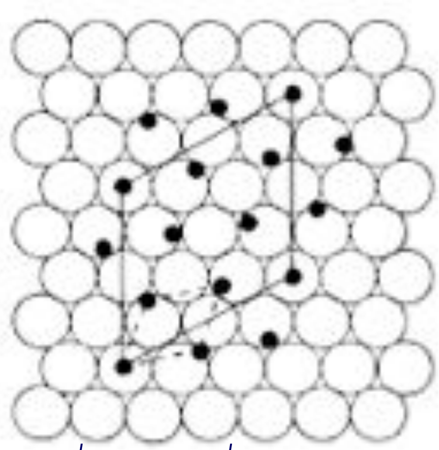
Modeling-guided design of a promoter

High CO coverages on Co

Surface Science (LEED)

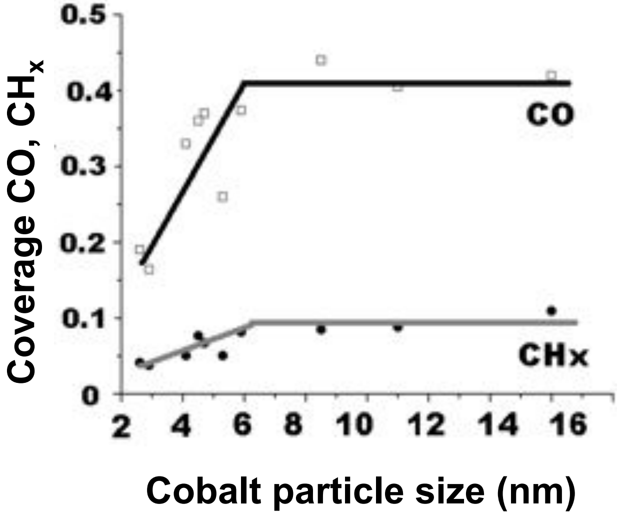


(√3 × √3)*R*30°
1.2 L CO, 100 K
1/3 ML CO



(2√3 × 2√3)*R*30°
2.2 L CO, 100 K
7/12 ML CO

SSITKA studies on supported Co catalysts

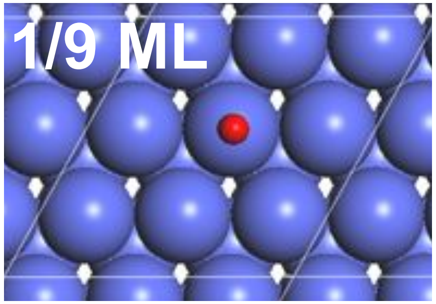


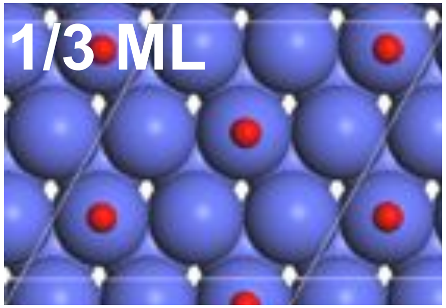
1.85 bar, 500 K

2 configurations observed under UHV conditions
SSITKA measures ~0.5 ML CO coverage on particles

Bridge, Comrie, Lambert, *Surf. Sci.* **1997**; Papp, *Surf. Sci.* **1983;**
Beitel et al., *JPC* **1996**, *JPCB* **1997;** den Breejen et al., *JACS* **2009**

Increasing coverage to 1/3 ML





	Pt-1/9	Co-1/9	Pt-1/3	Co-1/3
revPBE-vdW	-143	-130	-139	-135
Experimental	-142	-128		

revPBE-vdW – accurate adsorption enthalpies

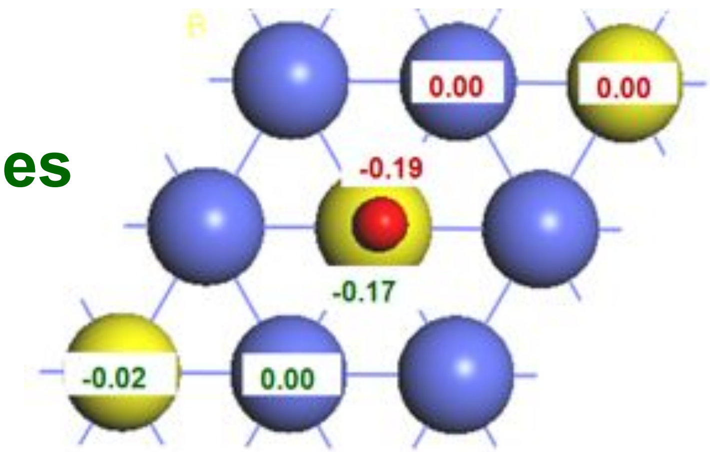
1/9 ML → 1/3 ML – attraction on Co, repulsion on Pt

Attraction → CO island formation (note: mixing entropy)

Increasing coverage to 1/3 ML

Effect of CO adsorption on Co/Pt charges

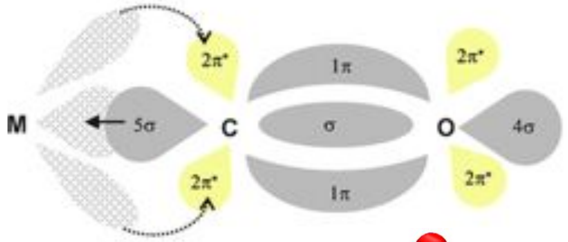
CO reduces charge on neighboring Co atoms, small effect for Pt



Change in Bader charge (Co / Pt)

Natural Bond Orbitals[1]

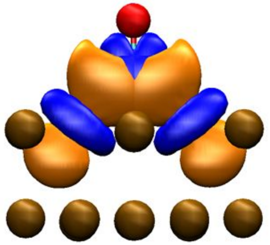
	Pt-1/9	Co-1/9	Pt-1/3	Co-1/3
$(5\sigma\text{-}d_{z2})^*$ occupancy	0.42	0.36	0.44	0.34
C-O $2\pi^*$ occupancy	0.19/0.19	0.29/0.29	0.19/0.19	0.28/0.28



NBO agrees with Blyholder picture

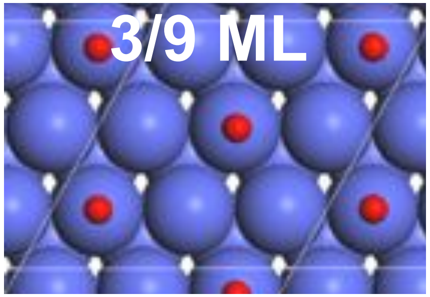
Reduced charge->lower Pauli repulsion (5σ)

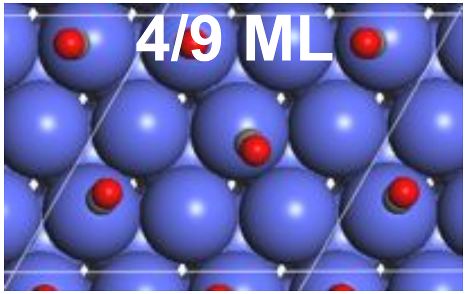
Back-donation to 2π* nearly affected

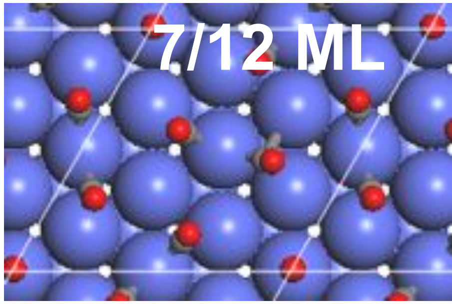


[1] Schmidt et al., *J. Chem. Theory Comput.* (2012); Blyholder (1961)

CO coverage on terraces. Phase transition







Differential E_{ads}	-135	-46	-75
ΔG_{ads}(500 K, 7 bar)	-65	+32	+6

Adsorption entropy: -140 to -150 J/mol K

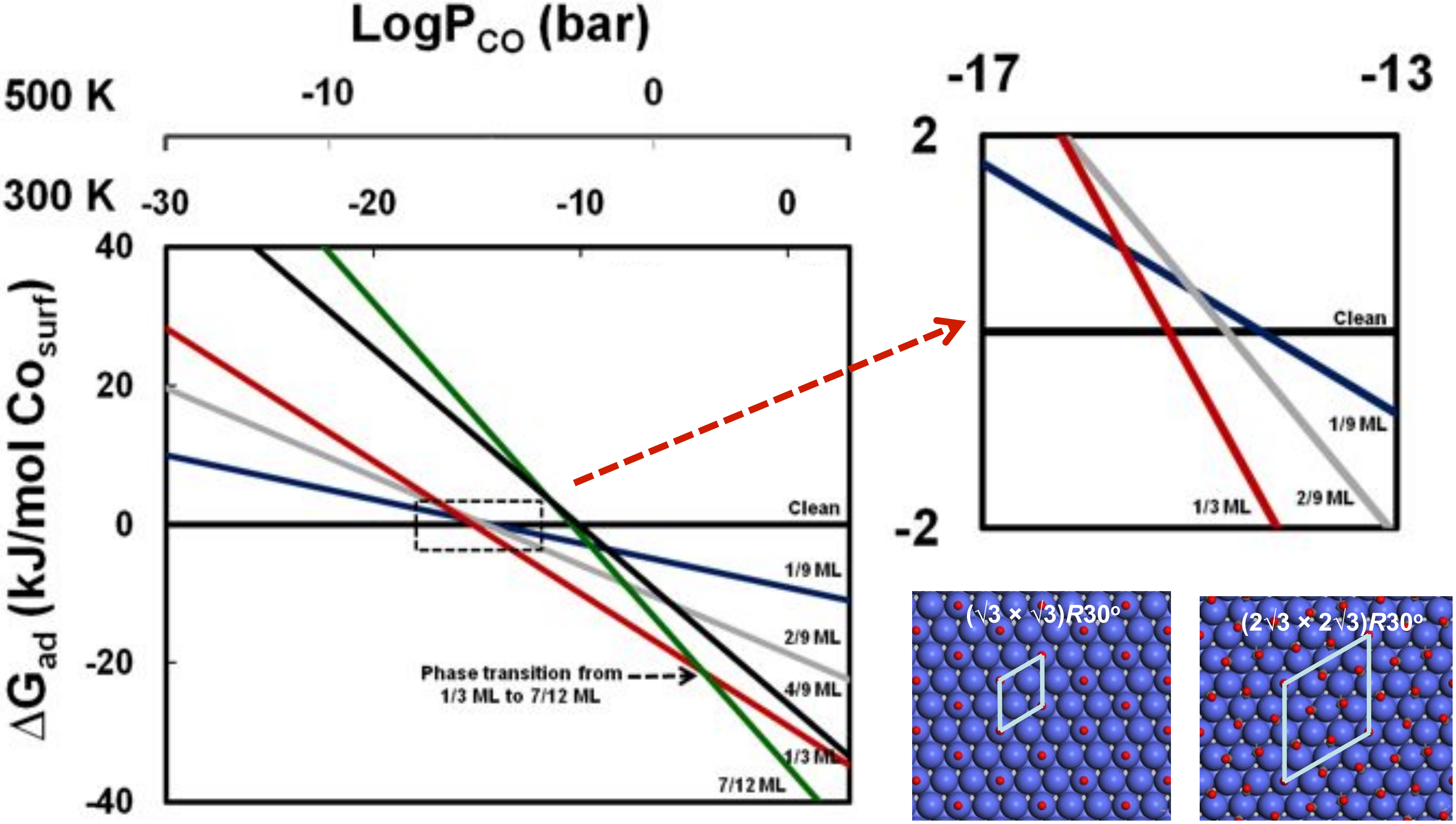
Stability: $\Delta G_{ads}(T, p) = \Delta H_{ads}^{0}(T) + T\Delta S_{ads}(T) + RT\ ln(p/p_0)$

Differential $E_{ads:}$ Co-1/3 ML CO + CO(g) → Co-x ML-CO

Co terraces saturated at 1/3 ML (500 K, 7 bar CO)

Phase transition to 7/12 ML, not gradual increase

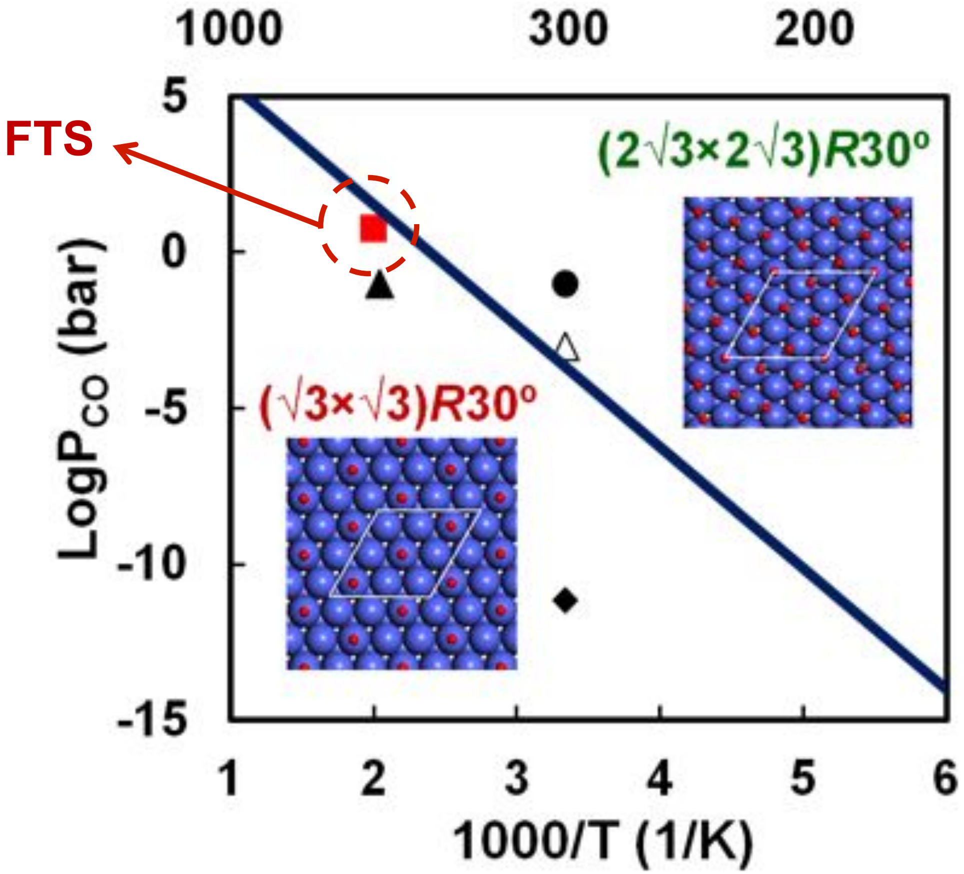
CO coverage on terraces. Phase transition



Low pressures: isolated (√3×√3)*R*30º-CO islands

Higher pressures: phase transition to (2√3×2√3)*R*30º-7CO phase

Phase diagram CO on Co terraces



Two phases on Co terraces, separated by a first-order phase transition

Only two phases observed experimentally (LEED, RAIRS)

Calculations reproduce exp. phase transitions

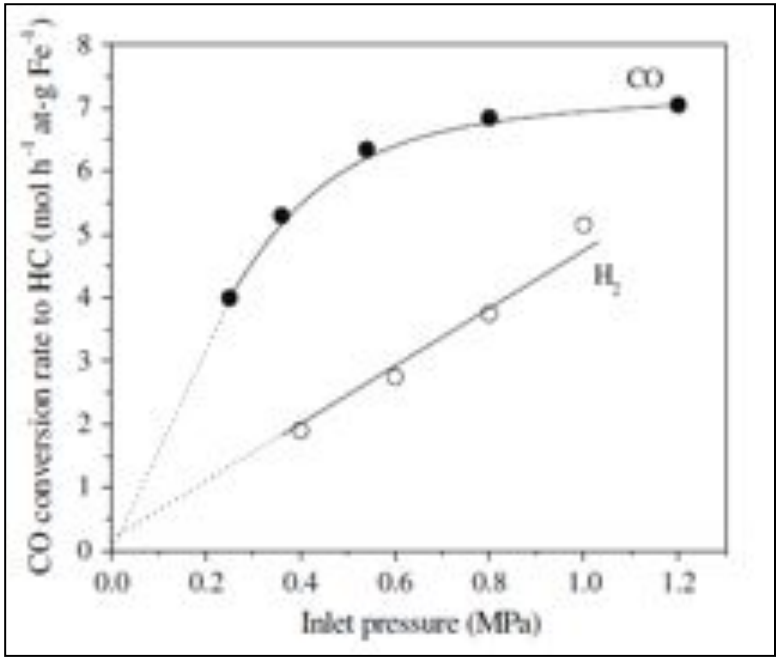
Coverage under FT: 1/3 ML or 7/12 ML

How does CO coverage affect kinetics?

