Activation of small molecules
-
Ethylene and Oxygen

16th December 2016

Elias Frei

Fritz Haber Institute, Inorganic Chemistry Department
efrei@fhi-berlin.mpg.de

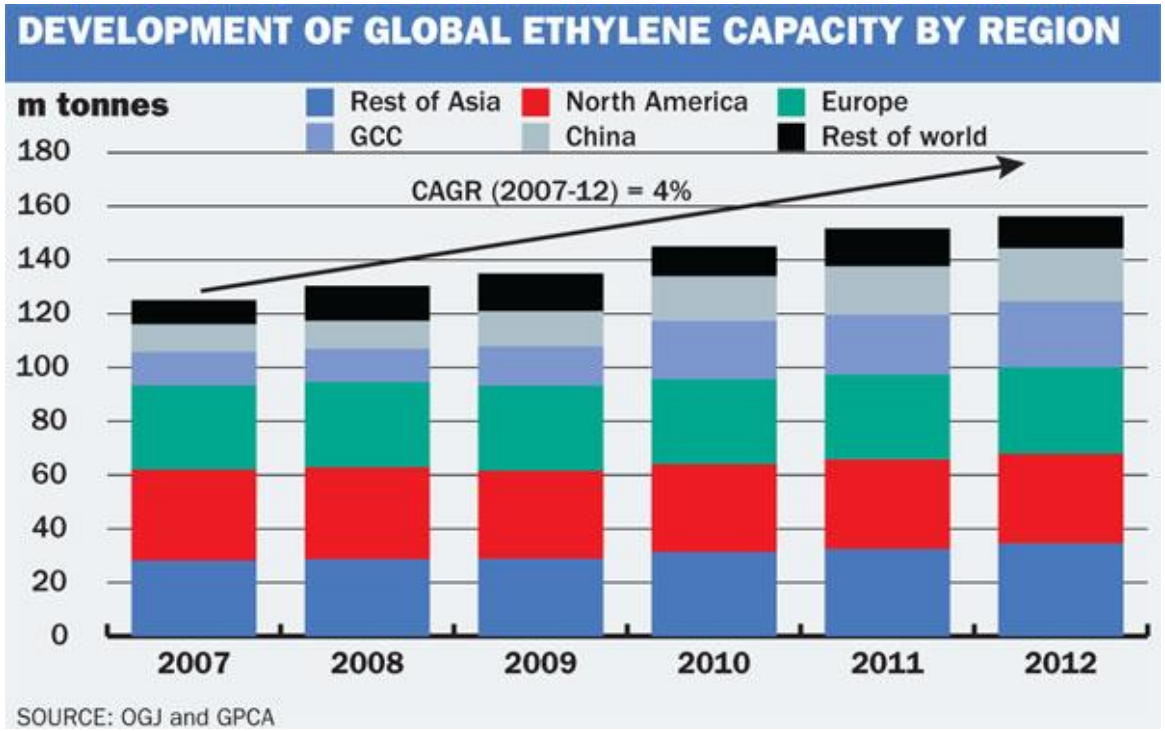
Literature

- 1. Handbook of Heterogenous Catalysis, G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp (2. ed.), Vol 7., 2008
- 2. Industrial Catalytic Processes, C.H. Bartholomew and R.J. Farrauto, Wiley 2006.
- 3. Industrial Organic Chemistry, K. Weissermel, H.-J. Arpe (4. ed), Wiley VCH 2003
- 4. Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis, S. Ted Oyama, Elsevier, 2008

