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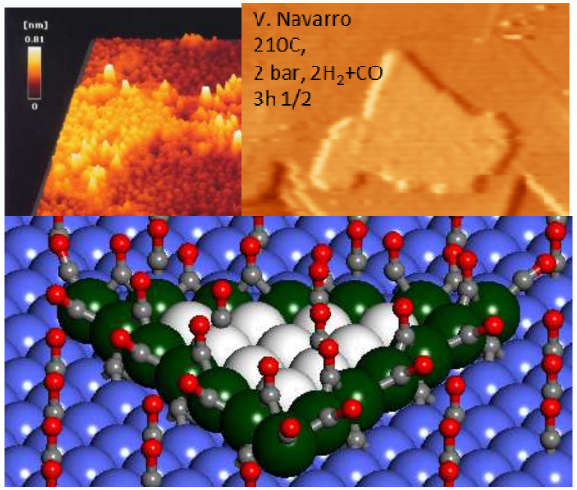
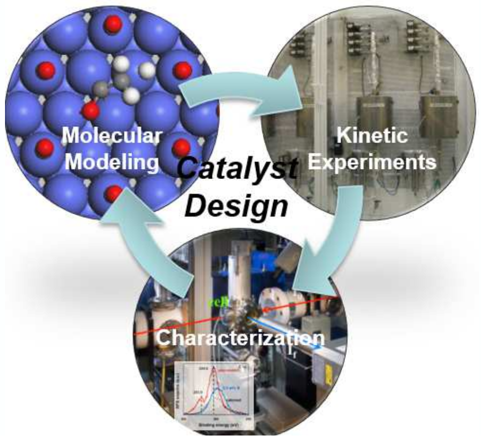
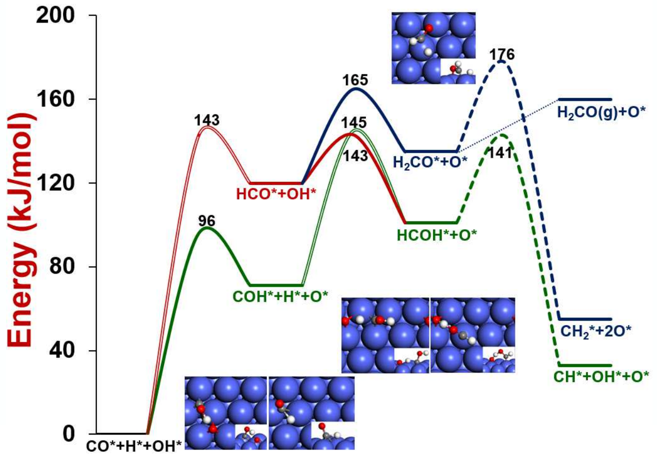
FACULTY OF ENGINEERING AND
ARCHITECTURE

# Catalyst structure and C-O activation during Fischer-Tropsch Synthesis







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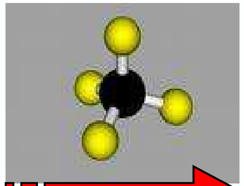
*Laboratory for Chemical Technology, Ghent University, Belgium*

*http://www.lct.UGent.be*

# Synthetic Fuels form Gas, Coal & Biomass



NG

GTL

SMR-CPO

Coal

CTL

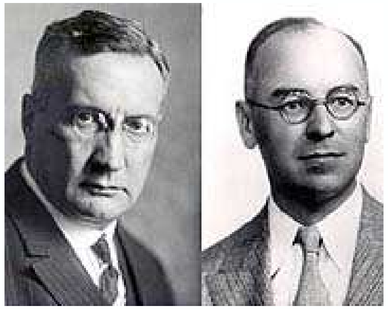
Gasification

Biomass

BTL

Gasification

Syngas



Fischer-Tropsch

**Overall reaction:**

$$\mathbf{CO + 2H_2 \rightarrow C_nH_{2n} + H_2O}$$

**Cobalt catalysts:**

High activity, high selectivity, low $CO_2$ production

Active sites? Mechanism?