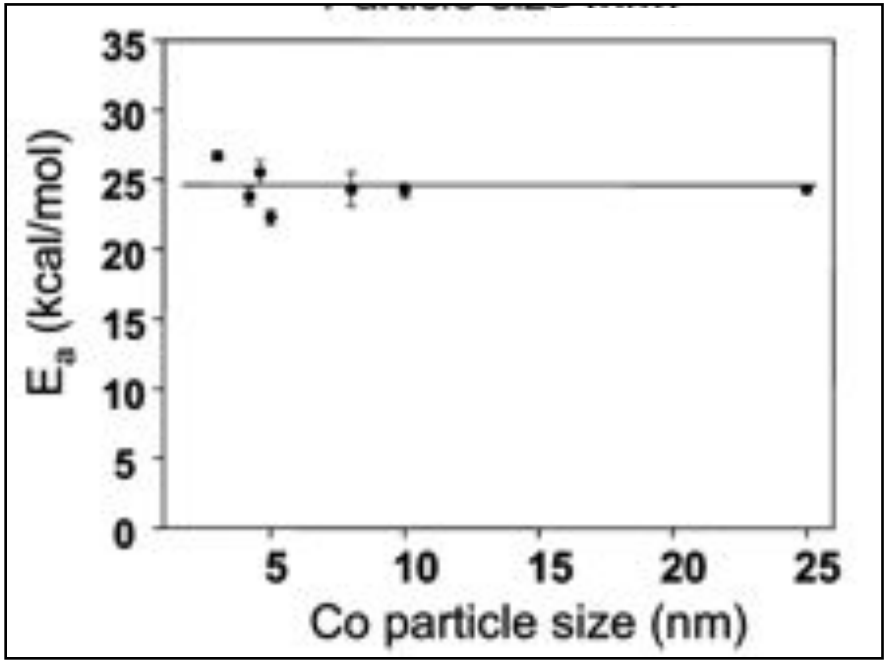
Zhou, Borgna, Saeys, J. Catal., **2013**; **Exp:** Bridge et al., Surf. Sci. **1977**; Beitel et al., JPC B **1997**

Kinetic Data for FTS

Reaction order and Activation energy



Iglesia et al., FTS over Fe at 235 ºC



Salmeron et al., 240 ºC and 1 bar

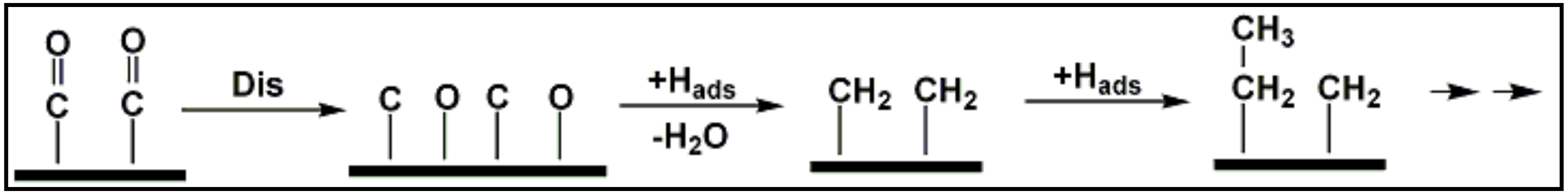
$$TOF = k_{surface}\,(K_{H2}\,p_{H2})^{1}\,(K_{CO}p_{CO})^{\sim 0}$$

$$E_{a,eff} = E_{surface} + \Delta H_{ads,H2} \qquad \Delta H_{ads,H2} \sim -50\ \text{kJ/mol}$$

$$E_{surface} \sim \underline{150\ \text{kJ/mol}}$$

Ojeda, Nabar, Milekar, Ishikawa, Mavrikakis, Iglesia, *J. Catal*. **2010;** Herranz, Deng, Cobot, Guo, Salmeron, *JPCB* **2009**

Carbide mechanism



- Brady-Pettit experiments with CH_2N_2: $CH_2 + CH_2$ coupling[1]

- C-C coupling on Co[2]:

  $RCH + C \rightarrow RCHC$ $E_a = 71$ kJ/mol

  $RCH + CH_2 \rightarrow RCHCH_2$ $E_a = 68$ kJ/mol

- CO dissociation on Co(0001):

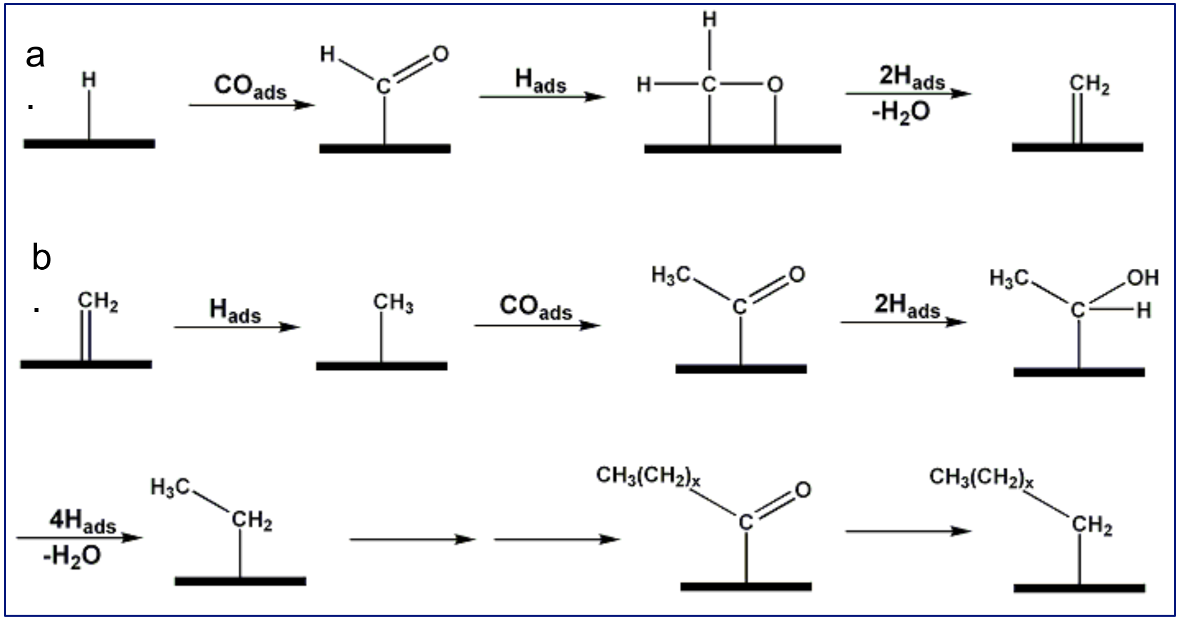
  $CO \rightarrow C + O$ $E_a = 218$ kJ/mol[3] and
  367 kJ/mol (high coverage)[4]

- CO dissociation slow → **low** C or CH_2 **coverage**

→**coupling slow compared to hydrogenation/termination**

1. Brady and Pettit, *JACS* **1980**; 2. Cheng, Hu, Ellis, French, Kelly, Lok, *J. Cat.* **2008**
3. Ge, Neurock, *JPC B* **2006**; 4. Ojeda, Nabar, Nilekar, Ishikawa, Mavrikakis, Iglesia, *J. Cat*. **2010**

CO insertion mechanism



a. H-assisted CO activation[1,2]

Hydrogenation lowers C-O dissociation to 82 kJ/mol[1]

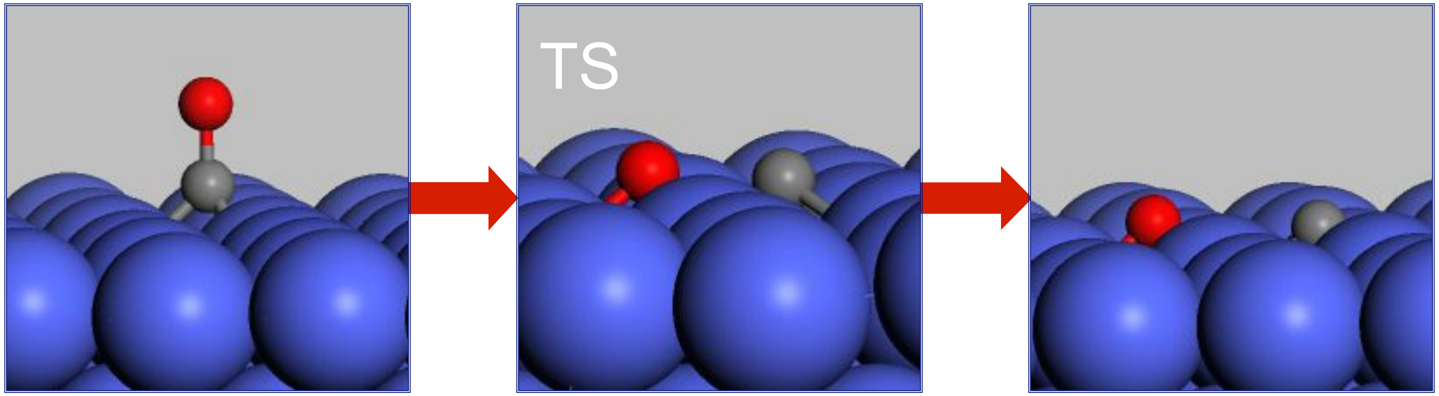
b. CO insertion (Pichler and Schulz, 1970)

RCH_2 + CO - High calculated barrier (182 kJ/mol[3])

Alternative CO insertion steps can be envisioned

1. Inderwildi, Jenkins, King, *JPCC* **2007**; 2. Ojeda, Nabar, Nilekar, Ishikawa, Mavrikakis, Iglesia, *J. Cat*. **2010**; 3. Cheng, Hu, Ellis, French, Kelly, Lok, *JPCC* **2008**

CO activation

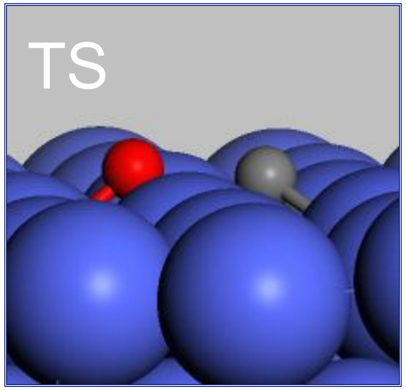


E_a: 220 kJ/mol
ΔH_r: +53 kJ/mol

Kinetically difficult due to high CO activation barrier
Should be zero order in p_{H2}

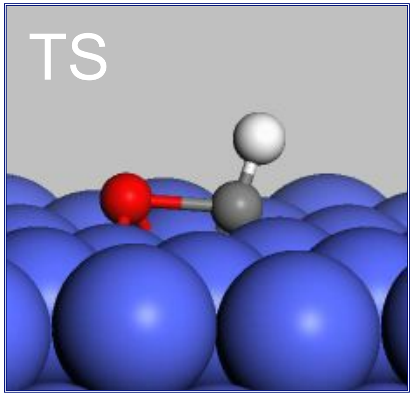
H-assisted CO activation

$CO \rightarrow C + O$



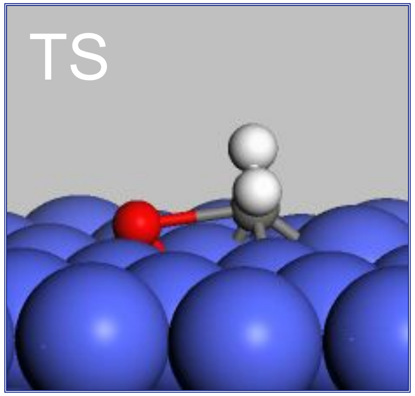
E_a: 220 kJ/mol
ΔH_r: +53 kJ/mol

$HCO \rightarrow CH + O$



E_a: 90 kJ/mol
ΔH_r: -97 kJ/mol

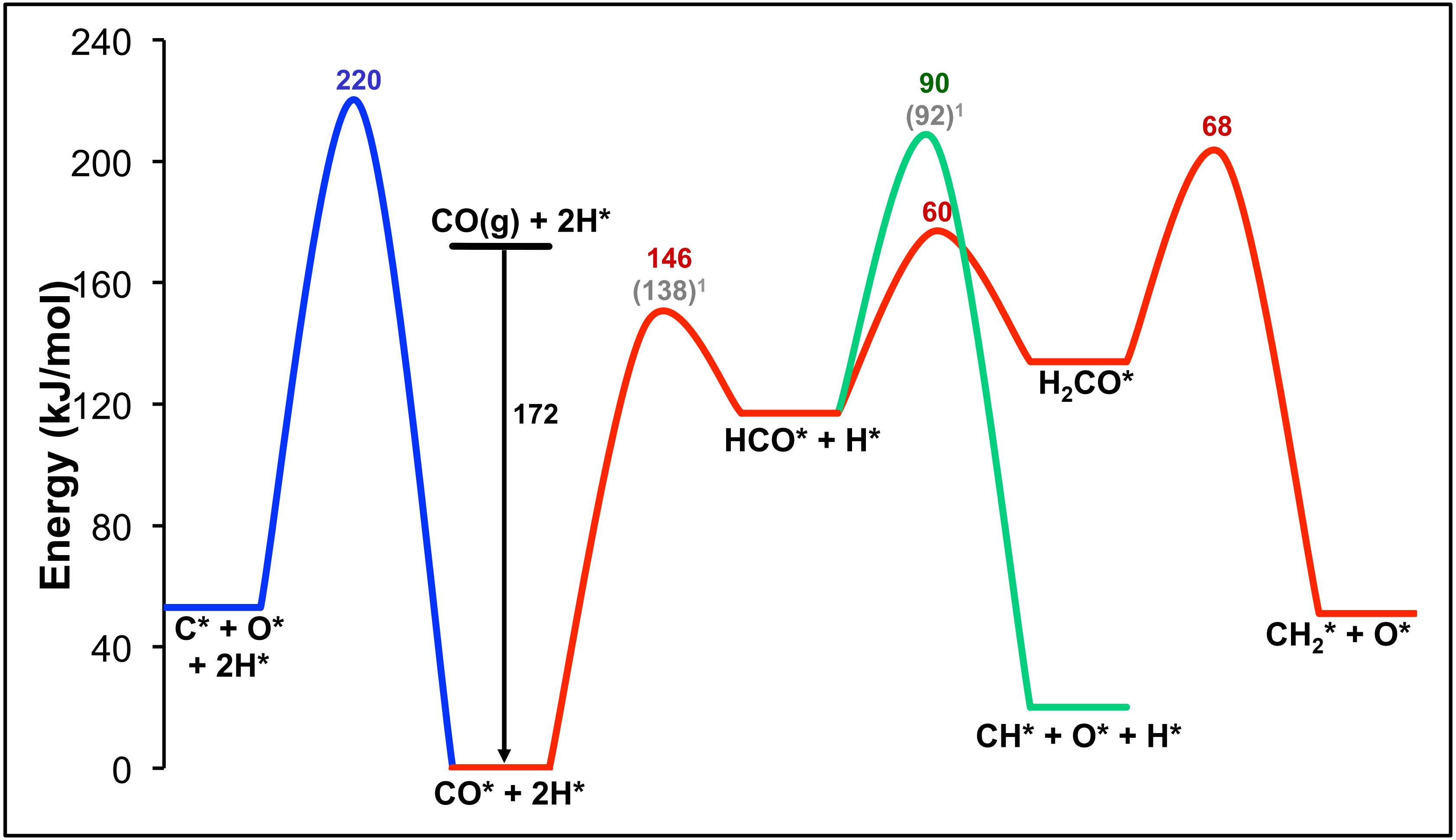
$H_2CO \rightarrow CH_2 + O$



E_a: 68 kJ/mol
ΔH_r: -83 kJ/mol

Hydrogenation lowers C–O dissociation barrier
Could be 0.5 to 1.0 order in p_{H2}

H-assisted CO activation: Energy Profile



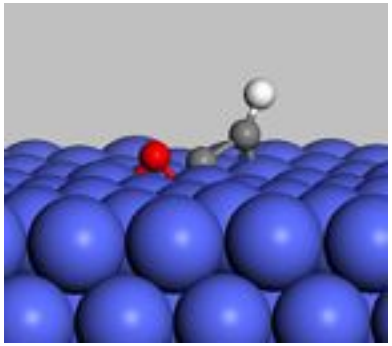
First hydrogenation difficult, but faster than CO activation

[1] Ojeda, Nabar, Nilekar, Ishikawa, Mavrikakis, Iglesia, *J. Catal*. **2010;** Zhuo, Tan, Borgna, Saeys, JPCC, **2009**

Effect of coupling on C–O dissociation barrier

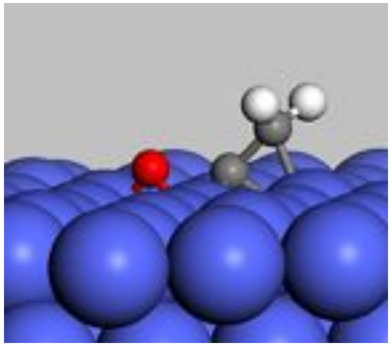
For RC=O

$CHCO \rightarrow CHC + O$



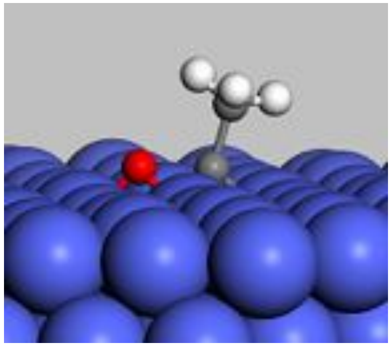
E_a: 180 kJ/mol
ΔH_r: -35 kJ/mol

$CH_2CO \rightarrow CH_2C + O$



E_a: 95 kJ/mol
ΔH_r: -72 kJ/mol
E_a: 70 kJ/mol, Jenkins et al.[1]

$CH_3CO \rightarrow CH_3C + O$



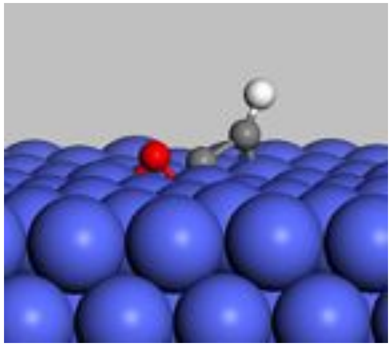
E_a: 72 kJ/mol
ΔH_r: -78 kJ/mol

Ref: Zhuo, Tan, Borgna, Saeys, *JPCC*, **2009**; Inderwildi, King, Jenkins, *PCCP* **2009**

Effect of coupling on C–O dissociation barrier

For RC=O

$CHCO \rightarrow CHC + O$



E_a: 180 kJ/mol
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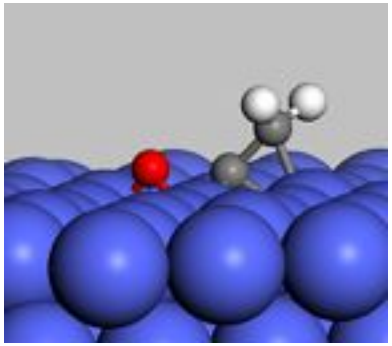
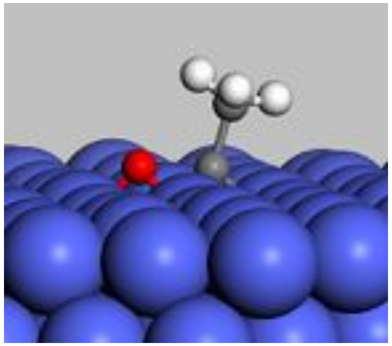


E_a: 95 kJ/mol
ΔH_r: -72 kJ/mol

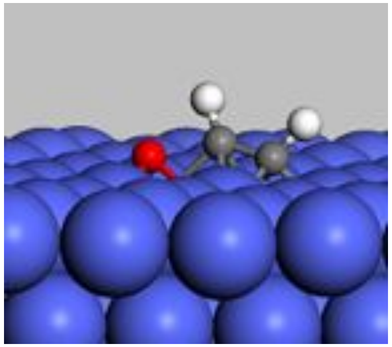
$CH_3CO \rightarrow CH_3C + O$



E_a: 72 kJ/mol
ΔH_r: -78 kJ/mol

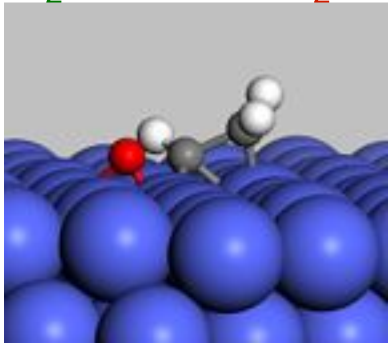
For RCH=O

$CHCHO \rightarrow CHCH + O$



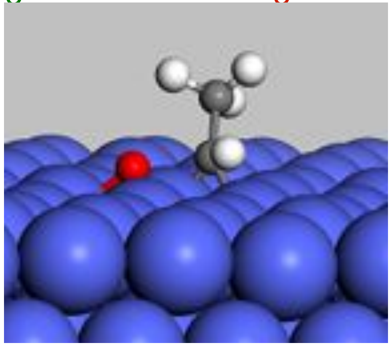
E_a: 70 kJ/mol
ΔH_r: -102 kJ/mol

$CH_2CHO \rightarrow CH_2CH + O$



E_a: 132 kJ/mol
ΔH_r: -18 kJ/mol

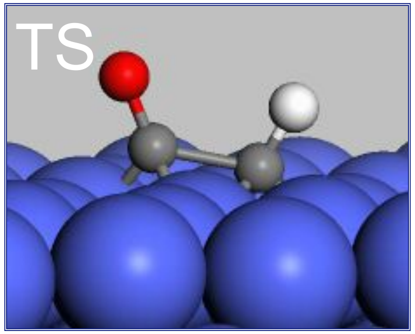
$CH_3CHO \rightarrow CH_3CH + O$



E_a: 61 kJ/mol
ΔH_r: -48 kJ/mol

CO insertion mechanism: C–C coupling

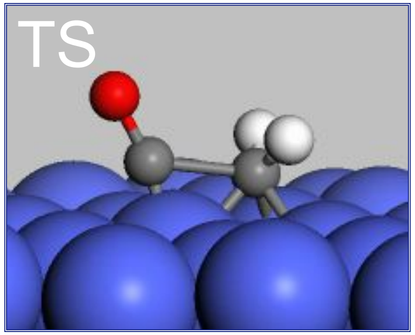
$CH + CO \rightarrow CHCO$



E_a: 96 kJ/mol

ΔH_r: +51 kJ/mol

$CH_2 + CO \rightarrow CH_2CO$

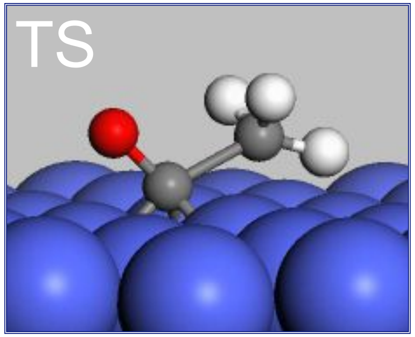


E_a: 74 kJ/mol

E_a: 53 kJ/mol, Jenkins et al.