+ references on the slides

Ethylene Production

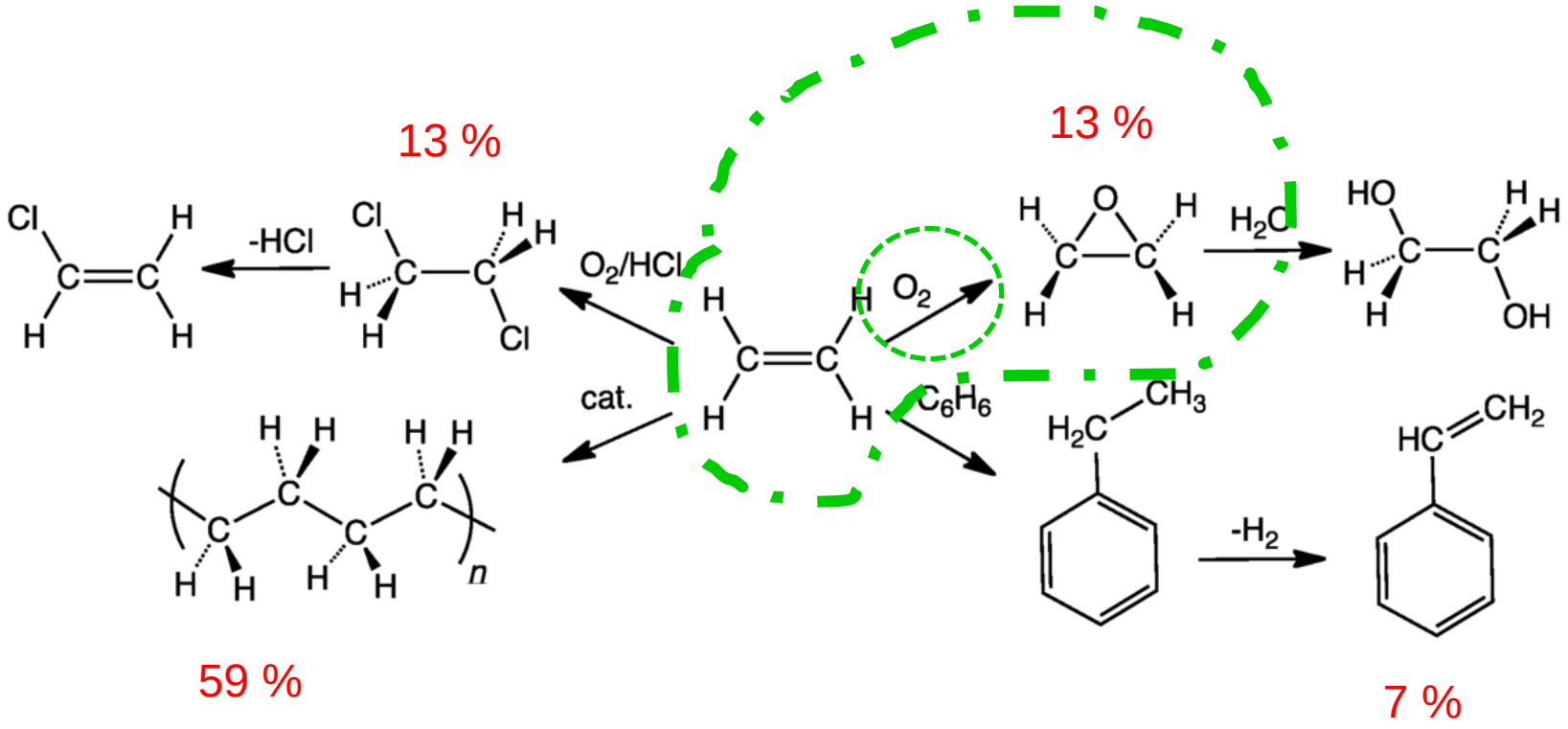
- By far the most important organic chemical compound ~ 150 Mio tons/a
- World scale plant 1 Mio t/a (1970: 300 kt/a)
- Ethylene production: Steam Cracker (https://youtu.be/QLmh0jJE2zE)



~4 % of Germany

http://www.researchandmarkets.com/research/2xl4dr/the_ethylene
The Ethylene Technology Report 2016: 7,000 $

Ethylene Conversion



Ethylene Oxide Production

- World production capacity ~ 17 Mio tons/a
- Plant size: 400 kt/a
- Ethylene production (60-70 % invest for ethylene):
  - 1863 Chlorohydrin process (Wurtz)