# From Molecules to Processes

1. Molecular-scale hypotheses about elementary steps, active sites, kinetics,…

**“Playing”**

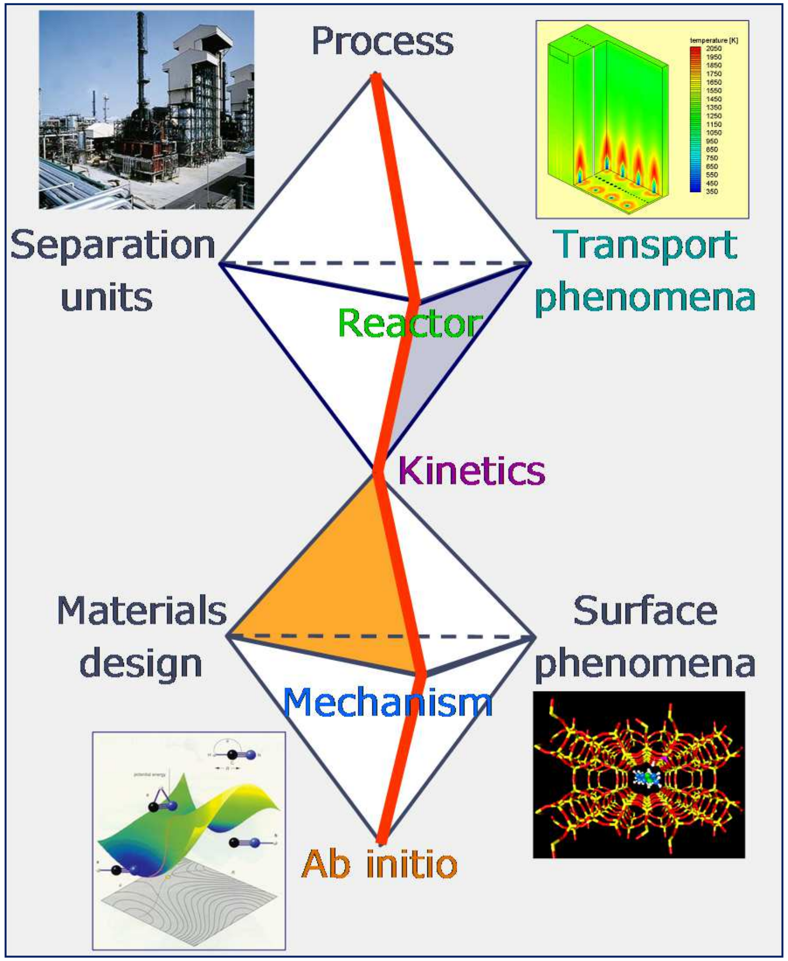
2. Modeling to evaluate

**“Insight”**

3. Kinetic model or improved catalyst (activity, stability)

**“Validate”**

4. Macro-scale experimental validation (intrinsic kinetics)



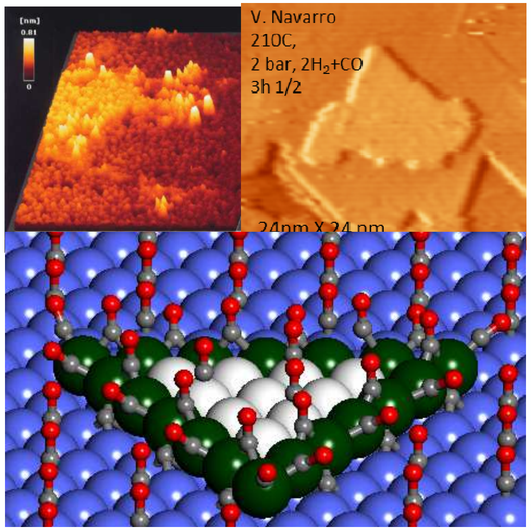
# Outline

## Structure: Reconstruction

Nature of experimentally observed islands

Origin of stability/formation

**Refs**: Banerjee *et al.*, *ACS. Catal.* **2015,** Banerjee *et al.*, *JPCL* **2016**

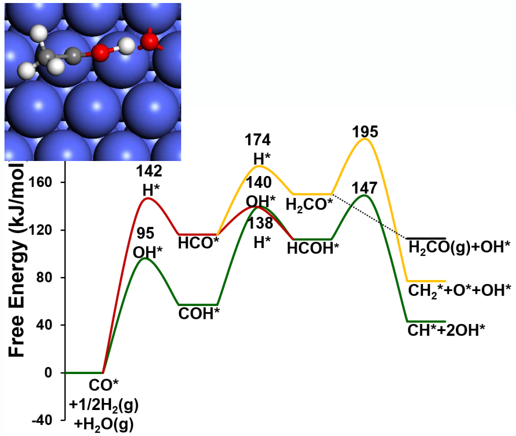


## Activity & Selectivity: Debate

CO insertion consistent with kinetic data

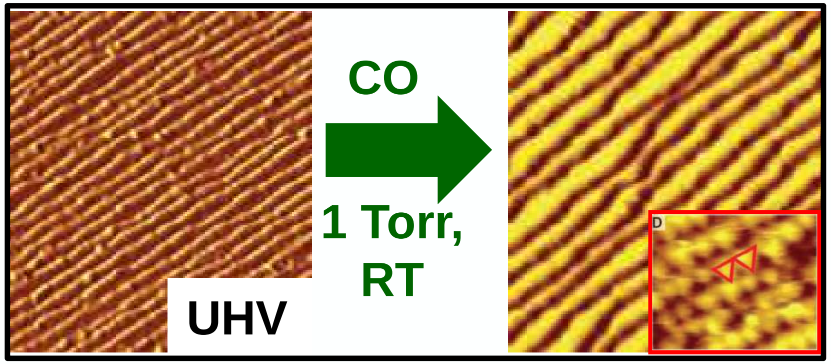
OH as hydrogenating species

**Refs**: Zhuo *et al.*, *JPCC* **2009**, Zhou *et al.*, *J. Catal.* **2013**, Gunasooriya *et al.*, *Surf. Sci.* **2015,** Gunasooriya *et al.*, *ACS Catal.* **2016**

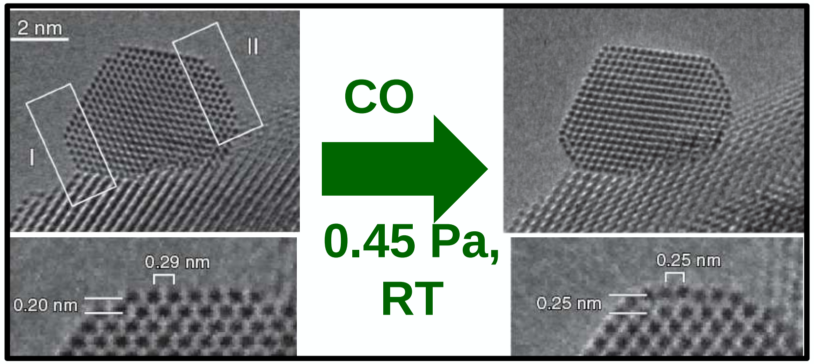


# Surface reconstructions

## Pt restructuring



## Au restructuring



- **Pt terraces form triangular nano-islands under CO**

  **Ref:** Somorjai *et al.*, *Science*, **2010**

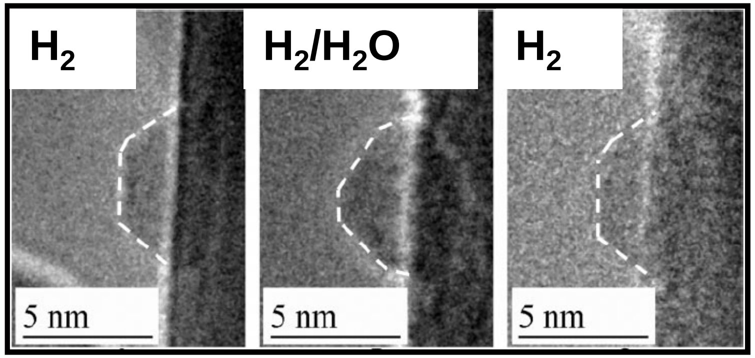
- **Au nanoparticles restructure driven by stronger adsorption on reconstructed surface**

  **Ref:** Yoshida *et al.*, *Science*, **2012**

- **Cu/ZnO/$Al_2O_3$ catalysts restructure reversibly under $H_2/H_2O$ at 1.5 mbar**

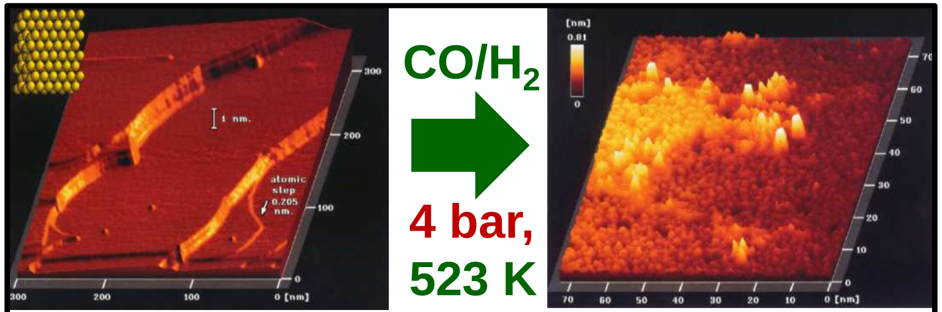
  **Ref:** Hansen *et al.*, *Science*, **2002**

## Cu restructuring



# Massive reconstruction under FT conditions

## STM images of effect of syngas on Co(0001)

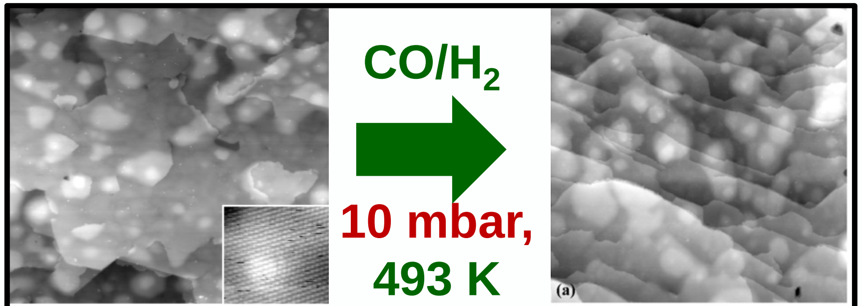


CO/H$_2$

4 bar,
523 K

**Islands**

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

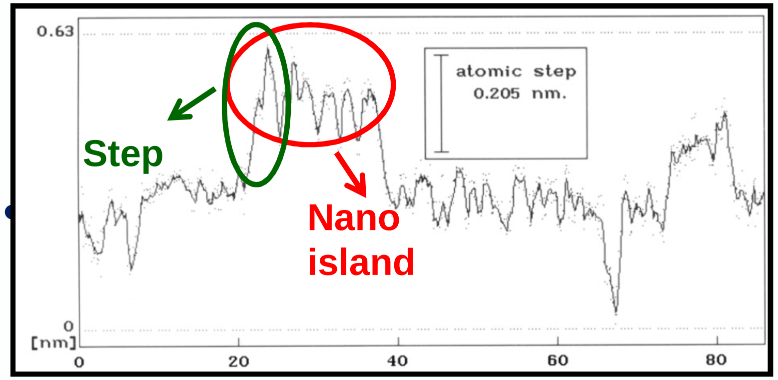


CO/H$_2$

10 mbar,
493 K

**No Islands**

**Ref:** Ehrensperger, Wintterlin, *J Catal*, **2014**



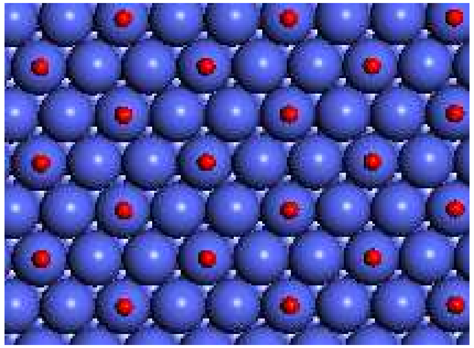
**Massive surface reconstruction at FT pressures**