ΔH_r: +60 kJ/mol

$CH_3 + CO \rightarrow CH_3CO$

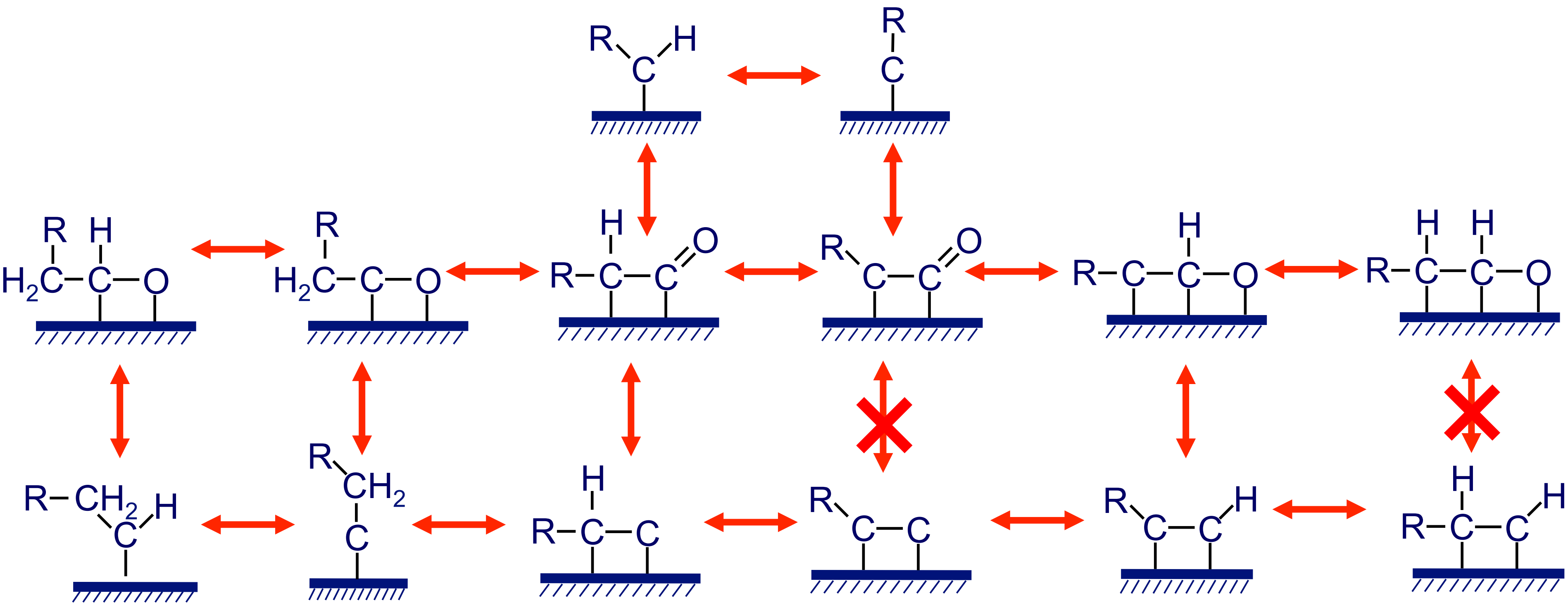


E_a: 180 kJ/mol

ΔH_r: +67 kJ/mol

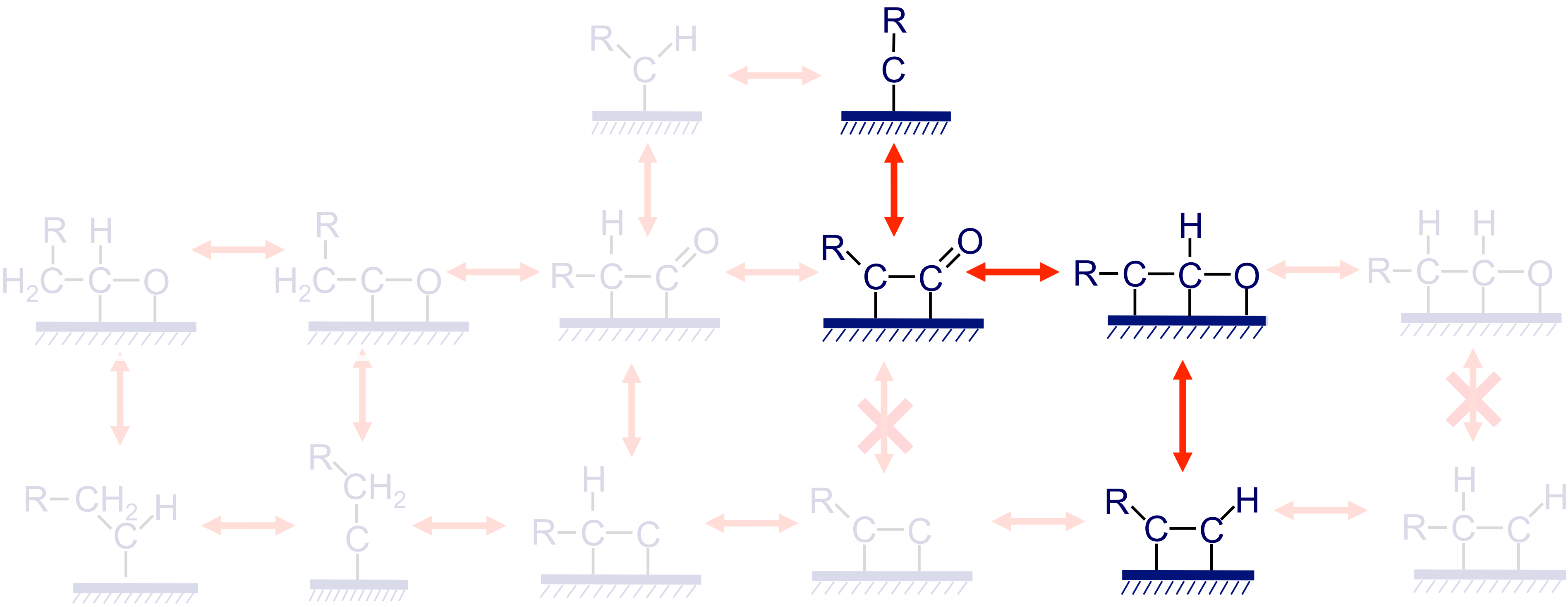
Zhuo, Tan, Borgna, Saeys, *JPCC*, **2009**

CO insertion mechanism: Hydrogenation steps



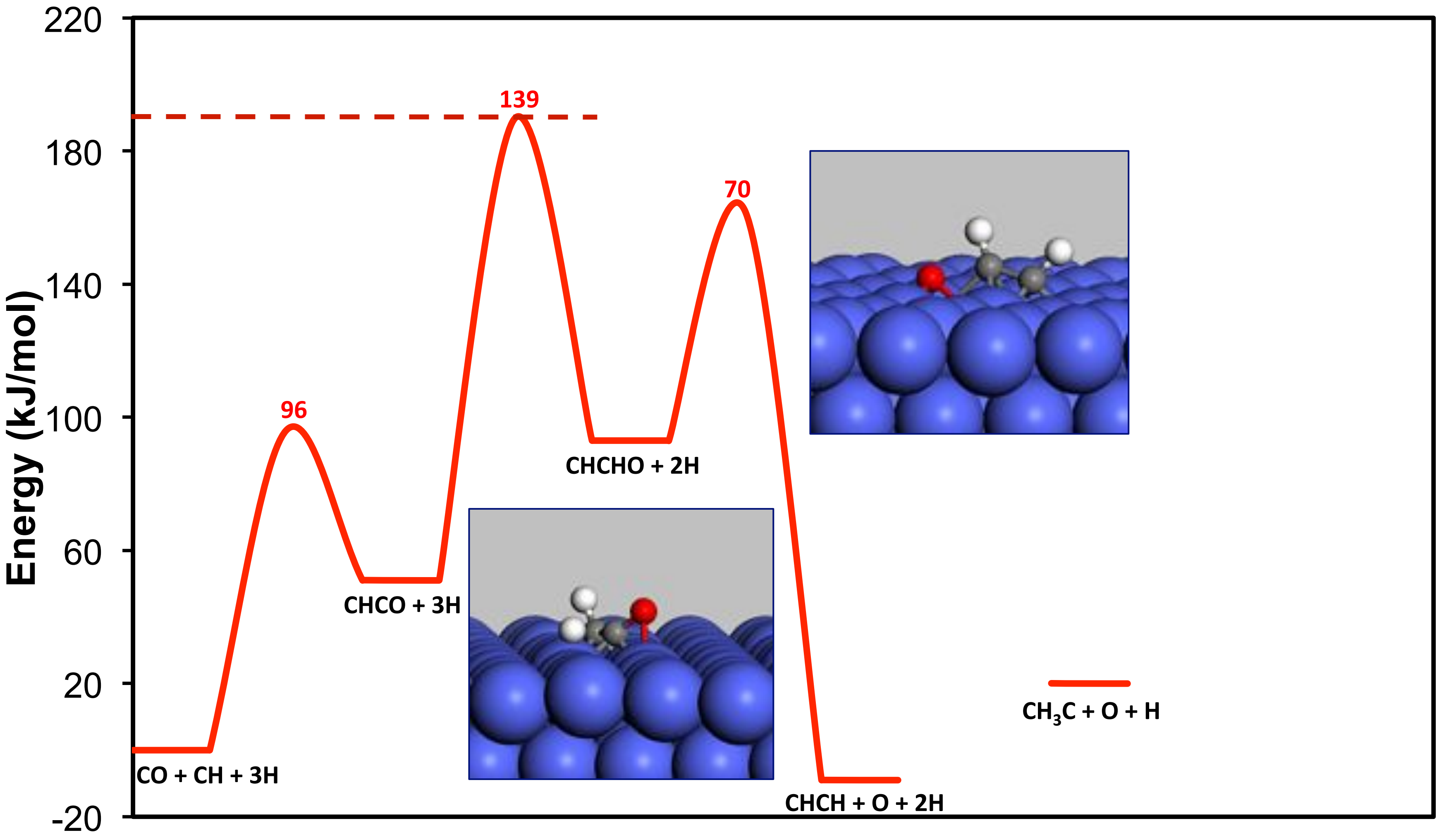
2 possible C-C coupling steps
4 possible C-O scission steps

CO insertion mechanism: RCCH-O Path



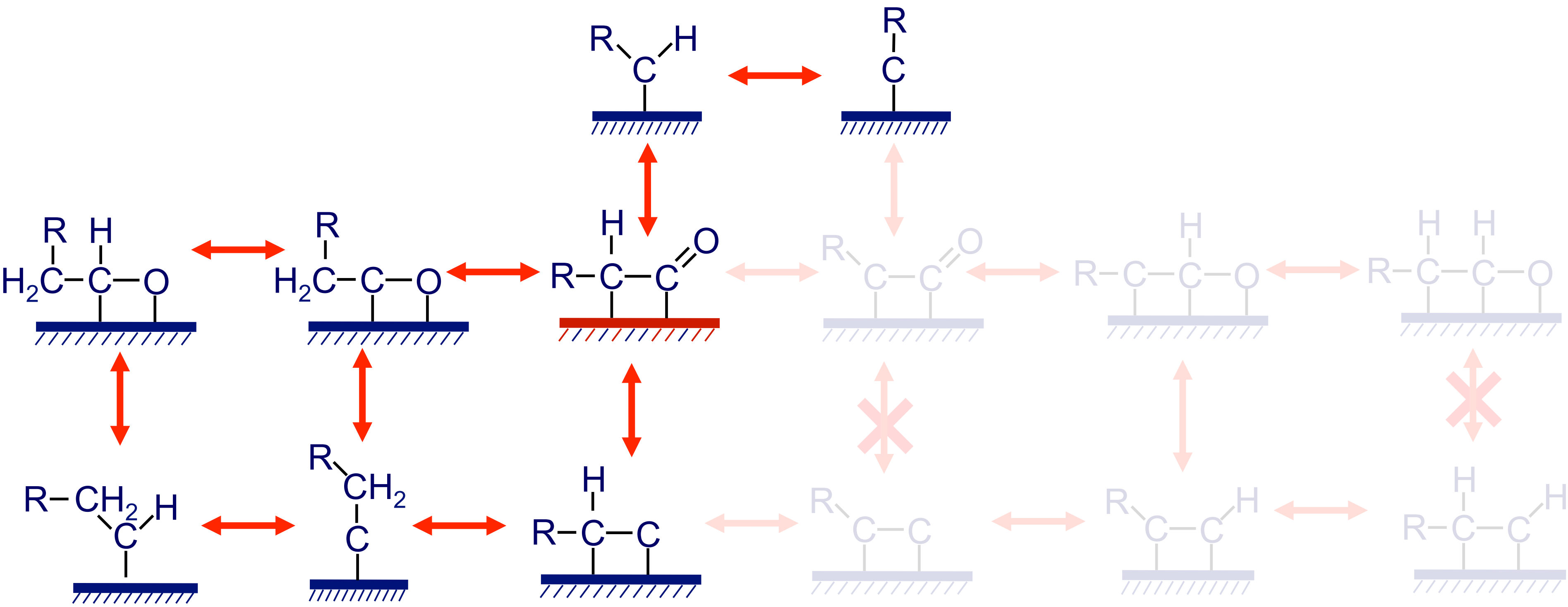
2 possible C-C coupling steps
4 possible C-O scission steps

CO insertion mechanism: RCCH-O Path



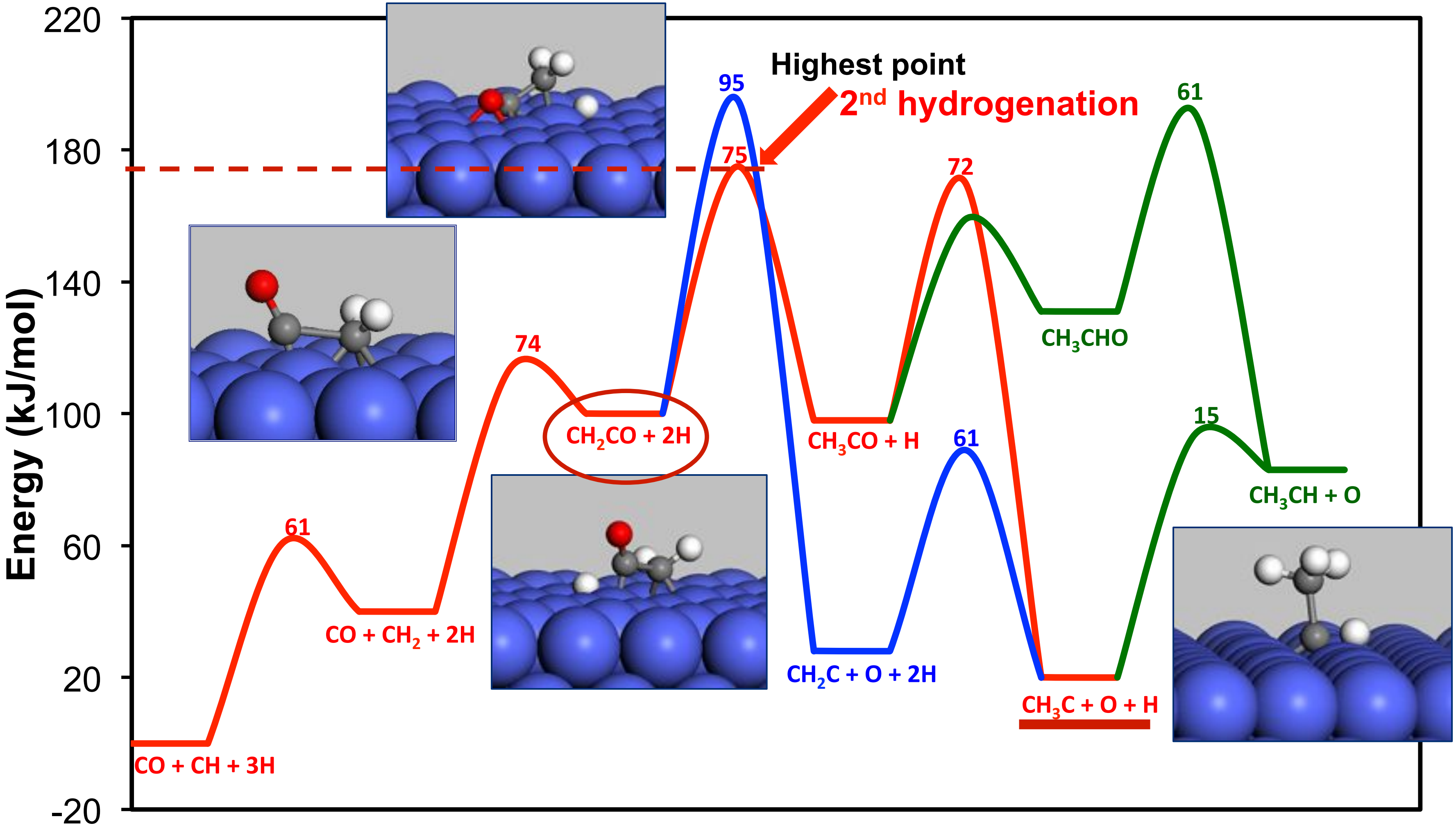
Effective barrier for surface reaction: 190 kJ/mol