**Triangular nano-islands (~2 nm diameter)**

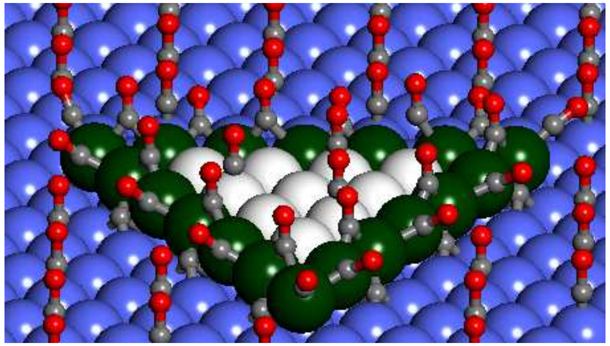
**What drives the formation of those islands?**

# Structure of Co islands

## Island formation under reaction conditions

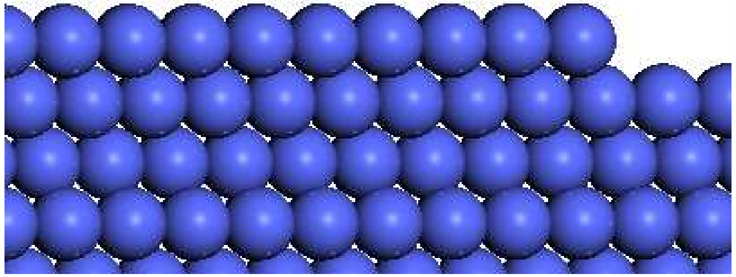


CO-covered terraces

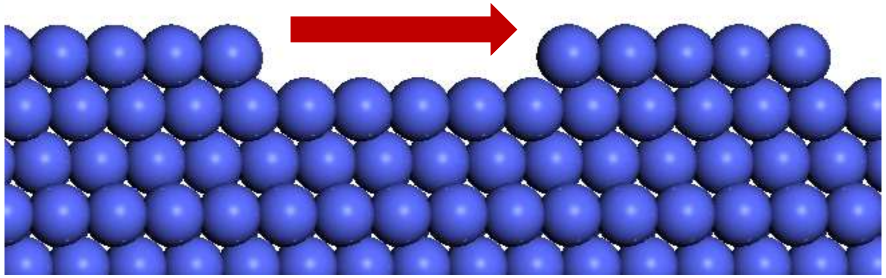


Covered islands

## Step creation



Clean Terraces



Formation of a step

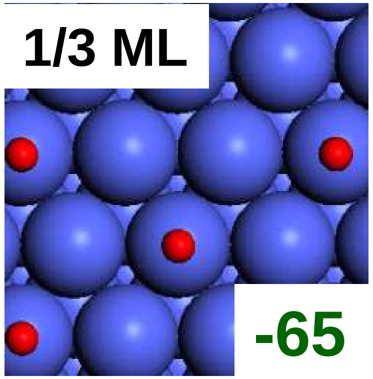
**Step creation: +85 kJ/mol step atoms (both sides)**

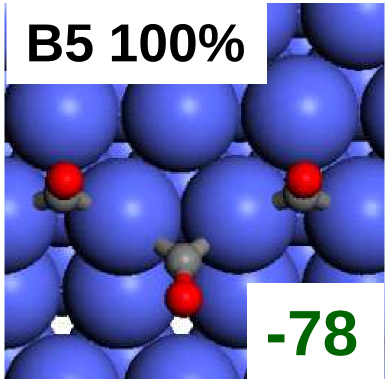
**Can we find adsorption combinations to overcome this penalty?**

# CO adsorption at step edges

**First principle CO adsorption free energy (~T, p, composition)**

$$\Delta G_{ads}(T, p_{CO}) = \Delta H_{ads}(T,p_{CO}) - T\Delta S_{ads}(T, p_{CO}) + RT \ln(1/p_{CO})$$





**$\Delta G_{rxn}$ to create step:**

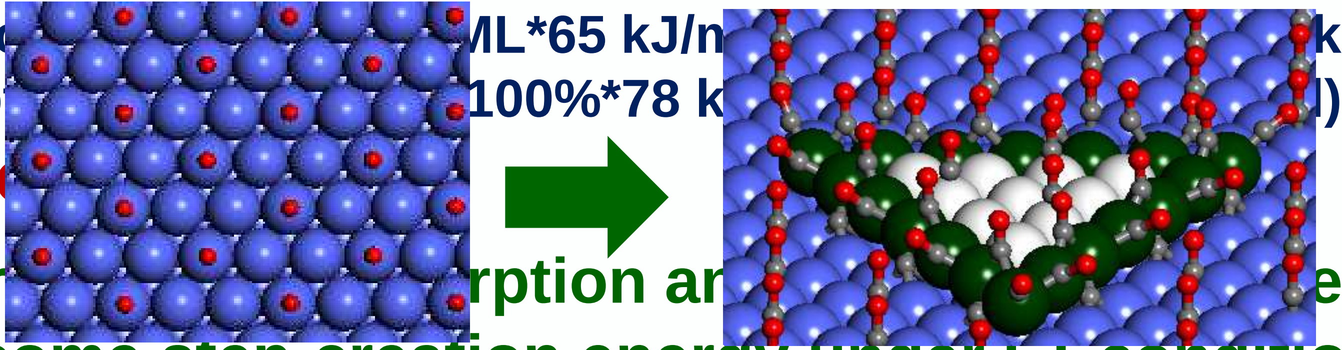
**Desorption o ML*65 kJ/n kJ/mol)**

**- CO adsorp 100%*78 k l)**

**~ 0 kJ/m**

**Str rption ar e**

**overcome step-creation energy under FT conditions**



**CO-covered terraces**

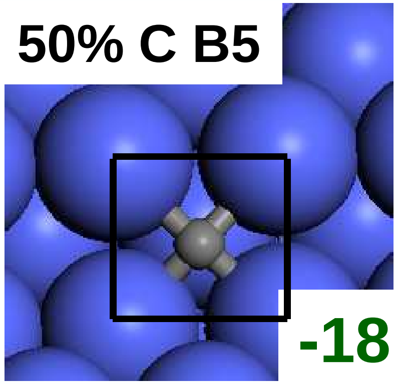
**Covered islands**

**Can we increase driving force?**

# Strong square-planar carbon adsorption

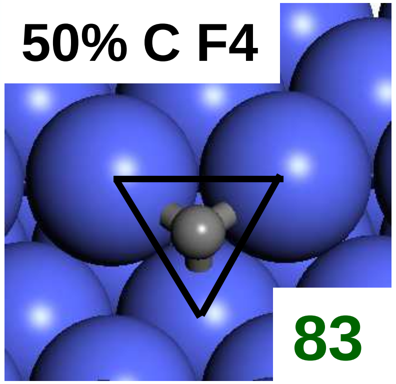
**Carbon stability:** $\Delta G_{rxn}$ for $CO(g) + H_2(g) \rightarrow [C]^* + H_2O(g)$

50% C B5



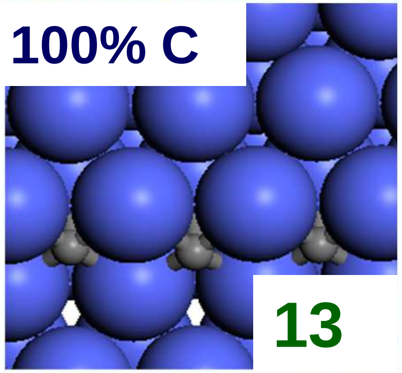
-18

50% C F4



83

100% C

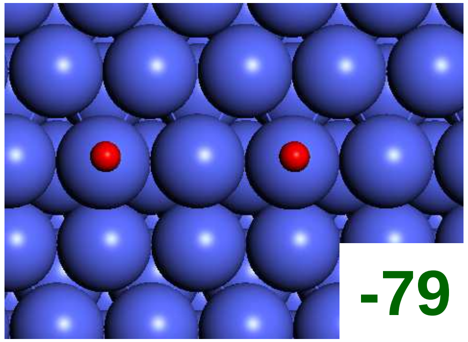


13

**square-planar carbon binds strongly at B5 site, C coverage beyond 50% not favorable, Sites available for reaction?**

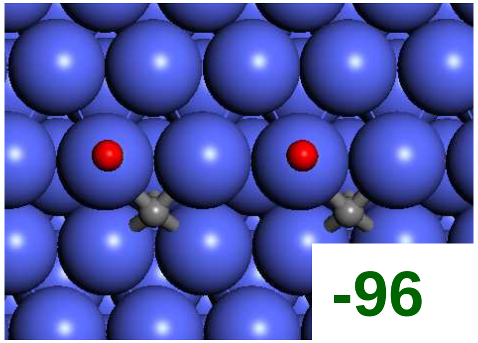
**CO stability:**

B5 50%



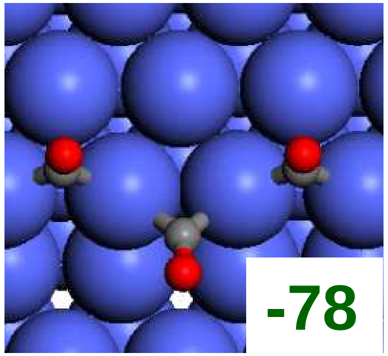
-79

50% C + 50% CO



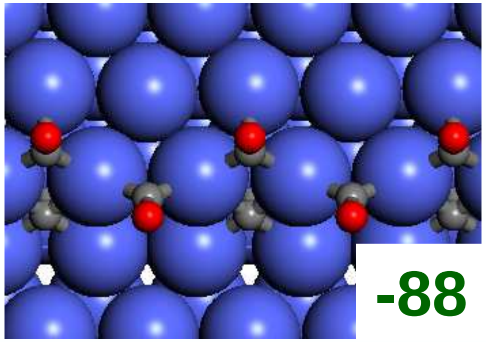
-96

B5 100%



-78

50% C + 100% CO

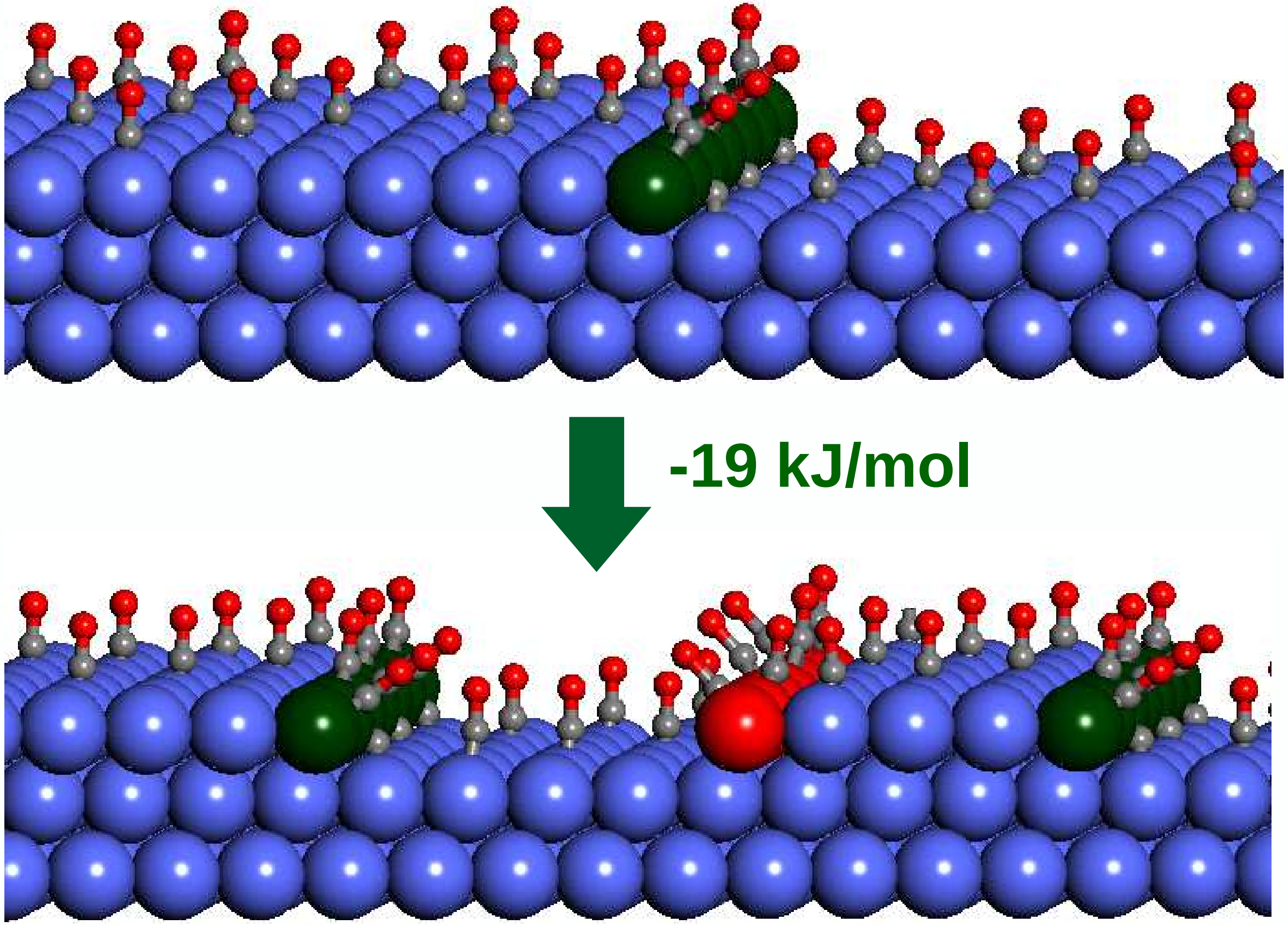


-88

**Square planar C increases CO stability**

**Refs:** Ciobica *et al.* **2008,** Tan, Xu, Chang, Borgna, Saeys, *J. Catal.*, **2010**

# Stability of C/CO covered B5 steps

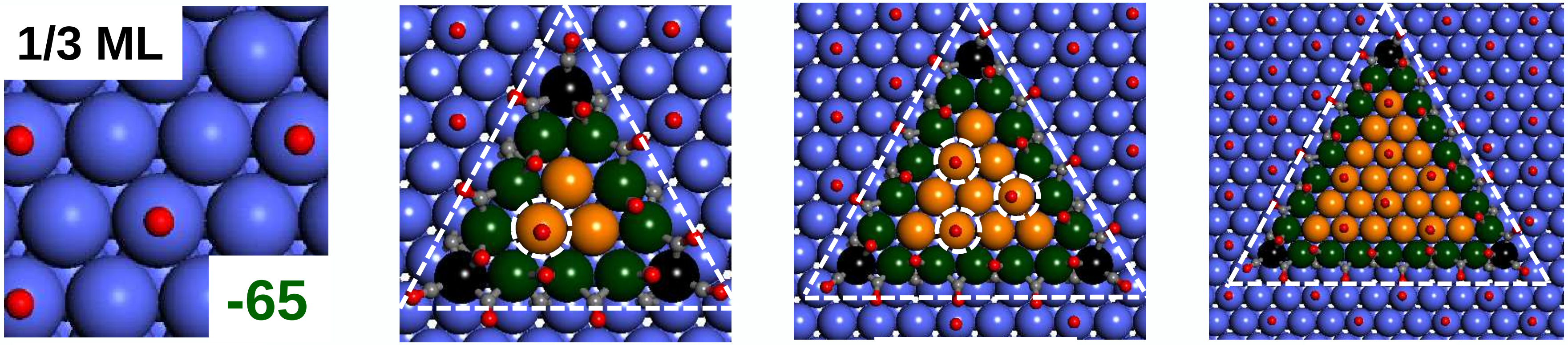


**50% C and 100% CO step edge coverage overcomes energy penalty to create steps and stabilizes B5**

**Ref:** Banerjee, Saeys *et al.*, *ACS Catal.* **2015**

# Creation of C/CO saturated B5 islands

## CO adsorption free energy at island terraces?



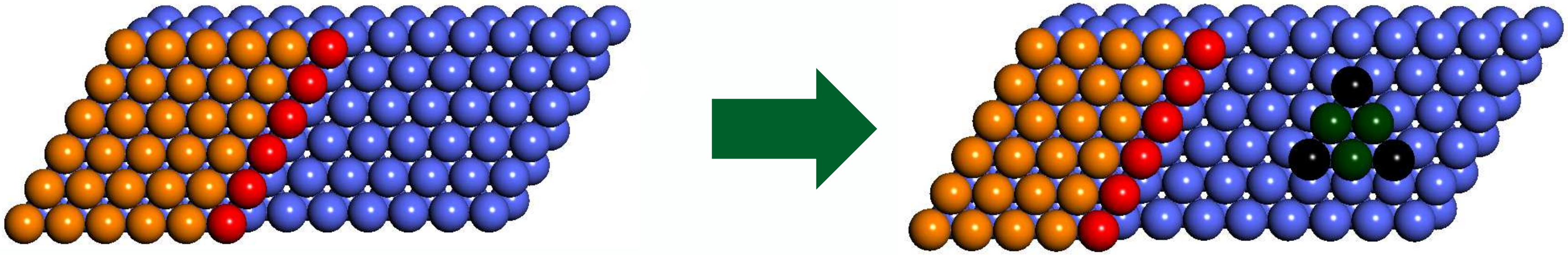
Terraces

$Co_{15}$

$Co_{28}$

$Co_{45}$