CO insertion mechanism: RCHCO paths



2 possible C-C coupling steps
4 possible C-O scission steps

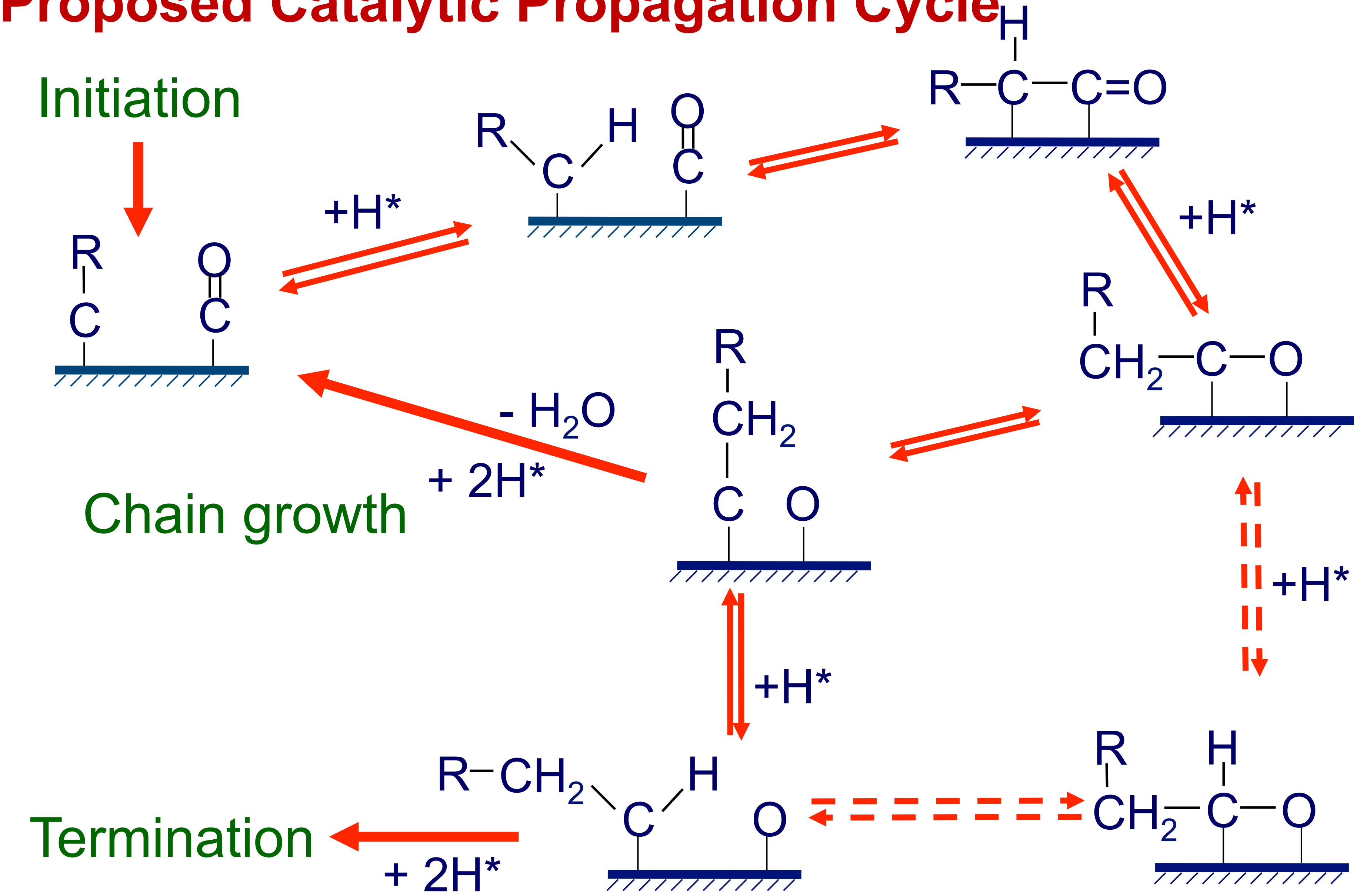
CO insertion mechanism: RCHCO paths



Propagation $E_{a,surface}$: 175 kJ/mol

Order in p_{H2} about 1.0

Proposed Catalytic Propagation Cycle

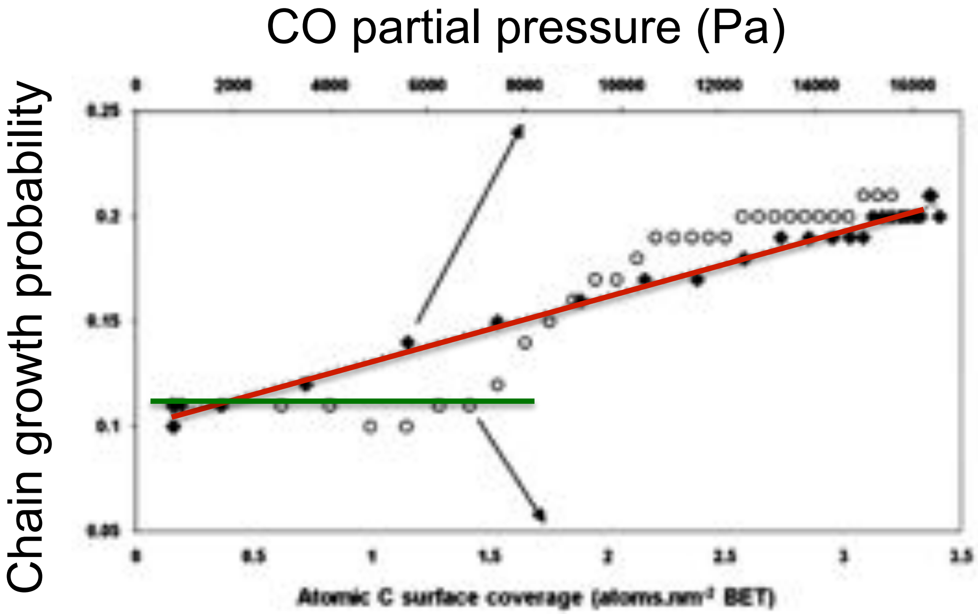


Initiation

Chain growth

Termination

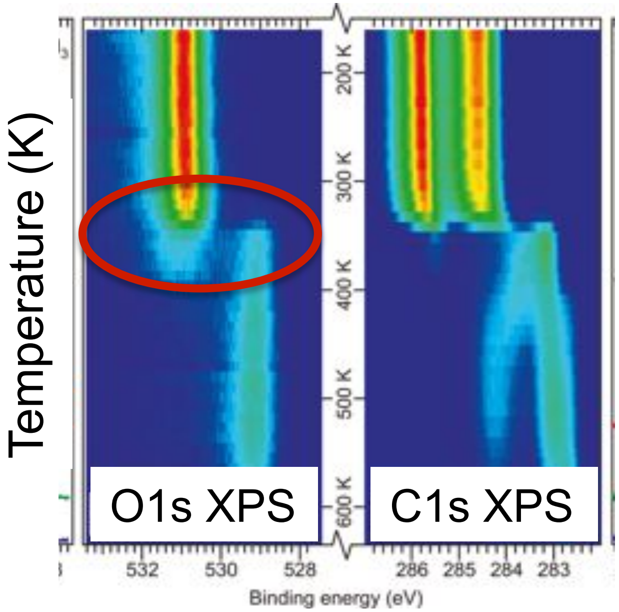
Experimental evidence for CO insertion mechanism



Transient kinetics on Co/MgO

Switch H_2/He -> H_2/CO/Ar

Chain growth ~ CO coverage



C-O scission in RCH_2C-O

Ethanol on Co(0001)

CH_3CHO* decomposes

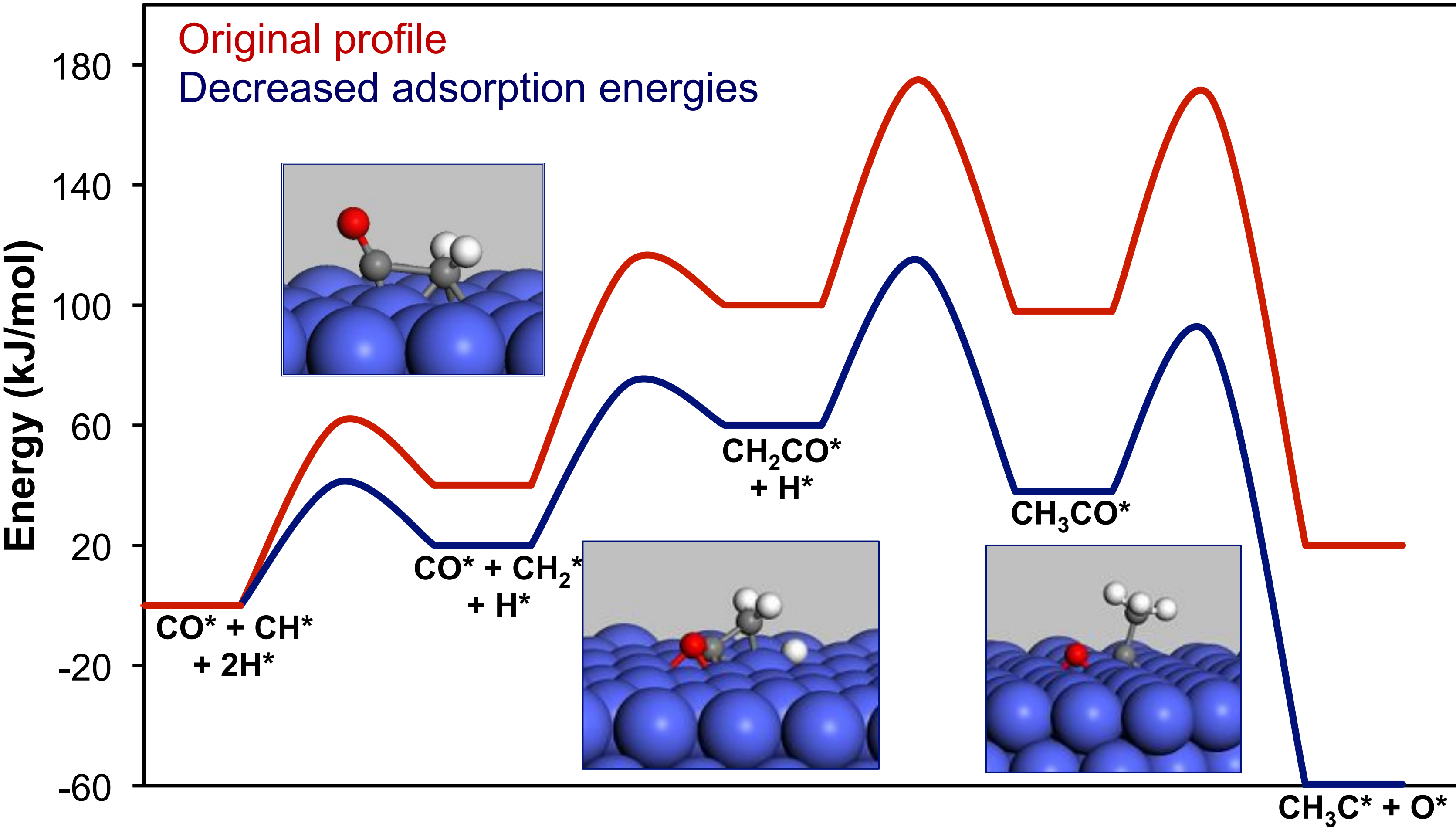
-> O at 370 K

CO* is chain growth monomer

Schweicher, Bundhoo, Kruse, *JACS* **2012;** Weststrate et al., *JPCL* **2010**

CO insertion mechanism: Effect of coverage

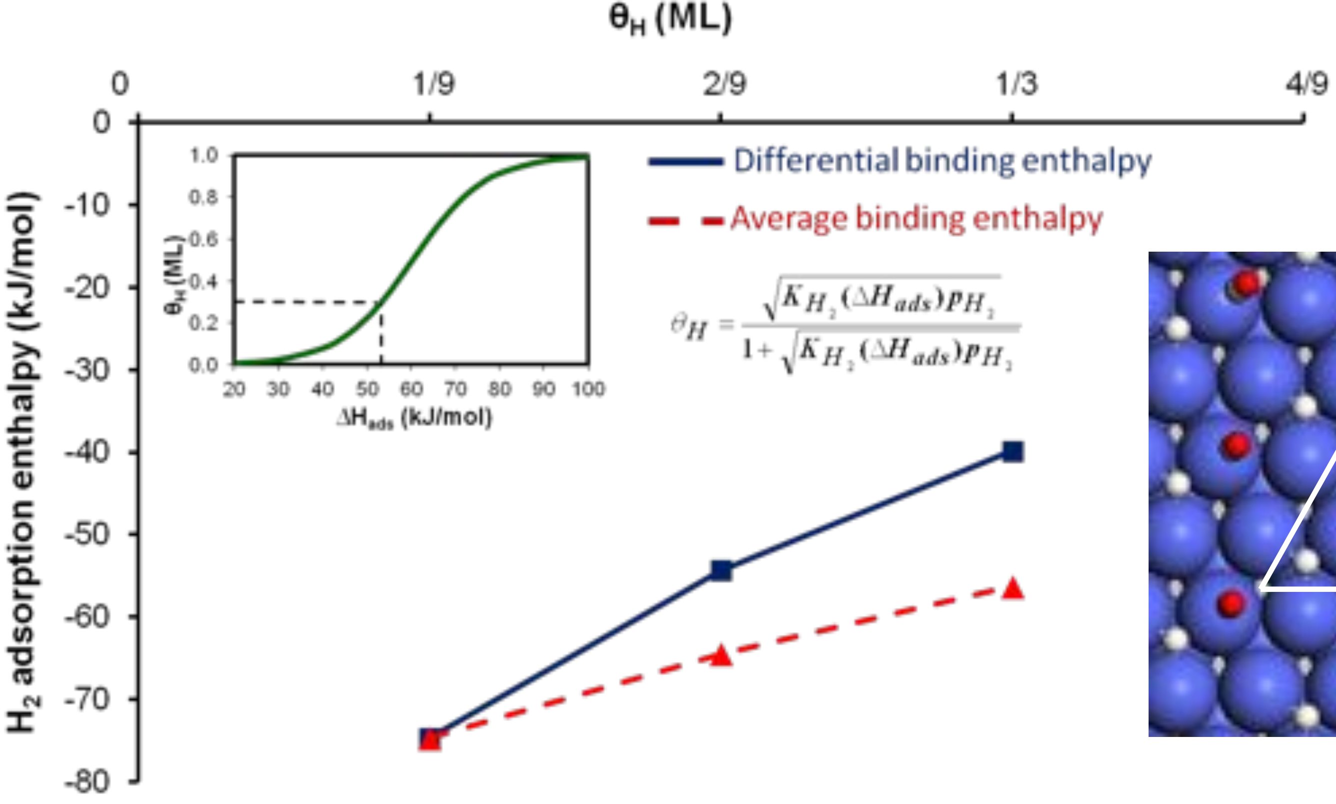
Energy profile: Decreased adsorption energies



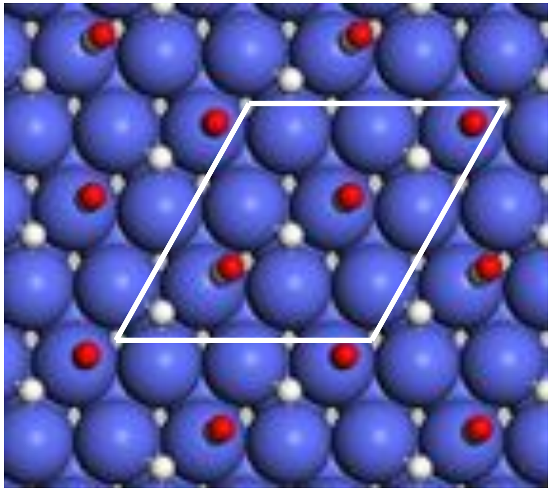
Original TOF: $3\ 10^{-7}\ s^{-1}$

TOF for “high coverage” cycle: $2\ 10^{-2}\ s^{-1}$

H Stability Diagram on (√3x√3)R30°-CO Co(0001)



$$\theta_H = \frac{\sqrt{K_{H_2}(\Delta H_{ads})p_{H_2}}}{1+\sqrt{K_{H_2}(\Delta H_{ads})p_{H_2}}}$$



CO destabilizes H atoms, from -121 kJ/mol on clean Co(0001)

H's populate hollow sites along CO diagonal

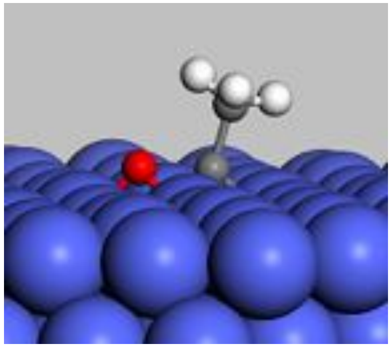
Binding energy decreases monotonically. No stable phases.