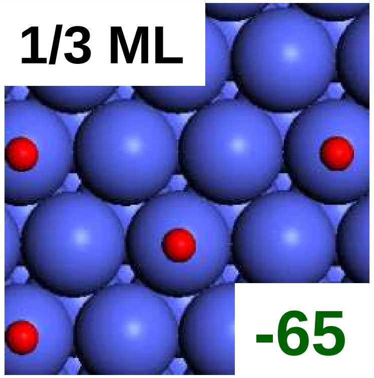
## How do islands form?



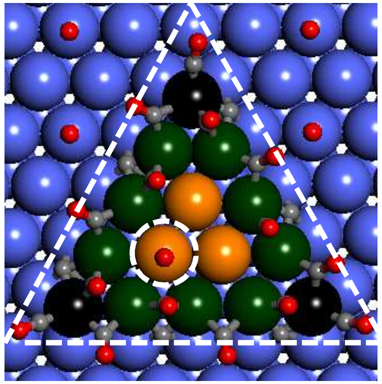
**Ref:** Banerjee, Saeys *et al.*, *JPCL* **2016**

# Creation of C/CO saturated B5 islands

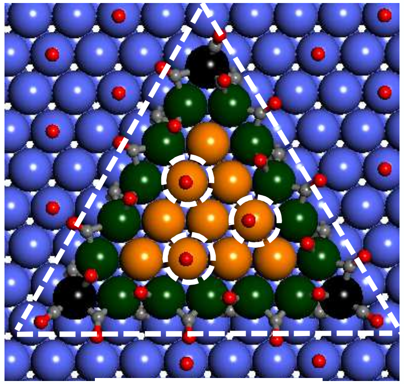
## CO adsorption free energy at island terraces?



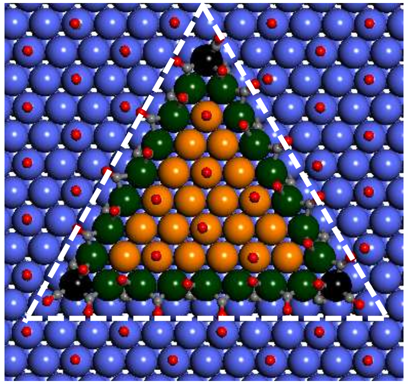
**Terraces**



**Co$_{15}$**



**Co$_{28}$**



**Co$_{45}$**

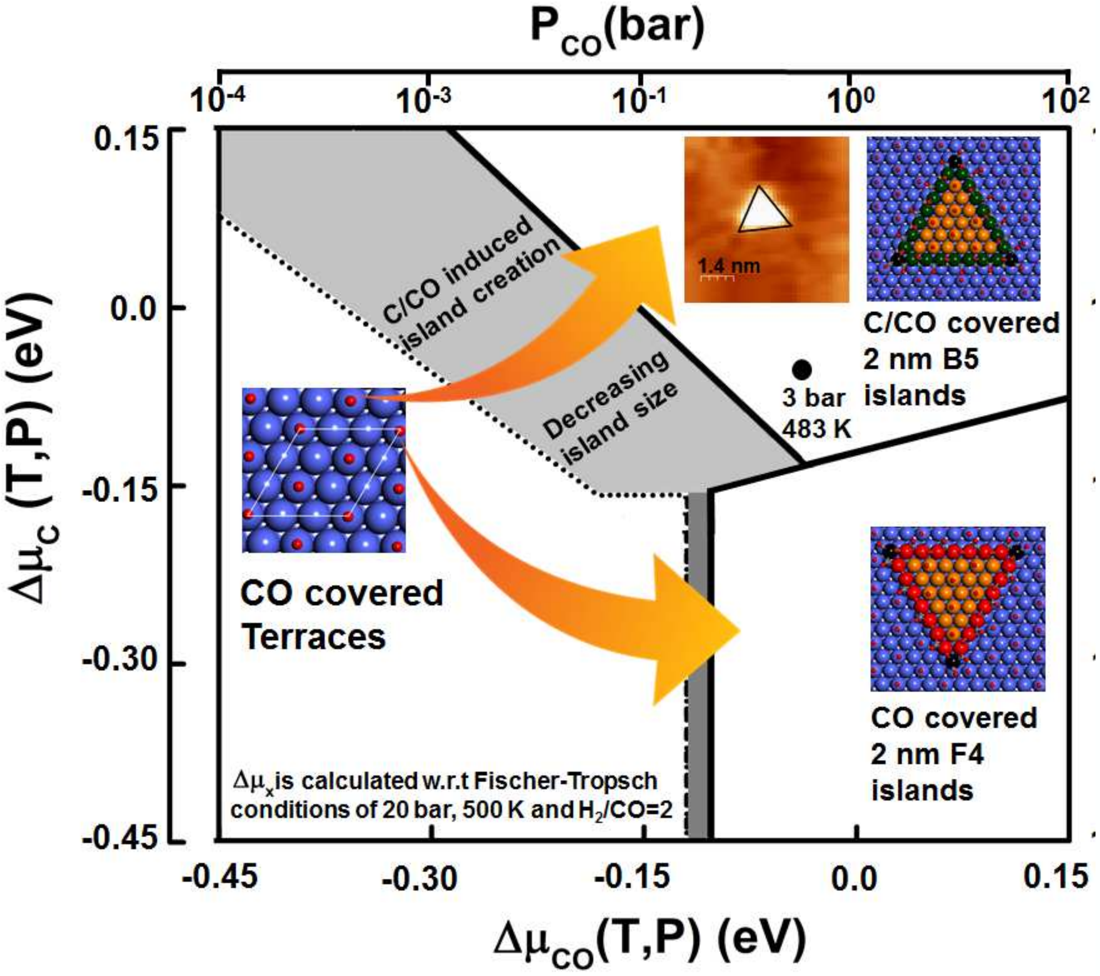
**Energy balance for B5 island of 45 Co atoms**:

Desorb CO from **66** terrace (indicated in white) sites: 66/3 x 65 = **+1430 kJ/mol**
Create **24** B5, 3 corners: 24 x 45 + 3 x 22 = **+1146 kJ/mol**
Adsorb CO on **21** island terrace sites: 21/3 x -65 = **-455 kJ/mol**
Adsorb 50%C/100%CO at **24** B5 sites: 9 x -18 + 18 x -88 = **-1746 kJ/mol**
Adsorb C/CO at **3** corners: 3 x -14+ 9 x -70 = **-672 kJ/mol**

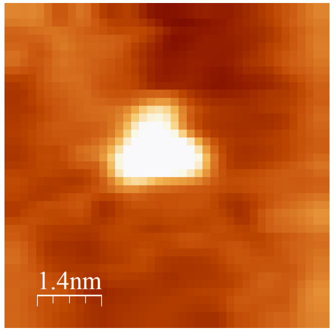
**Overall: -297 kJ/mol islands or -6.6 kJ/mol Co atom for Co45**
**-393 kJ/mol islands or -6.2 kJ/mol Co atom for Co66**
**-126 kJ/mol islands or -4.5 kJ/mol Co atom for Co28**

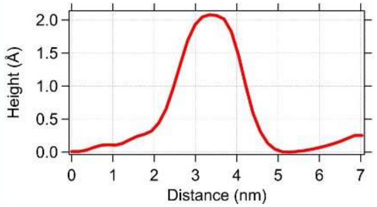
**Ref:** Banerjee, Saeys *et al.*, *JPCL* **2016**

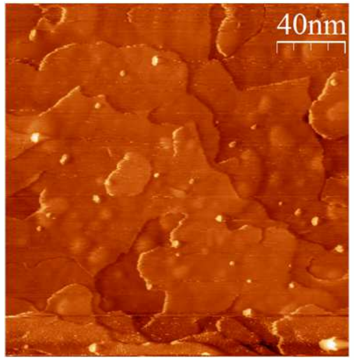
# Effect of reaction conditions on island stability

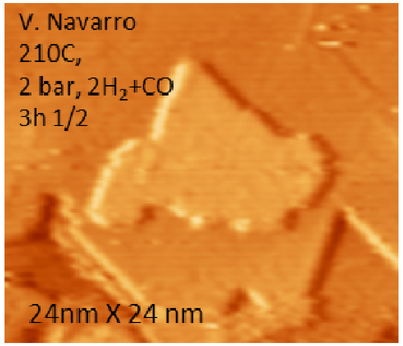


$\Delta\mu_x$ is calculated w.r.t Fischer-Tropsch conditions of 20 bar, 500 K and $H_2$/CO=2



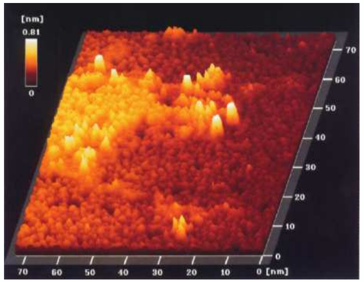






V. Navarro
210C,
2 bar, $2H_2$+CO
3h 1/2

24nm X 24 nm



**High CO, C chemical pot. drives $Co_{45}$ island formation**
**Lower C chemical pot. → lower C stability → larger islands**

*** $\mu_{C/CO}$=0 at FT conditions (500 K, 20 bar, 60% conversion)**

**Ref:** Banerjee, Saeys *et al.*, *JPCL* **2016**

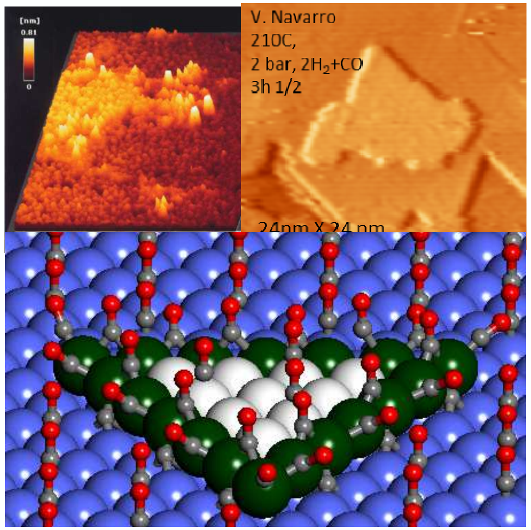
# Outline

## Structure: Reconstruction

Nature of experimentally observed islands

Origin of stability/formation

**Refs**: Banerjee *et al.*, *ACS. Catal.* **2015,** Banerjee *et al.*, *JPCL* **2016**

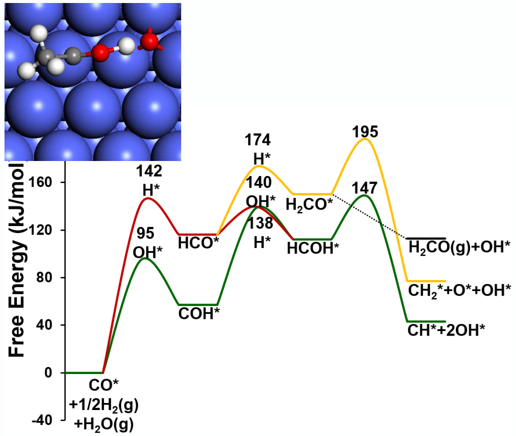


## Activity & Selectivity: CO insertion and role of OH

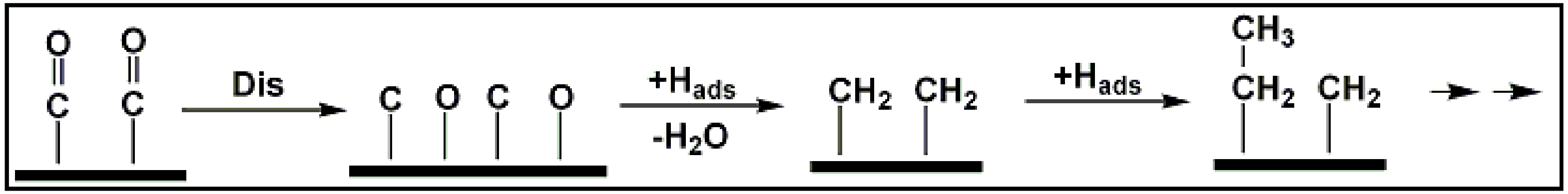
CO insertion consistent with kinetic data

OH as hydrogenating species

**Refs**: Zhuo *et al.*, *JPCC* **2009**, Zhou *et al.*, *J. Catal.* **2013**, Gunasooriya *et al.*, *Surf. Sci.* **2015,** Gunasooriya *et al.*, *ACS Catal.* **2016**



# Mechanistic proposals: Carbide mechanism



**$CH_x$-$CH_x$ coupling**

Brady-Pettit experiments with $CH_2N_2$: $CH_x$ + $CH_x$ coupling

C-C coupling on Co:

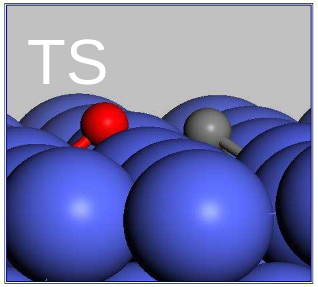
$RCH + C \rightarrow RCHC$ $E_a = 71$ kJ/mol

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

Need fast CO dissociation for **high $CH_x$ coverage**

**CO dissociation on Co(0001) terraces:**

**235 kJ/mol > 150 kJ/mol**



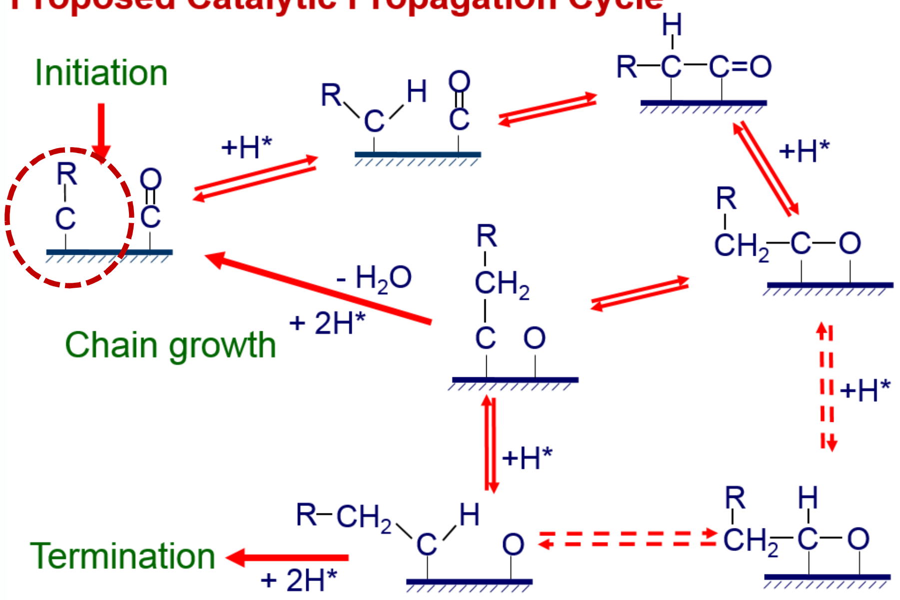
CO dissociation slow → **low** C or $CH_x$ **coverage**