Langmuir isotherm with coverage dependent BE -> θ_H=0.3 ML

C–O dissociation on (√3x√3)R30°-CO Co(0001)

For RC=O

$CH_3CO \rightarrow CH_3C + O$

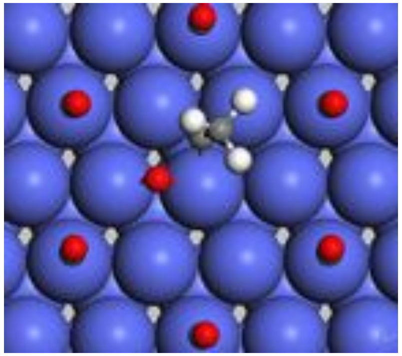


E_a: 72 kJ/mol

ΔH_r: -78 kJ/mol

C–O scission barrier increases

$CH_3CO \rightarrow CH_3C + O$

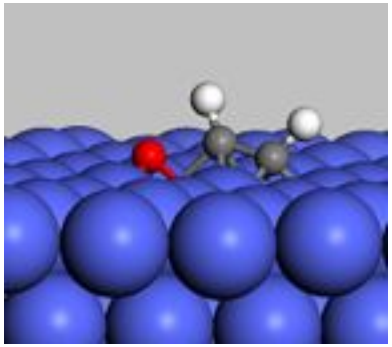


E_a: 89 kJ/mol

ΔH_r: -56 kJ/mol

For RCH=O

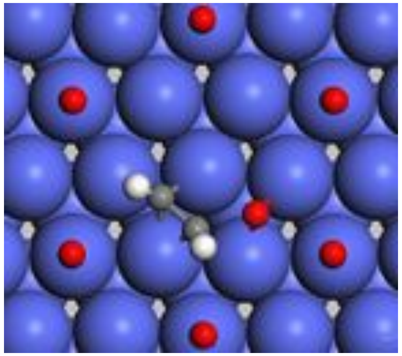
CHCHO → CHCH + O



E_a: 70 kJ/mol

ΔH_r: -102 kJ/mol

CHCHO → CHCH + O

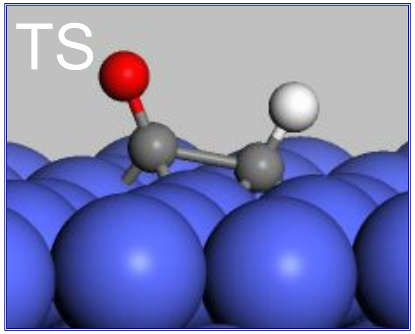


E_a: 105 kJ/mol

ΔH_r: -88 kJ/mol

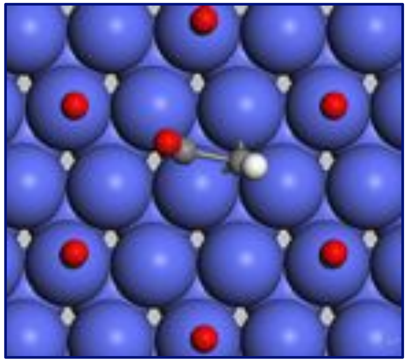
C–C coupling on (√3x√3)R30°-CO Co(0001)

CH + CO → CHCO



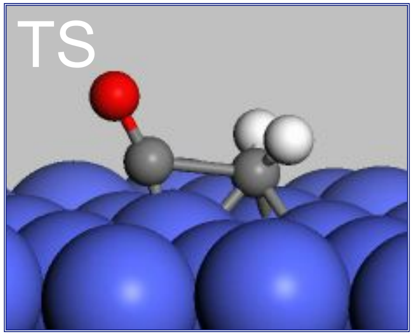
E_a: 96 kJ/mol
ΔH_r: +51 kJ/mol

C–C coupling barrier decreases

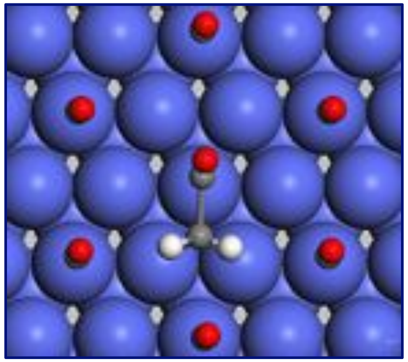


E_a: 89 kJ/mol
ΔH_r: +55 kJ/mol

CH_2+ CO → CH_2CO



E_a: 74 kJ/mol
ΔH_r: +60 kJ/mol

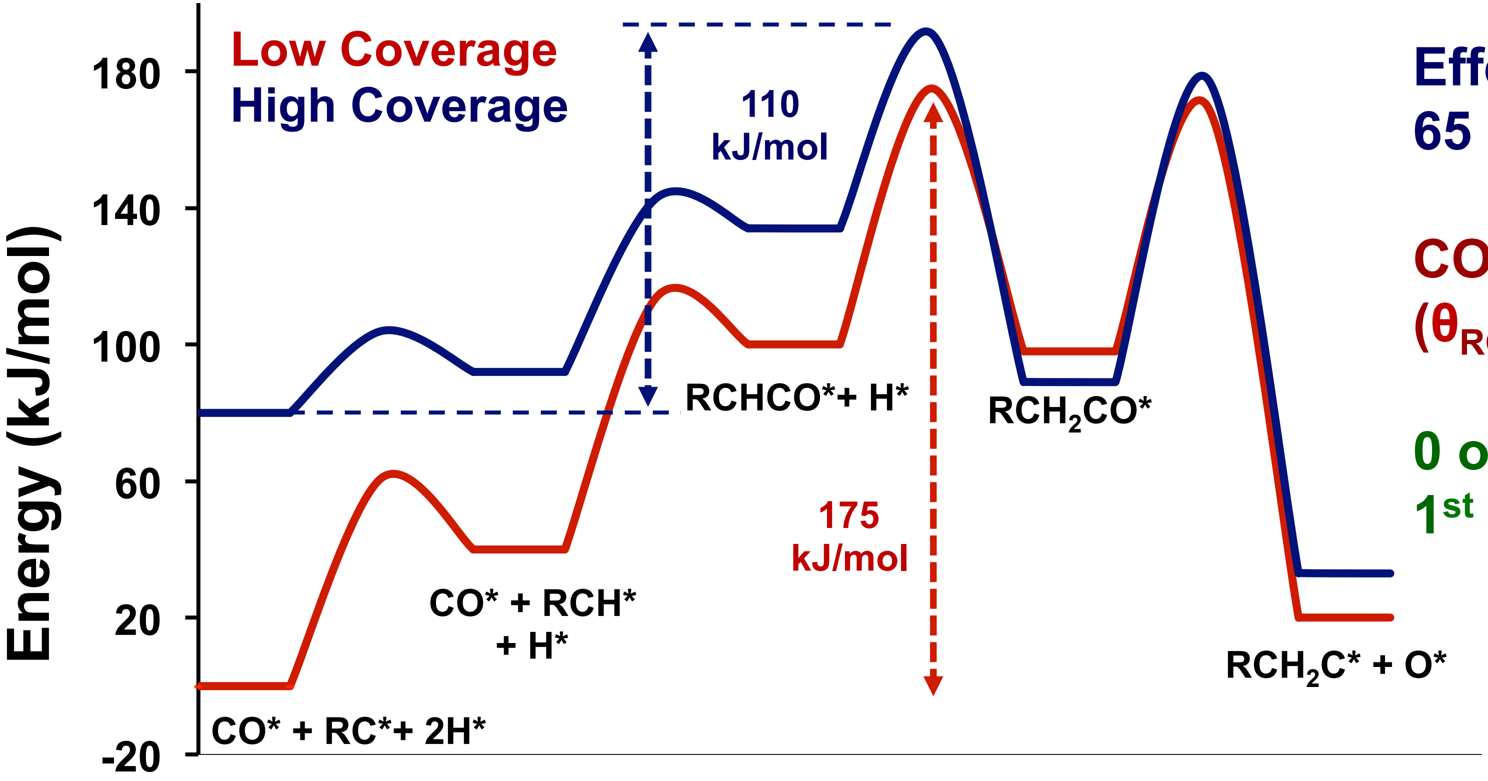


E_a: 51 kJ/mol
ΔH_r: +42 kJ/mol

Ref: Zhuo, Borgna, Saeys, J. Catal. 2013

CO insertion mechanism: Effect of coverage

CO insertion: $RCH_x + CO \rightarrow RCH_xCO \rightarrow RCH_xC + O$



Effective barrier 65 kJ/mol lower

CO TOF ~ 0.01 s^{-1} (θ_{RC} = 0.1 ML)

0 order in CO, 1st order in H_2

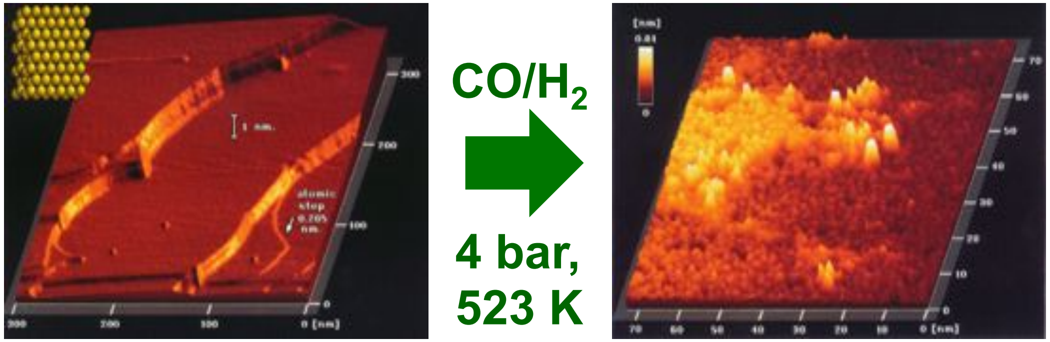
Initiation: How are CH* groups formed?

Coverage: Is 0.1 ML RC* reasonable?

Zhou, Borgna, Saeys, J. Catal., **2013**

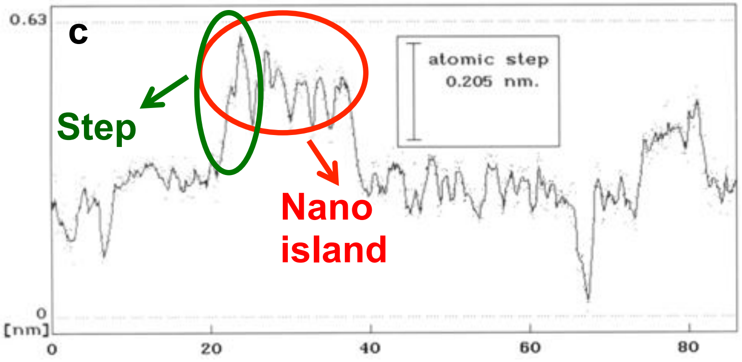
Massive reconstruction under FT conditions

STM images of Co(0001) single crystal



CO/H_2

4 bar, 523 K



Surface reconstruction and Co mobility

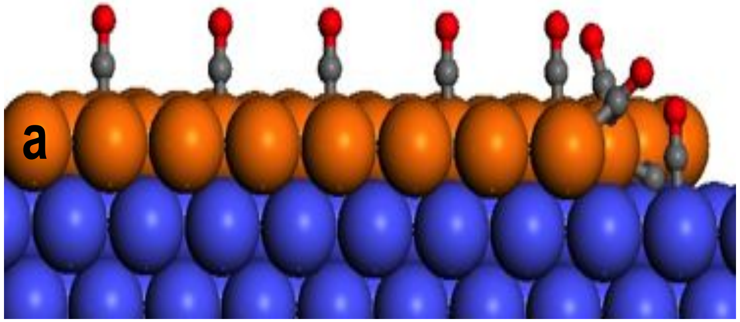
Monolayer nano-islands (~2 nm diameter) formed during FT synthesis

What drives the formation of those islands?

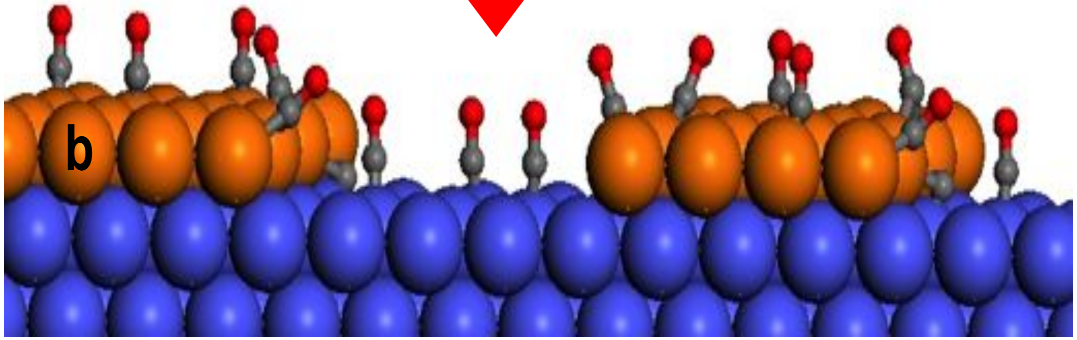
Wilson, de Groot, *J Phys Chem,* **1995**

Stability of Co islands

Step creation and island formation during FT



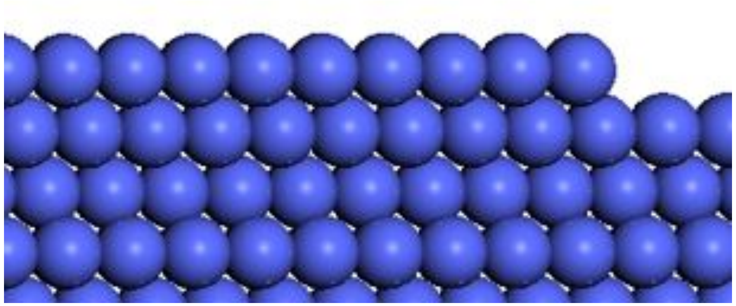
CO-covered terraces



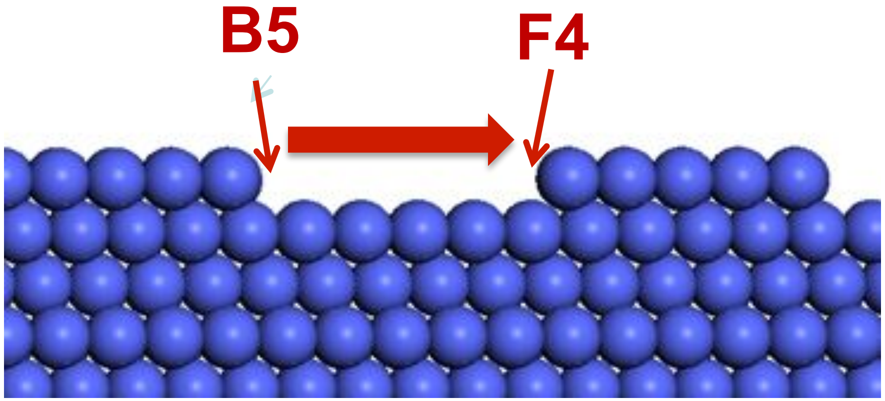
CO-covered nano-islands

Stability of Co islands

Step creation

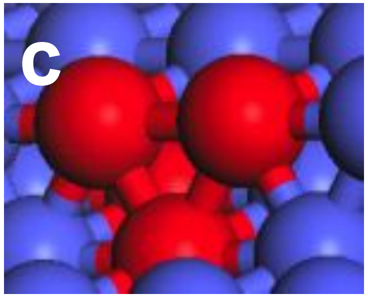


Clean Terraces

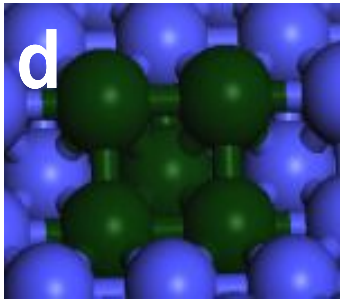


Formation of a step

Step creation: +80 kJ/mol step atoms (both sides)



F4 site



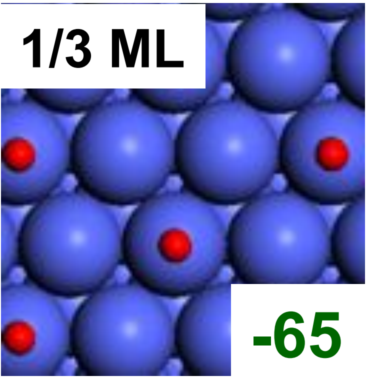
B5 site

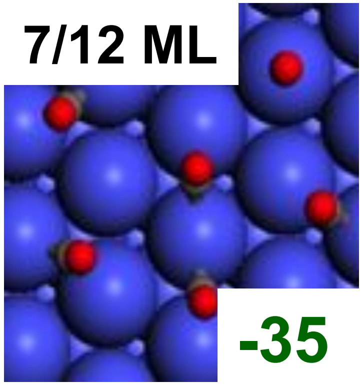
Does stronger adsorption stabilize the steps?

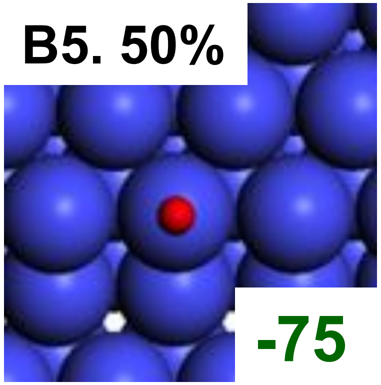
CO adsorption at step edges

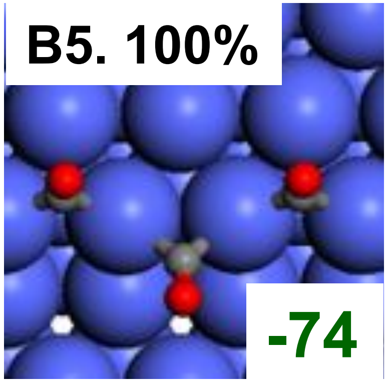
First principle CO adsorption free energy

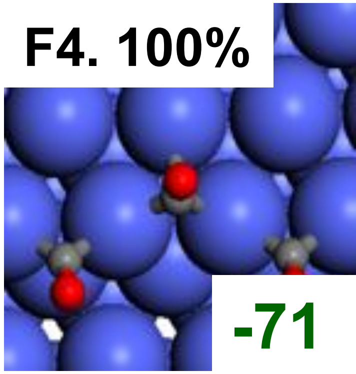
$$\Delta G_{ads}(T, p_{CO}) = \Delta H_{ads}(T,p_{CO}) – T\Delta S_{ads}(T, p_{CO}) + RT\ \ln(p_{co}/p_{o})$$











ΔG_{rxn} to create step:

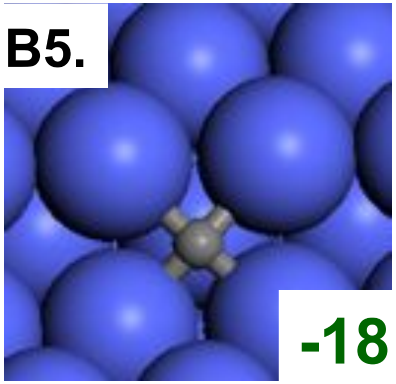
Desorption of CO (3 rows*1/3 ML*65 kJ/mol) + Step creation (80 kJ/mol)
- CO adsorption at B5 and F4 (100%*74 kJ/mol +100%* 71 kJ/mol)

~ 0 kJ/mol steps

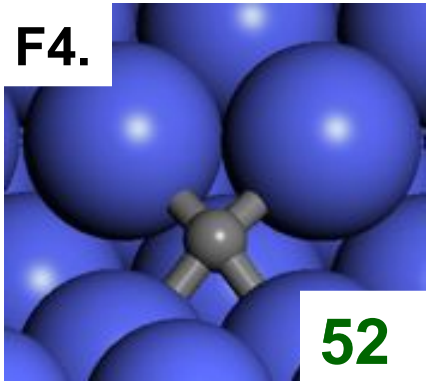
Stronger CO adsorption and high CO coverage overcome step-creation energy under FT conditions

Strong carbon adsorption

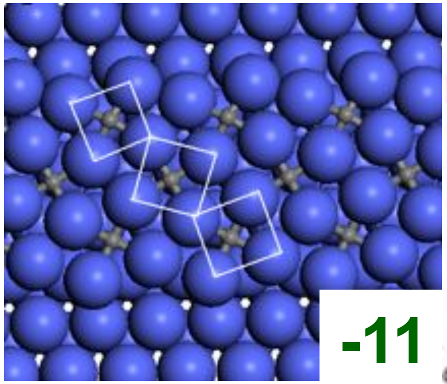
Carbon stability: ΔG_{rxn} for $CO(g) + H_2(g) \rightarrow [C]^* + H_2O(g)$



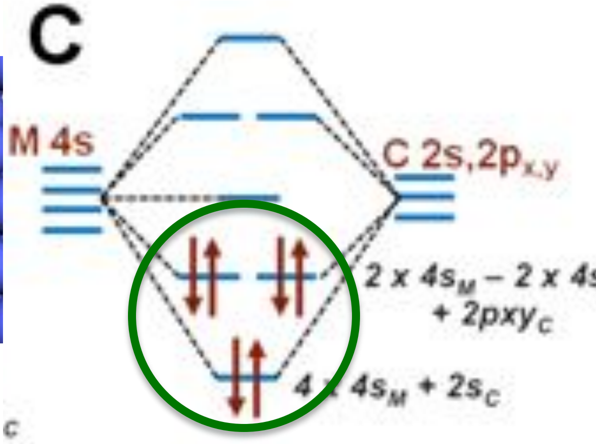
Carbon at B5 steps

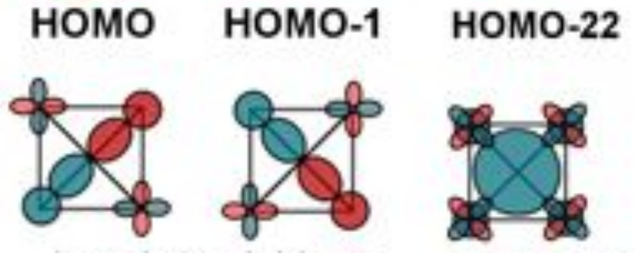


Carbon at fourfold steps



Surface carbide on islands





4n+2 Huckel rule
-> σ-aromaticity

Under FT conditions, Square planar carbon binds strongly at B5 site

Unique stability (cf. graphite: -47 kJ/mol) due to sigma aromaticity.