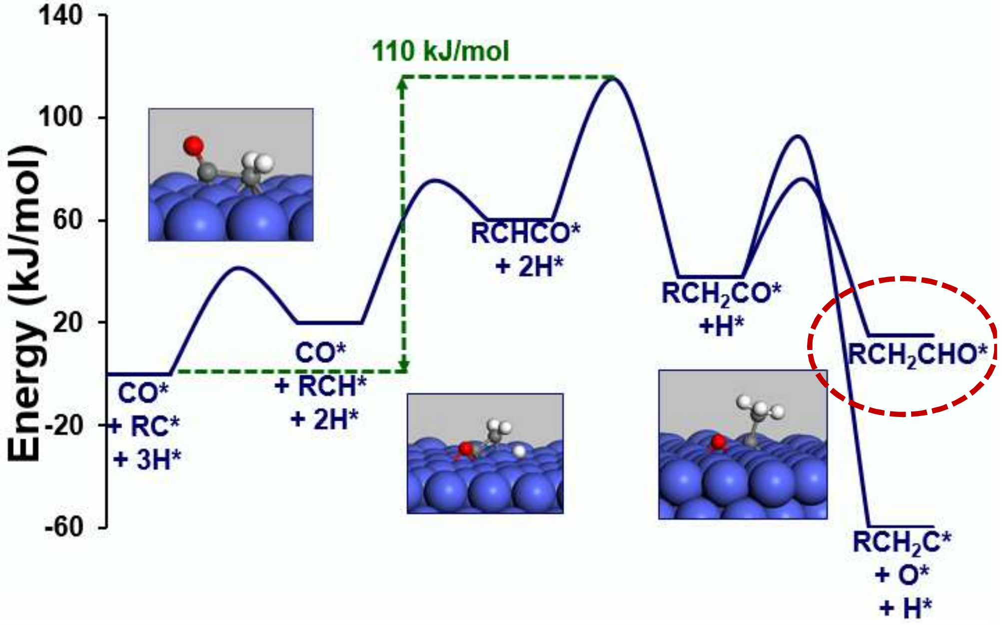
→**coupling slow compared to termination by hydrogenation**

**Refs:** Brady, Pettit, *J. Am. Chem. Soc.*, **1980**; Lok *et al.*, *J. Catal.* **2008**

# Mechanistic proposals: CO insertion mechanism

**Proposed Catalytic Propagation Cycle**





**C-O activation after C-C bond formation**

Proposed by Pichler and Schulz, 1970

$RCH_2$ + CO → **180 kJ/mol**, **but** RCH + CO much easier (60 kJ/mol)

Proposed cycle → **effective barrier 110 kJ/mol < 150 kJ/mol,**

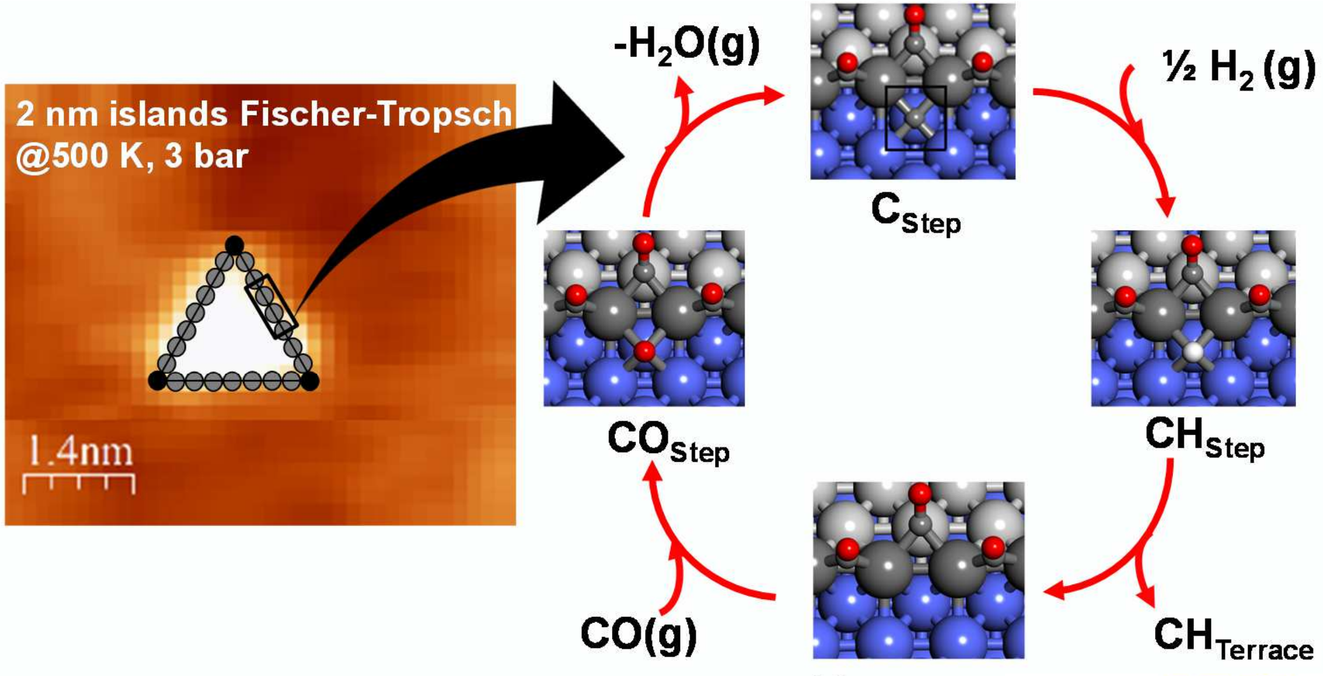
TOF ~ 4 x $10^{-2}$ $s^{-1}$

Need formation of **first CH**

**Oxygenate selectivity – acetaldehyde formation**

**Refs:** Pichler & Schulz, *Chem. Ing. Tech.*, **1970**; Zhou *et al.*, *J. Phys. Chem. C*, **2008** & *J. Catal.*, **2013**