Tan, Xu, Chang, Borgna, Saeys, *J. Catal.*, **2010**; Alexandrova, Saeys, in preparation

What is the C/CO coverage at B5 steps?

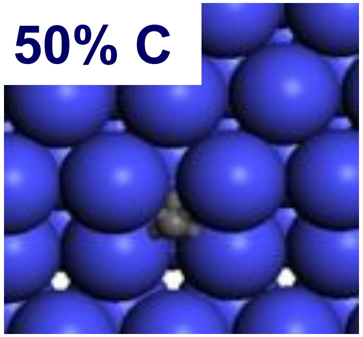
Carbon stability:

ΔG_{rxn} for $CO(g) + H_2(g) \rightarrow [C]^* + H_2O(g)$

Increase in C step coverage beyond 50% is not favorable

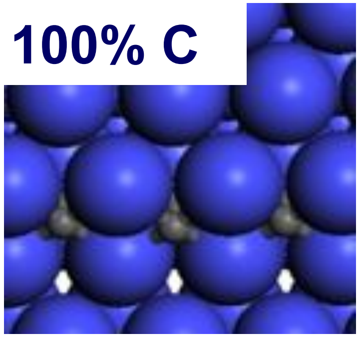
Can be understood from σ-aromaticity

50% C



-18

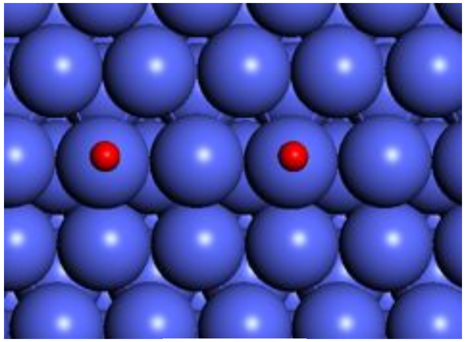
100% C



13

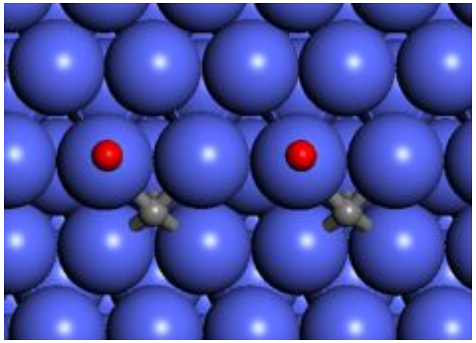
CO stability:

B5 50%



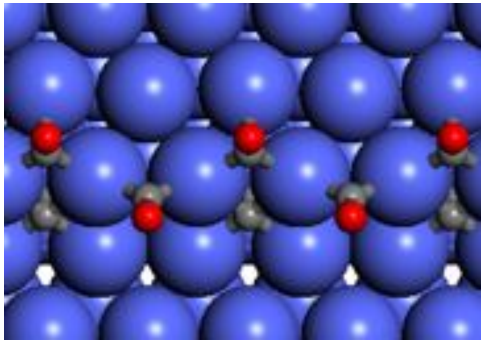
-75

50% C + 50% CO



-96

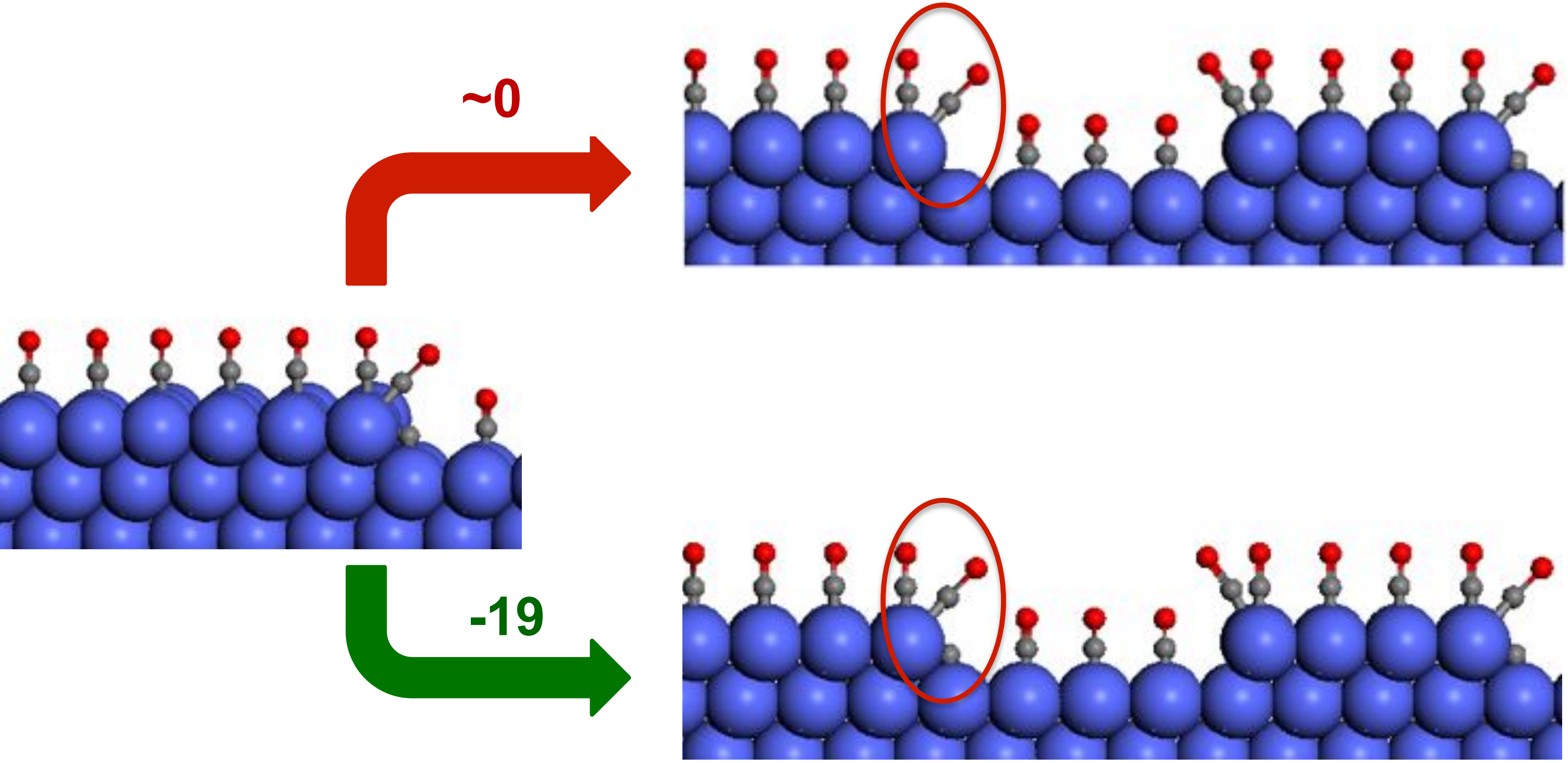
50% C + 100% CO



-84

Square planar C increases CO stability

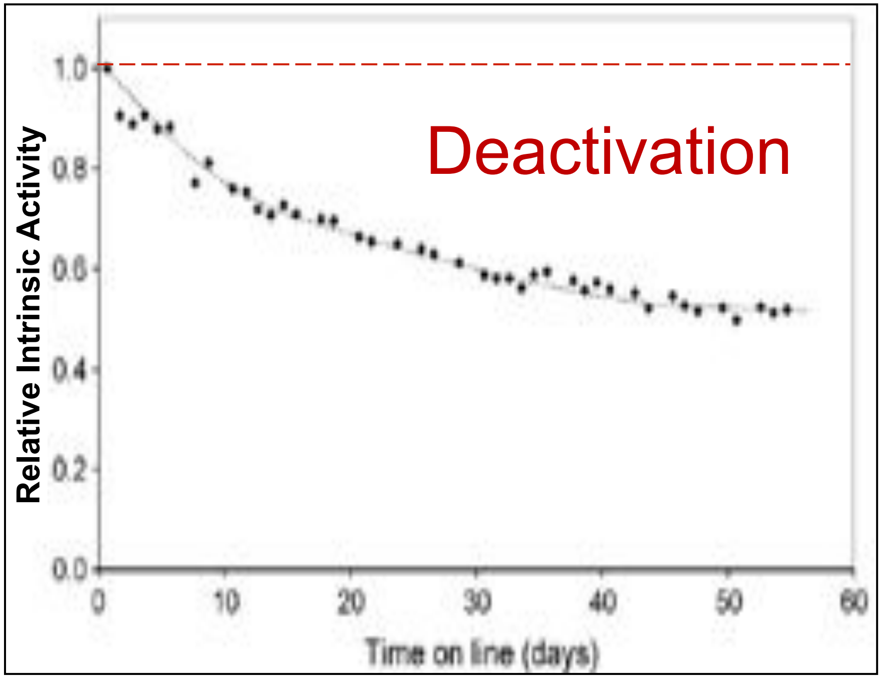
Stability of covered steps



50% C and 100% CO step edge coverage overcome energy penalty to create steps and stabilizes B5

Deactivation of Co catalysts during FTS

100 bbl/day bubble column pilot plant

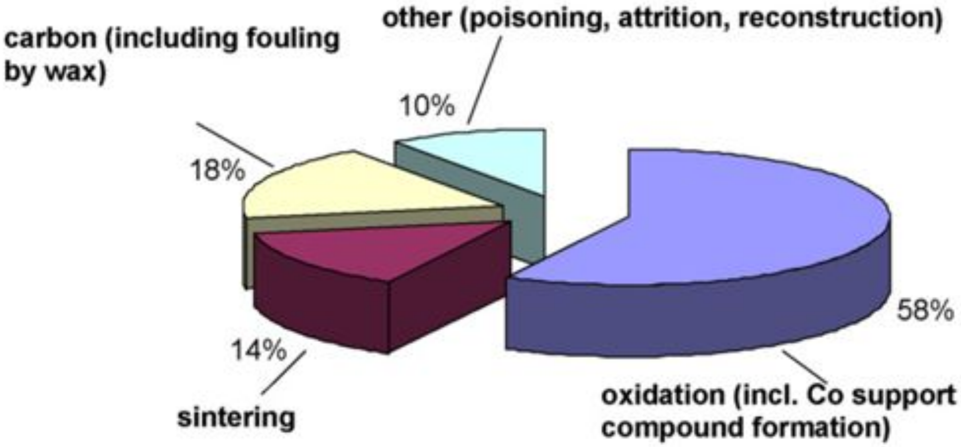


Conditions: 230 °C, 20 bar, $H_2/CO = 2$

Saib et al., *Appl. Catal. A*, **2006**
Moodley et al., *Appl. Catal. A*, **2009**
Saib et al., *Catal. Today*, **2010**

Slow deactivation under industrial FTS conditions

Various mechanisms have been proposed

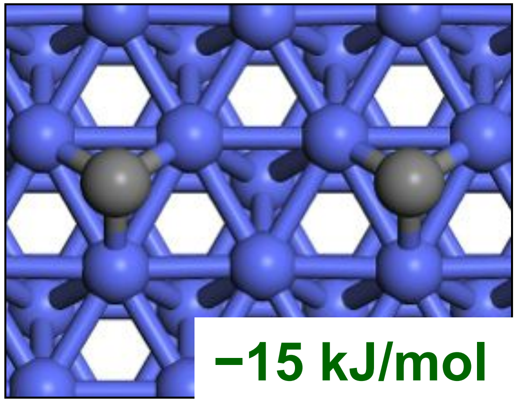


Stability of carbon species

Stability relative to a synthesis gas reservoir (PBE functional)

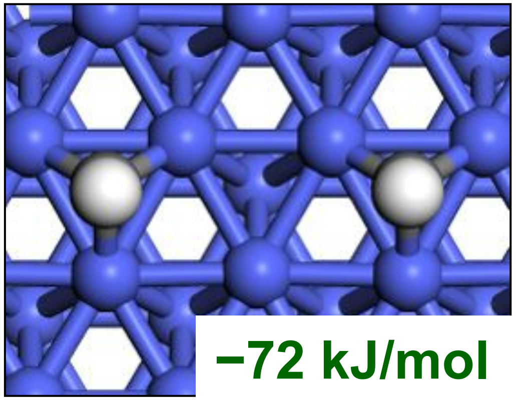
ΔG_{rxn}(220 ºC, 20 bar) for $CO(g) + (x/2+1)H_2(g) \longrightarrow [CH_x]^* + H_2O(g)$

Surface carbon



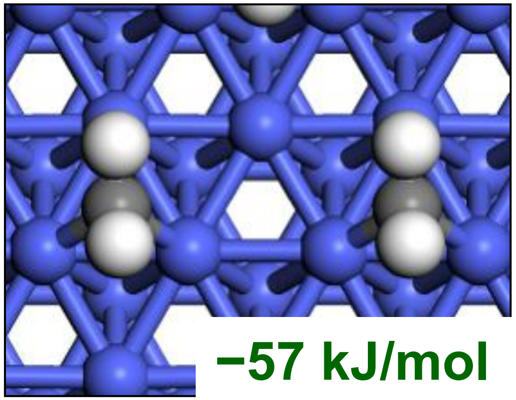
−15 kJ/mol

Surface CH



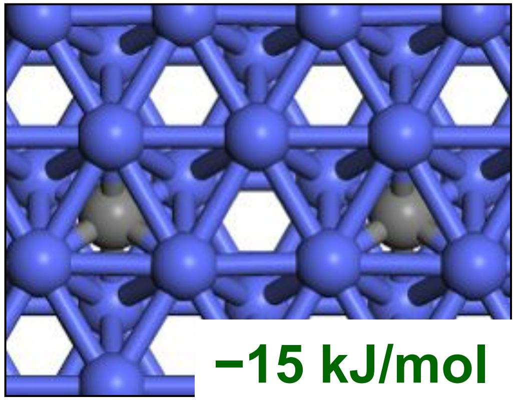
−72 kJ/mol

Surface CH_2



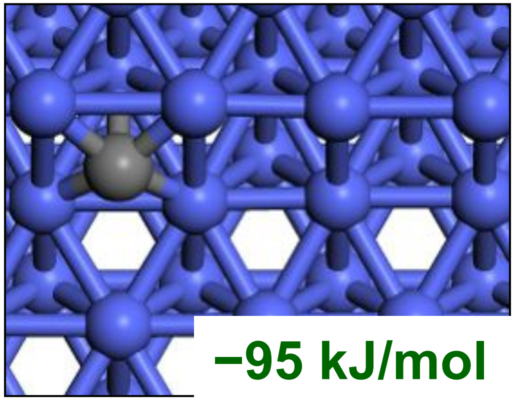
−57 kJ/mol

Subsurface carbon



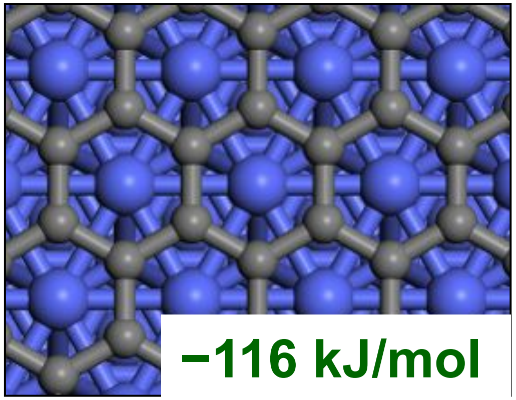
−15 kJ/mol

Step



−95 kJ/mol

Graphene



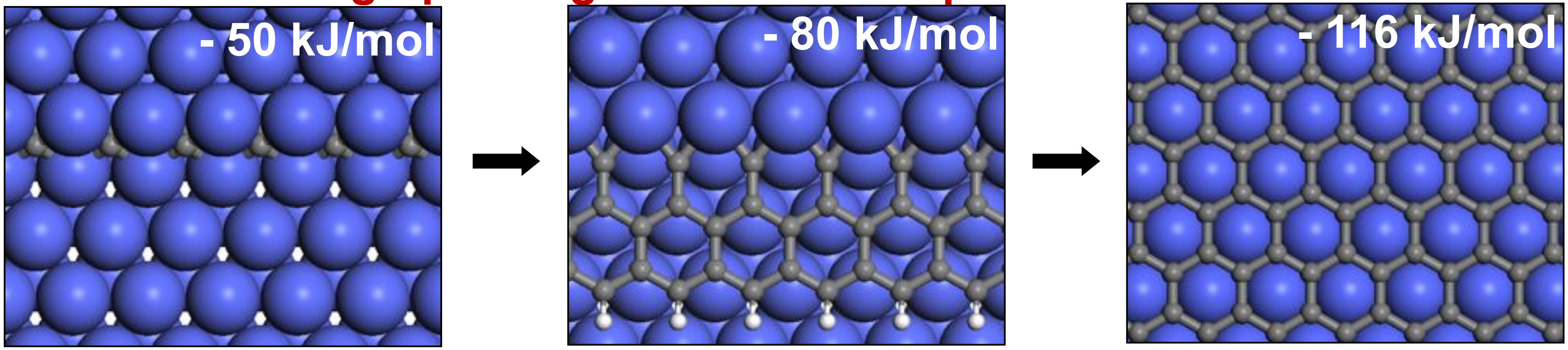
−116 kJ/mol

Stability of carbon species

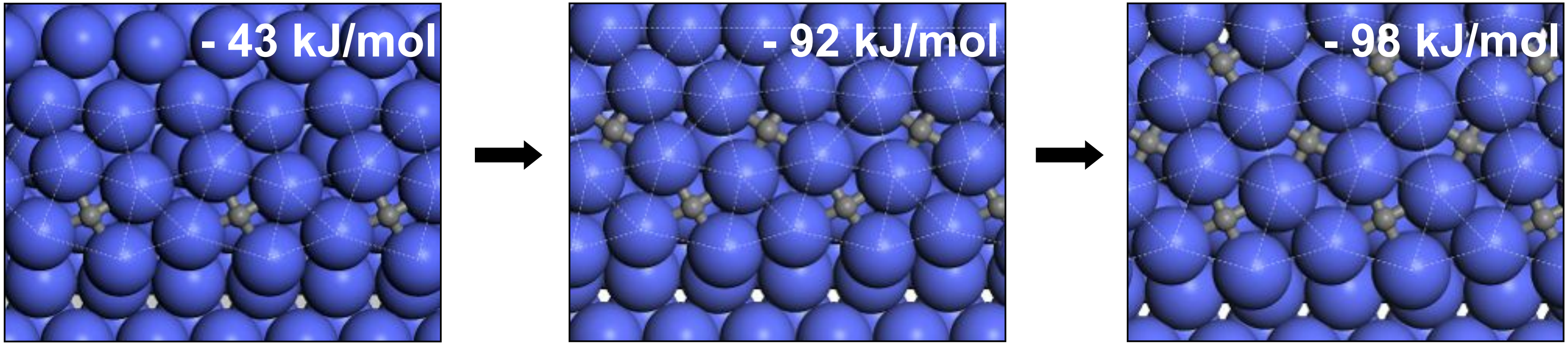
Stability relative to a synthesis gas reservoir

$$\Delta G_{rxn}(220\ ^{\circ}\mathrm{C},\ 20\ \mathrm{bar})\ \text{for}\ CO(g) + (x/2+1)H_2(g) \longrightarrow [CH_x]^* + H_2O(g)$$

Nucleation and graphene growth out of steps



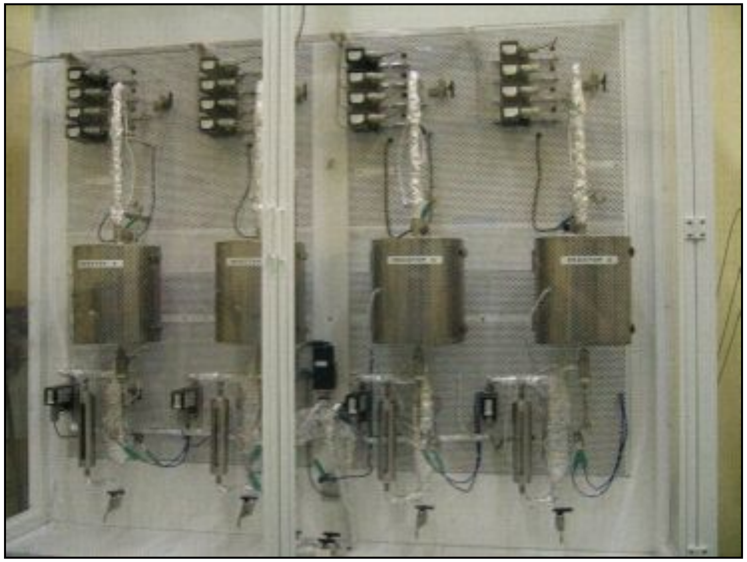
Diffusion into steps: p4g clock reconstruction



Experimental Procedure

Catalyst preparation

- 20 wt% Co/γ-Al_2O_3 catalyst, with 0.05 wt% Pt to improve reducibility
- Slurry impregnation of γ-Al_2O_3 with $Co(NO_3)_2$ and $[Pt(NH_3)_4](NO_3)_2$
- Calcination in air at 400 ºC for 2 hrs
- Reduction at 500 ºC for 12 hrs in 50 Nml/min H_2



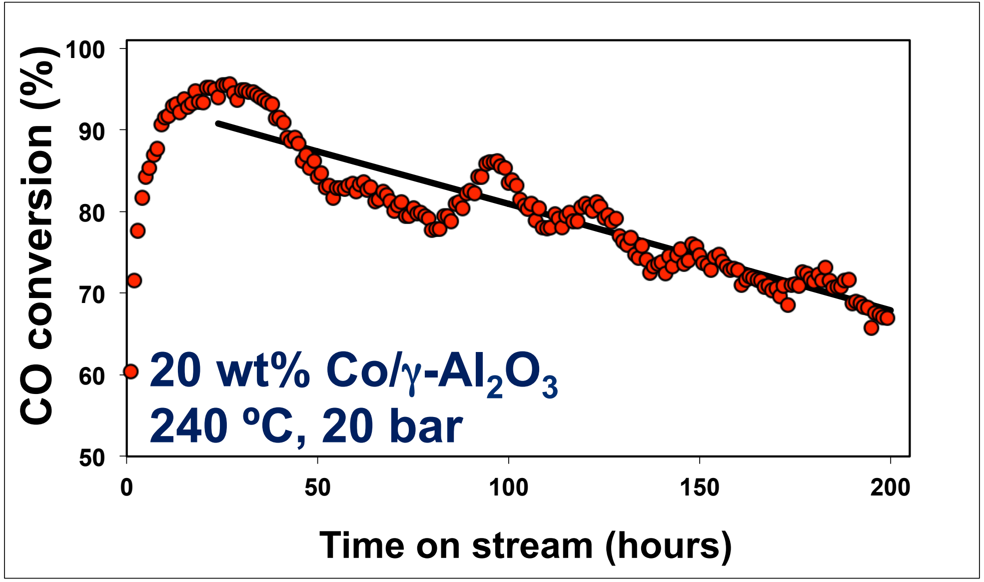
Catalyst testing

- 1 g catalyst and 18 g SiC in fixed bed
- Particle size: 212 – 300 µm
- 240 ºC, 20 bar, $H_2/CO = 2$
- W/F = 7.5 g_{cat}h/mol, high CO conversion

Heat and mass transfer limitations

- Different particle size – no effect on rate
- Bed temperature gradient < 1ºC

Experimental Validation and Characterization

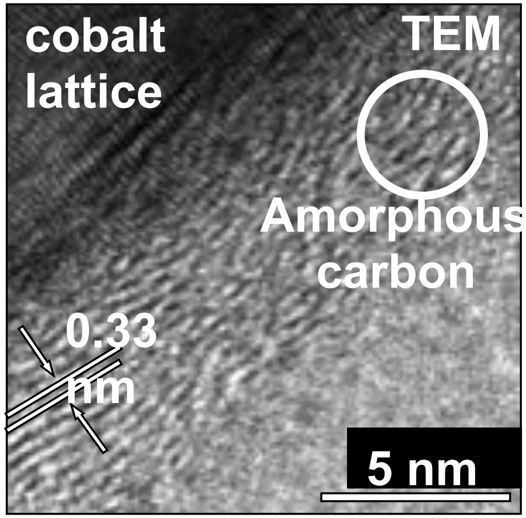


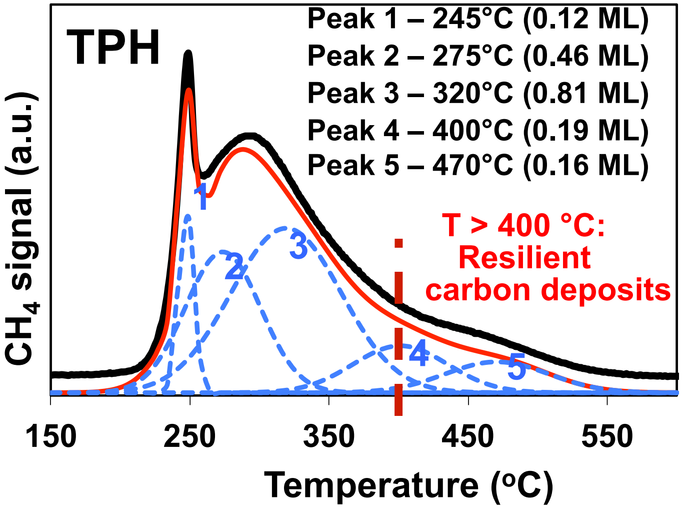
Gradual deactivation over 1 week

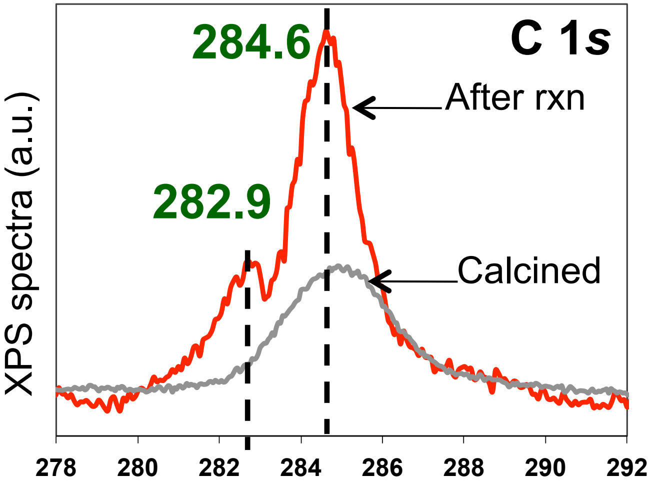
-Deactivation is attributed to resilient carbon deposits (by TEM and TPH)

- Two types of resilient carbon species (by XPS)

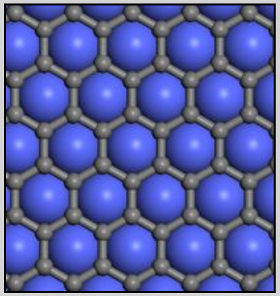
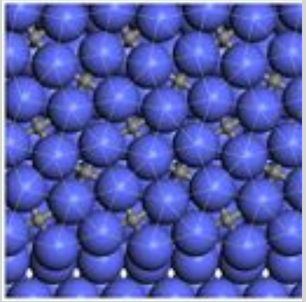
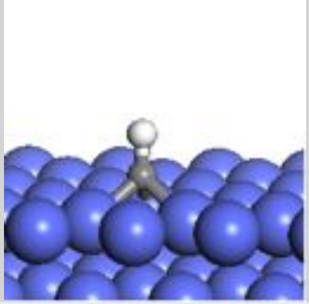
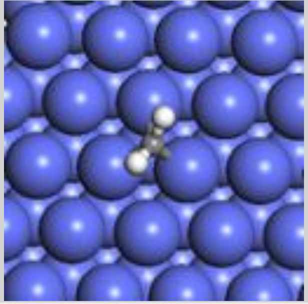
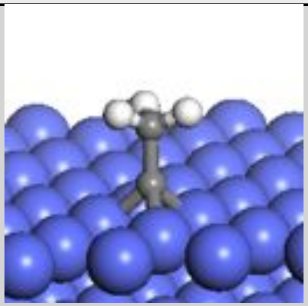
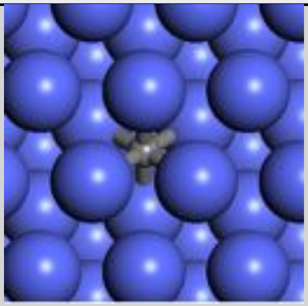
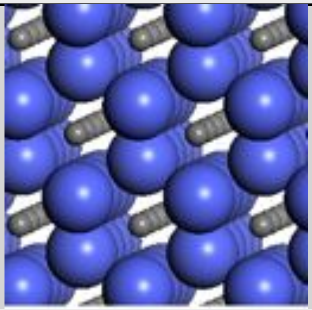
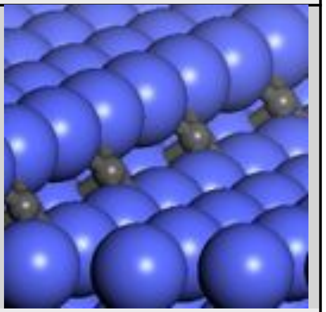
Ref: Tan et al., *J. Catal.* **2010**







Stability and C 1s BE for C species

	Graphene	**p4g carbide**	**CH at hcp**	**CH_2 at hcp**
Structure				
Calculated C 1s BE (eV)	**284.5**	**283.3**	283.6	**284.8**
Stability (kJ/mol)	**−116**	**−98**	−72	**−57**
	CCH_3 at hcp	**Subsurface carbon**	**Bulk carbide (Co_2C)**	**Carbon at B5 step**
Structure				
Calculated C 1s BE (eV)	**284.1 (C)** **285.1 (CH_3)**	283.9	**283.2**	284.0
Stability (kJ/mol)	−90	−15	**+16**	−95

Summary: Carbon Deposition Mechanism

Computational study

Carbon diffuses *into* steps and initiate a clock reconstruction

Nucleation and growth of H-terminated graphene *out of* steps

Calculated C 1s energies: 283.3 eV and 284.5 eV

Experimental study

CO conversion decreases by 25 % after 1 week

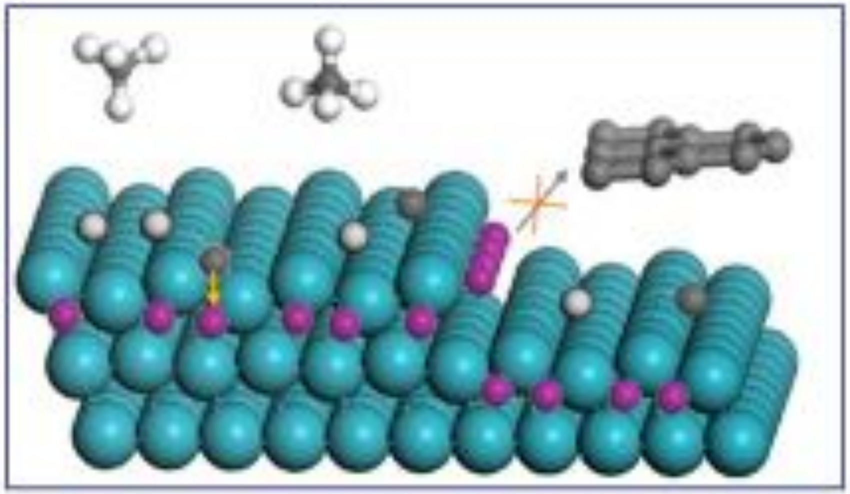
XPS: 2 types of carbon: “carbidic” and “poly-aromatic”

Experimental XPS for C 1s: 282.9 eV and 284.6 eV

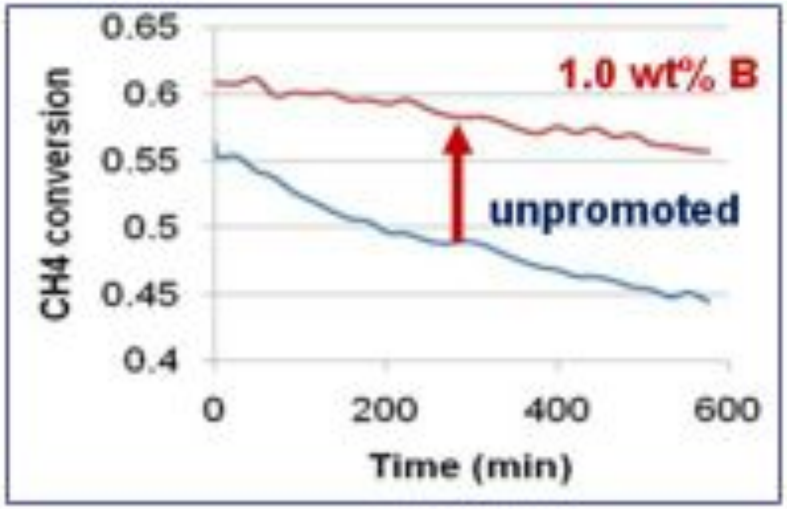
Can we improve stability of supported Co catalysts?

Ref: Tan, Xu, Chang, Borgna, Saeys, *J. Catal.* **2010**

Effect of Boron on Stability of Ni catalysts



Xu and Saeys, *J. Catal.*, **2006**



Xu *et al.*, *J. Catal.*, **2009**

DFT: Boron reduces carbon nucleation and growth on Ni catalysts by blocking nucleation sites

Experiments: Boron reduces the deactivation rate and carbon deposition by a factor 3, and slightly increases activity

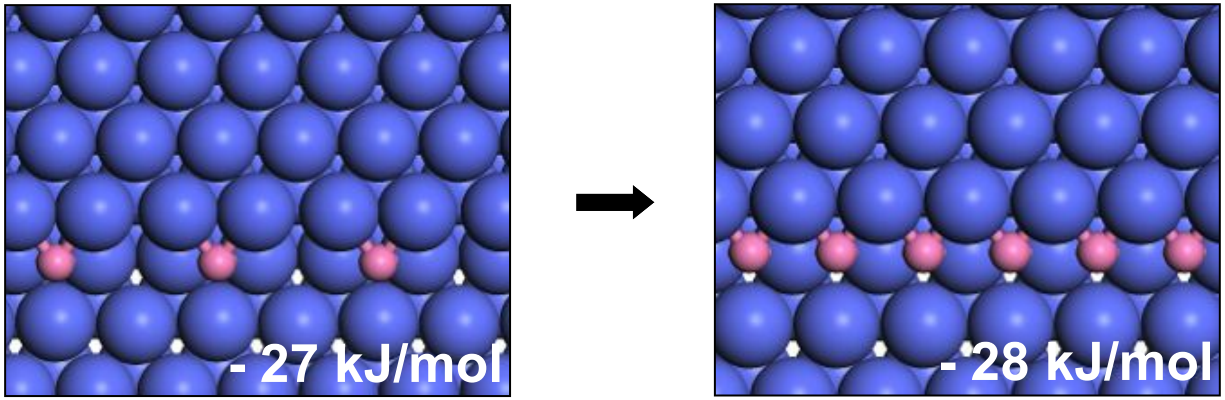
Would this work for Co?