# Mechanistic proposals: At islands?

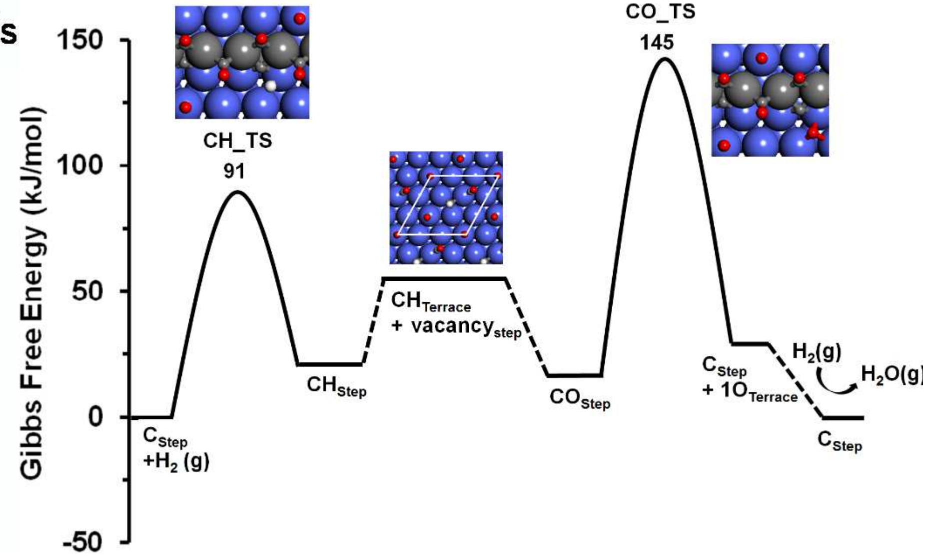


$C_{B5} \rightarrow CH_{B5}$

$CH_{B5} \rightarrow CH_{terrace}$

$CO(g) \rightarrow CO_{B5}$

$CO_{B5} \rightarrow C_{B5}$



**Overall free energy barrier**
**~ 125 kJ/mol**

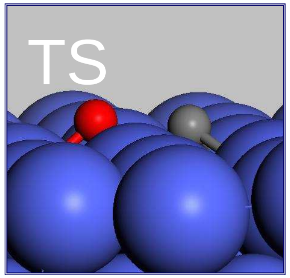
**TOF$_{CO}$ ~ 1 x 10$^{-2}$ s$^{-1}$**

**Refs:** Banerjee, Saeys *et al.*, submitted

# Mechanistic proposals: H-assisted?

## Direct C-O dissociation

CO* → C* + O*  235 kJ/mol at low CO coverage,
254 kJ/mol at 1/3 ML CO coverage



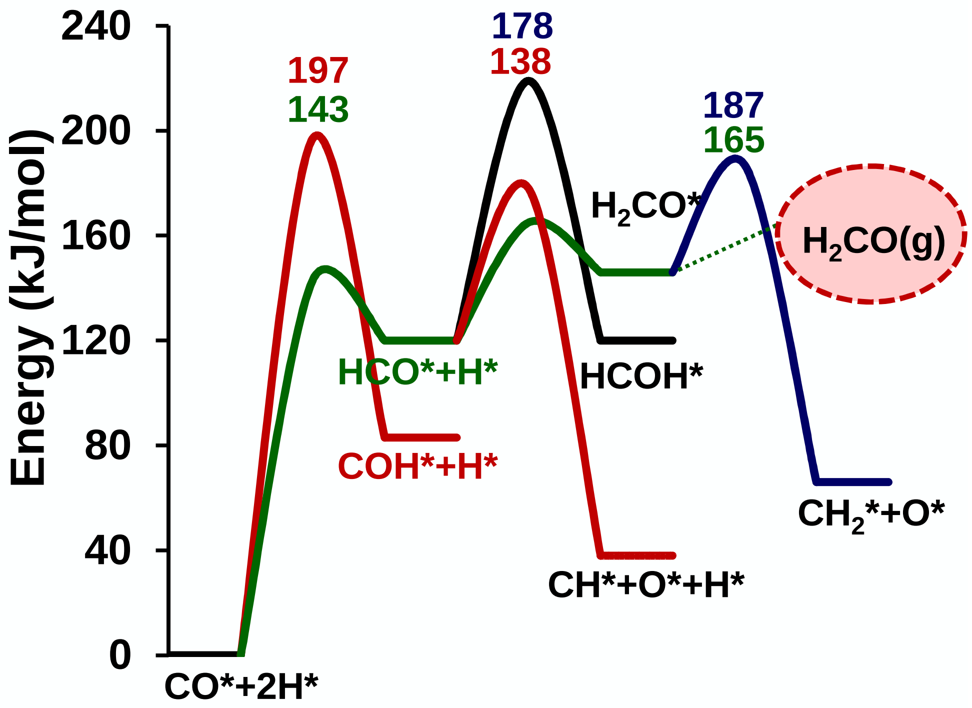
## H-assisted C-O dissociation

### Hydrogenation

CO* + H* → HCO* or COH*
HCO* + H* → $H_2CO$* or HCOH*

### C-O scissions

HCO* → HC* + O*
$H_2CO$* → $CH_2$* + O* or **$CH_2O(g)$**
HCOH* → HC* + OH*



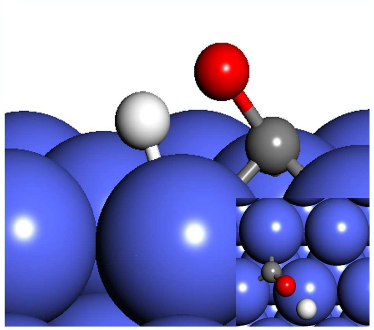
**High effective barriers, $CH_2O(g)$ formaldehyde formation**

**Ref:** Gunasooriya, Saeys *et al.*, *ACS Catal.* **2016**

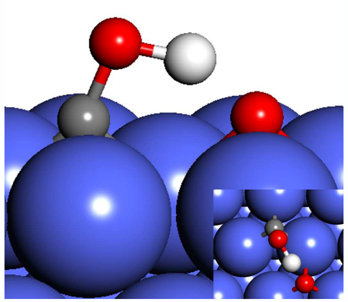
# Mechanistic proposals: OH-assisted?

## COH* formation

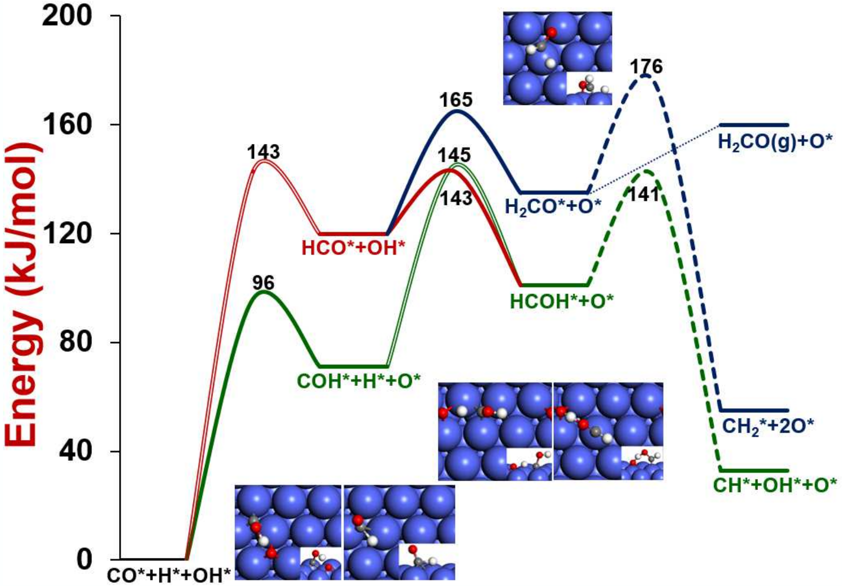
CO*+H*



CO*+OH*



| | | |
|---|---|---|
| $E_a$ | 197 | 96 |
| $\Delta G_a$ | 189 | 94 |



**HCOH formation favored over $H_2CO$ formation**

**CH-OH dissociation rate limiting**

**Effective barrier ~150 kJ/mol. TOF ~ 5 x10$^{-3}$ s$^{-1}$**

**CO TOF/CH formation = 10**

**Ref:** Gunasooriya, Saeys *et al.*, *ACS Catal.* **2016**

# μKinetic model: In Progress

$CO + H_2$

Direct CO activation

Chain growth

Product formation

OH-assisted CO activation

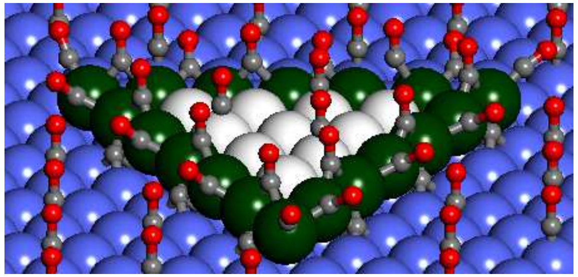
Chain growth

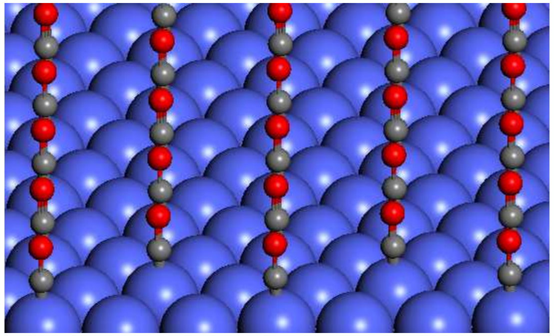
Product formation

O removal

$H_2O$
$CO_2$

$C_nH_{2n+2}$
$+ C_nH_{2n}$





- ✓ Detailed kinetic modeling

# Conclusions

Reconstruction of Co terraces driven by synergistic adsorption of σ-aromatic square planar C and CO at B5 sites

Mechanism,
Carbide: NO on terraces
CO insertion: YES, but first step?
CO activation at islands: YES, but do they exist?
H-assisted CO activation: NO, wrong product
OH-assisted CO activation: MAYBE,…

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