Stability of Boron on Co

Stability of boron under FTS conditions

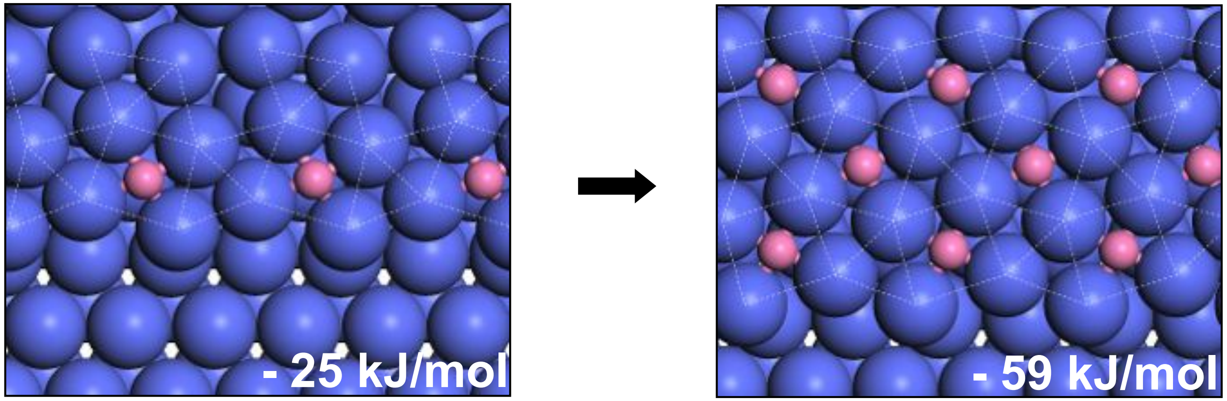
ΔG_r for $1/2\ B_2H_6(g) \rightarrow B^* + 3/2\ H_2(g)$

Step sites



Increased stability for nearest neighbors: B-B interaction

p4g clock

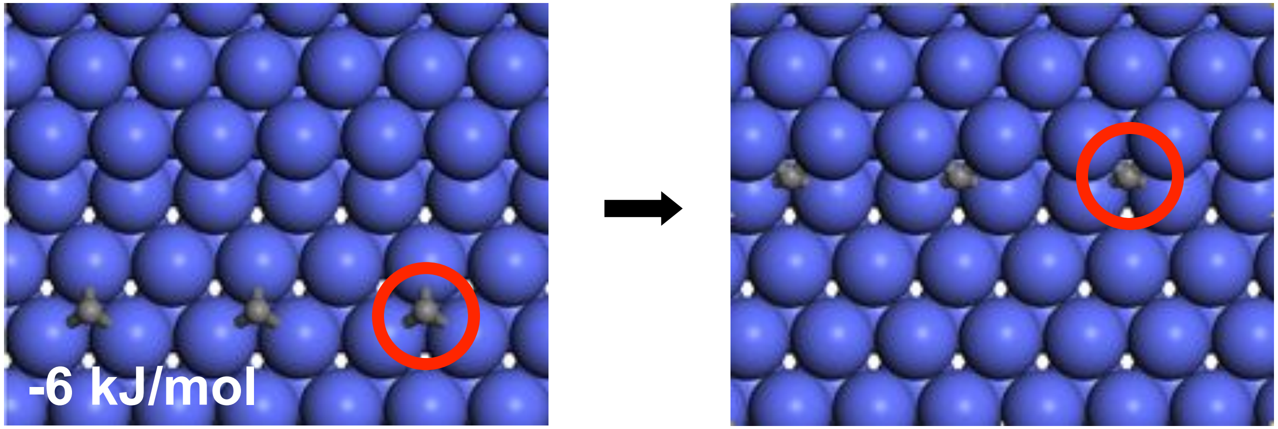


Boron very stable at p4g clock

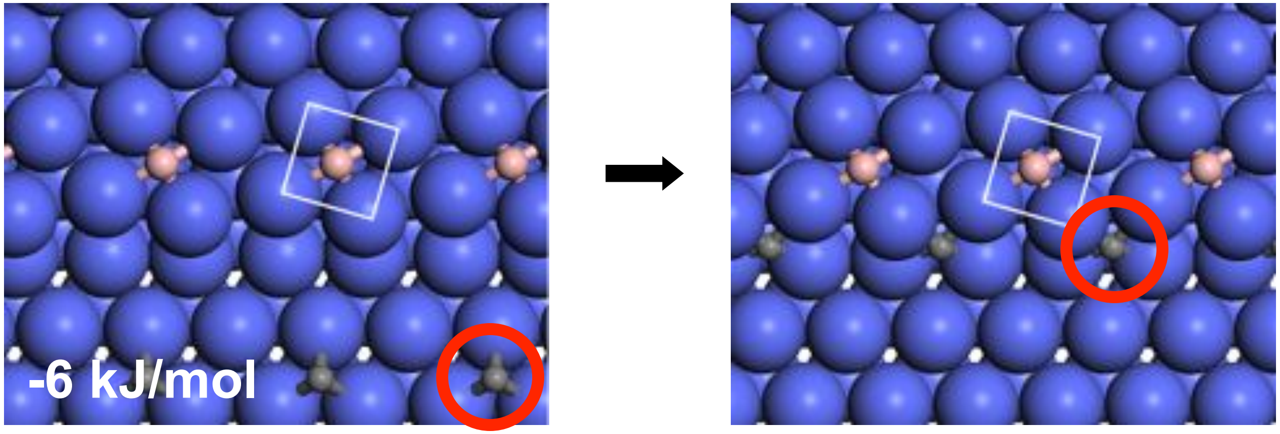
Boron mimics carbon binding preference – AA?

Effect of Boron on Carbon Stability

Effect of boron on carbon diffusion from terrace to step site



$\Delta E_r = -57$ kJ/mol



$\Delta E_r = +109$ kJ/mol

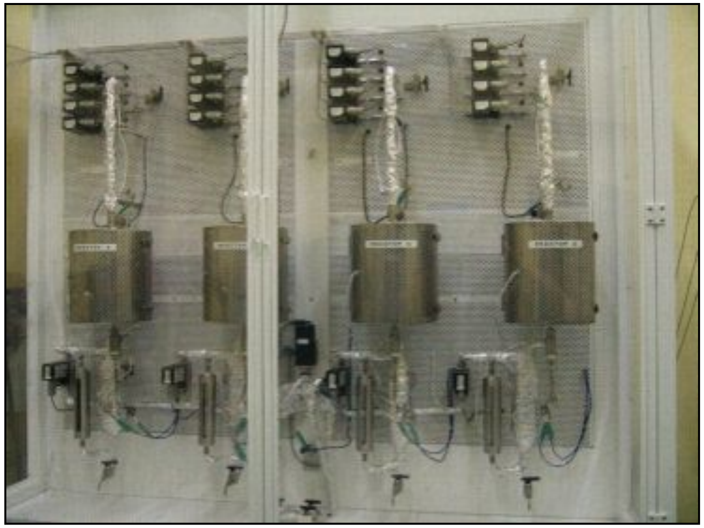
Experimental Procedure

Catalyst preparation

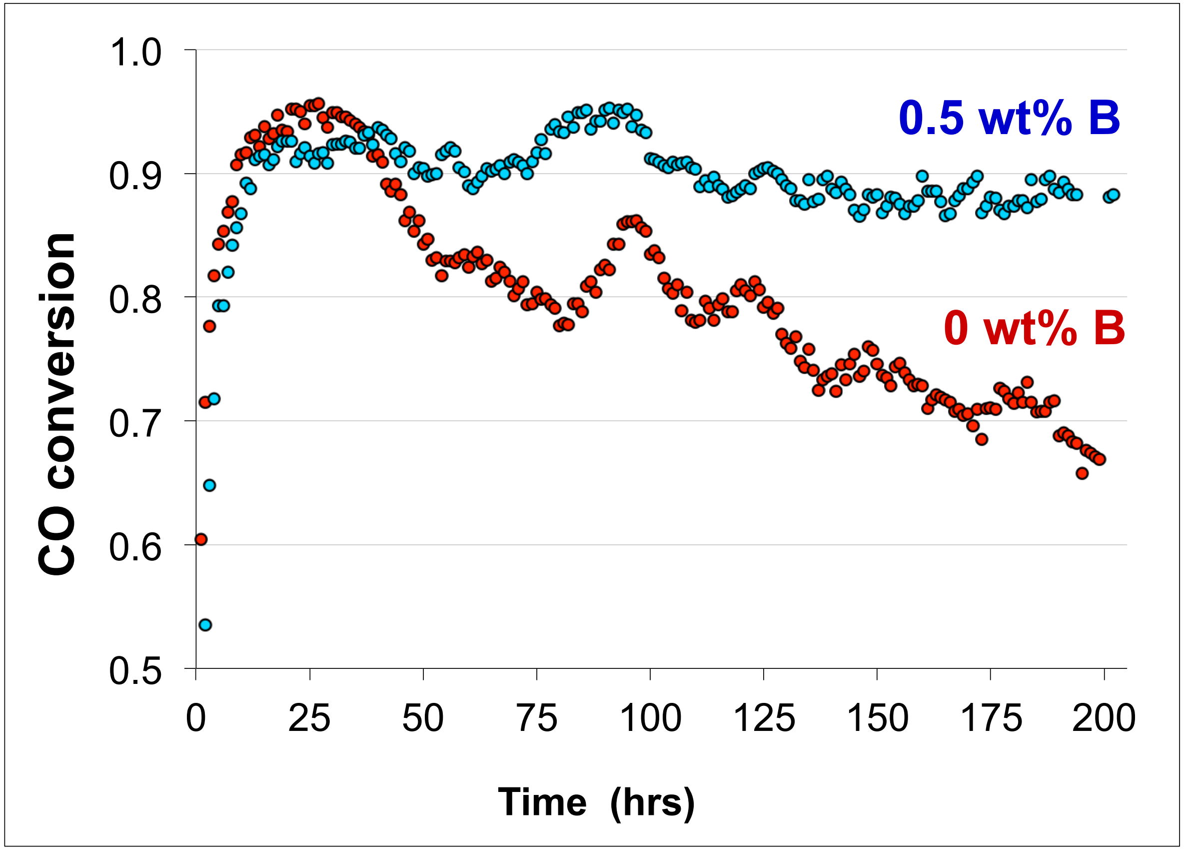
- 20 wt% Co/γ-Al_2O_3, 0.05 wt% Pt catalyst promoted with boron
- Two step impregnation of γ-Al_2O_3 with (i)$Co(NO_3)_2$ and **(ii)H_3BO_3**
- Calcination in air at 400 ºC for 2 hrs
- Reduction at 500 ºC for 12 hrs in 50 Nml/min H_2

Catalyst testing

- 1 g catalyst,18 g SiC in fixed bed reactor
- Particle size: 212 – 300 μm
- 240 ºC, 20 bar, $H_2/CO = 2$
- W/F = 7.5 g_{cat}h/mol, high CO conversion



Effect of Boron on CO conversion



Deactivation rate coefficient

B (wt%)	$k*10^{-4}$ (hr^{-1})
0	17
0.5	2.7

HC selectivity	0 wt% B	0.5 wt% B
C_1	24	22
$C_2 – C_4$	16	17
C_{5+}	60	61
α	0.70	0.71

0.5 wt% B reduces deactivation rate by factor 6

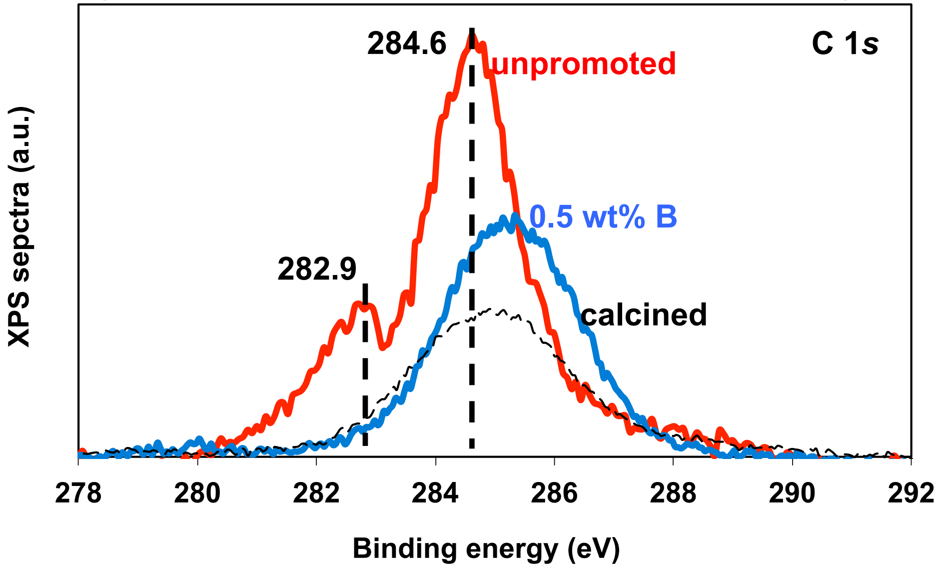
CO conversion maintained at 90%

HC selectivity relatively unaffected

Ref: Tan, Chang, Borgna, Saeys, J. Catal. (2011)

Post-reaction characterization

X-ray Photoelectron Spectroscopy



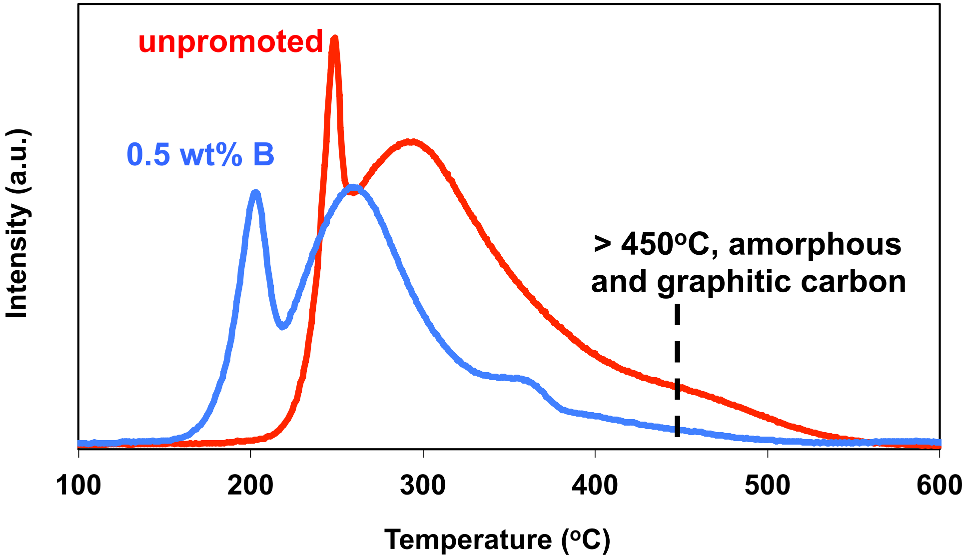
Promotion with 0.5 wt% B

Reduces XPS intensity

Peak at 282.9 eV undetectable

No graphite in HR-TEM

Temperature Programmed Hydrogenation



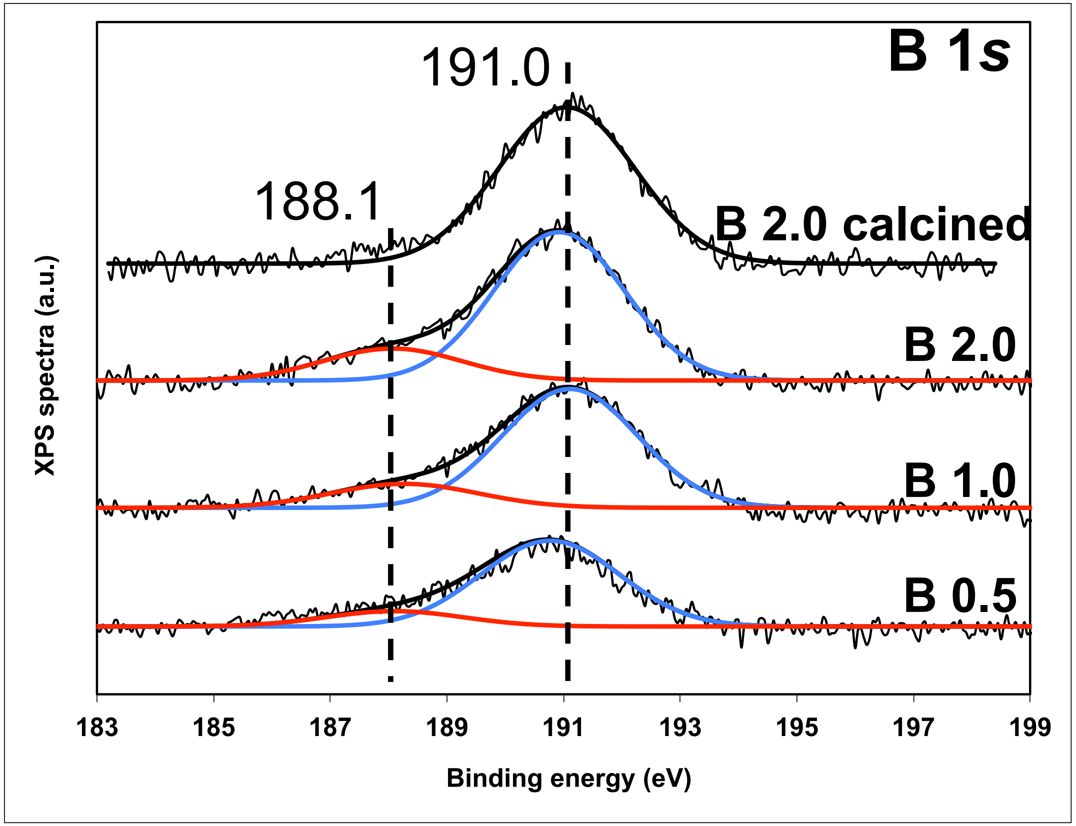
Promotion with 0.5 wt% B

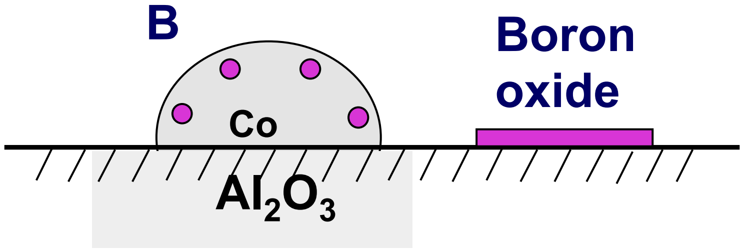
Total amount of CH_4 reduced

Less resilient carbon formed

Characterization: Formation of Cobalt Boride

B 1s X-ray Photoelectron Spectra





Peak at 191.0 eV
boron oxide

Peak at 188.1 eV
cobalt boride
187.8 eV from DFT-PBE

10% of boron oxide reduced
Only B atoms interacting with Co particles can be reduced

Conclusions

Modeling realistic coverages (*Operando*) affects kinetics and brings predicted kinetic parameters close to experiment

CO insertion mechanism via RCH + CO is a viable mechanism on Co terraces, consistent with kinetic data

Unique stability of C/CO at B5 site overcomes step creation penalty and drives formation of Co islands of specific size

Boron mimics the binding characteristics of carbon, is stable on Co, and can selectively block nucleation sites.

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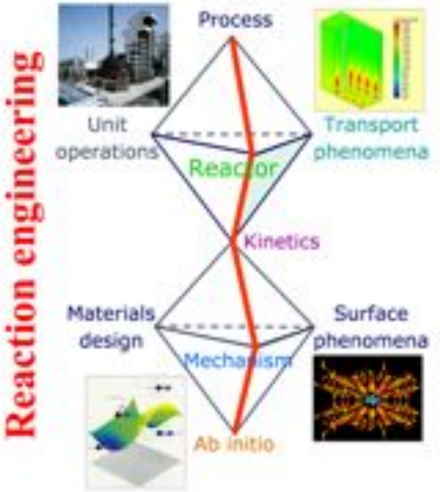

Odysseus program

Design of Selective Catalytic Processes

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