$Cl_2 + H_2O \rightarrow \mathbf{HOCl} + HCl$

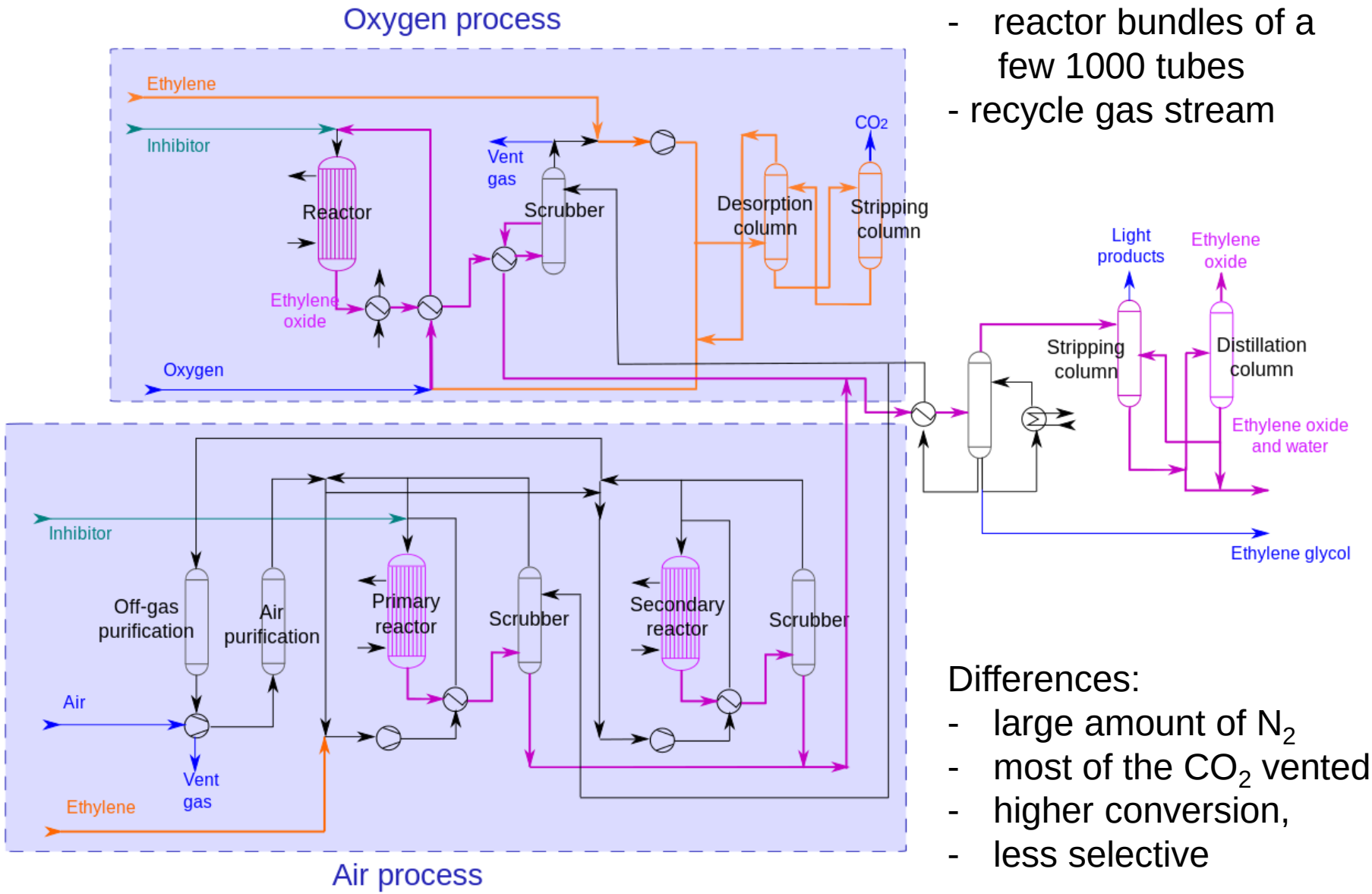
$CH_2{=}CH_2 + HOCl \rightarrow \mathbf{OH{-}CH_2CH_2{-}Cl}$ (4-6 % ethylene)

$OH{-}CH_2CH_2{-}Cl + Ca(OH)_2 \rightarrow \mathbf{H_4C_2O} + CaCl_2$ (30 % $Ca(OH)_2$ at 100 °C)

⇨ 80 % S(EO)

  - 1931 Direct oxidation with air (Lefort, Union Carbon → Dow)
  - 1958 Direct oxidation with O_2 (Shell patent)

Catalyst: Ag supported on Al_2O_3 + promotors



Both:

- reactor bundles of a few 1000 tubes
- recycle gas stream

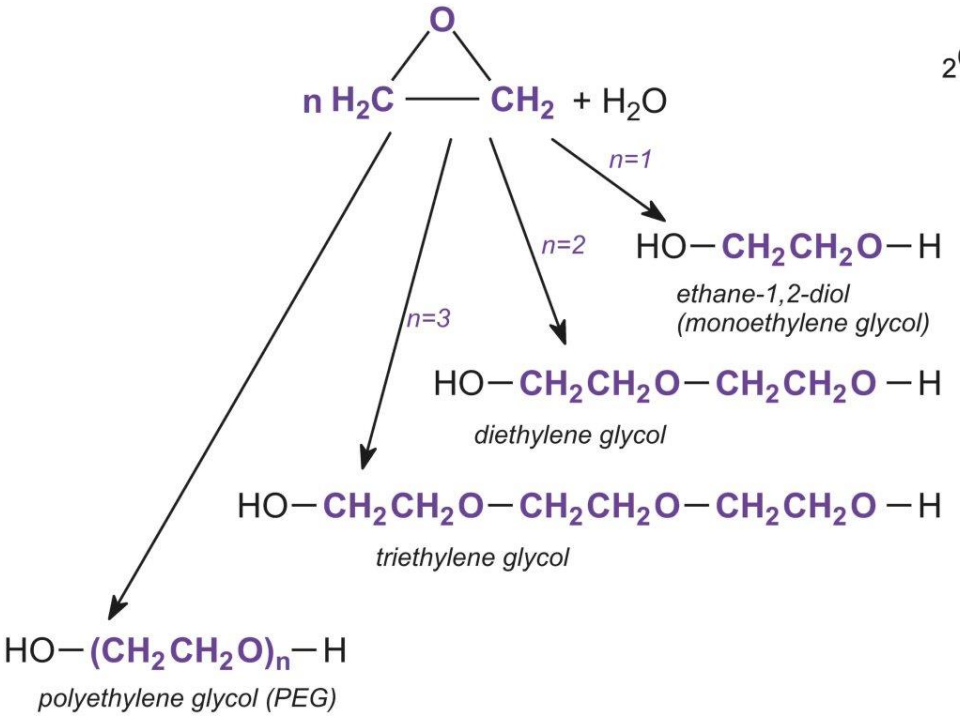
Differences:

- large amount of N_2
- most of the CO_2 vented
- higher conversion,
- less selective

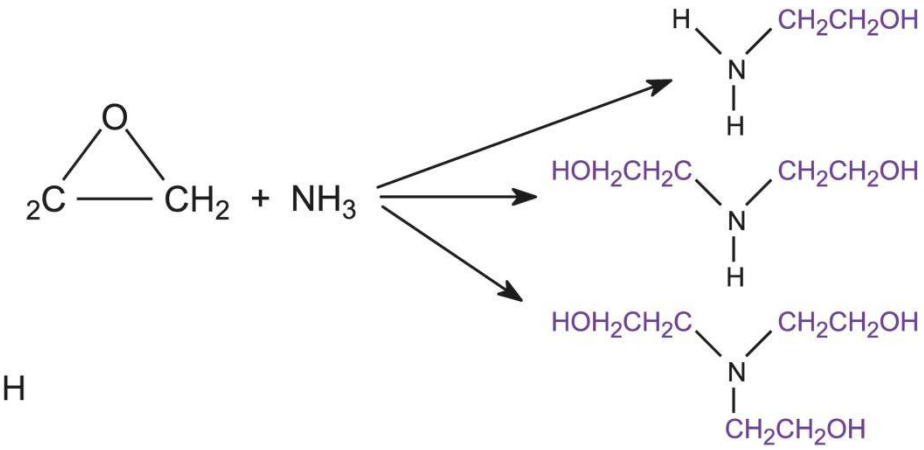
G. O. Curme: Glycols, Reinhold Publ. Co., New York 1952, pp. 74 – 113.

Rebsdat *et al.,* Ullmanns Encycl. Industrial Chemistry, Wiley-VCH **2012**, 547-572

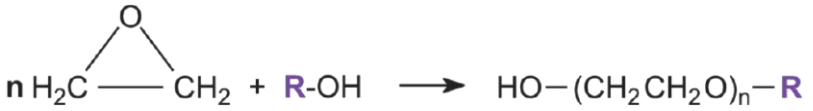
Ethylene Oxide Conversion



~ 67 % glycol + 12 % derivatives



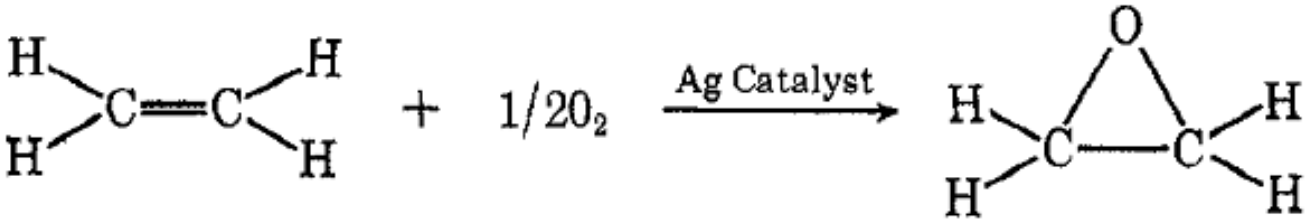
~ 7 % ethanolamine



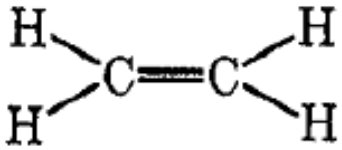
~ 13 % ethoxylates

http://www.essentialchemicalindustry.org/chemicals/epoxyethane.html

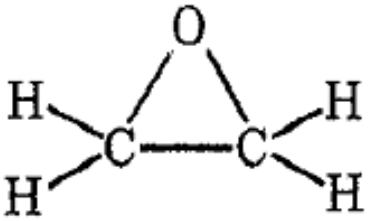
Ethylene + Oxygen



$+ \quad 1/2 O_2$ (1) **-105 kJ/mol**



$+ \quad 3 O_2 \xrightarrow{\text{Ag Catalyst}} 2CO_2 + 2H_2O$ (2) **-1327 kJ/mol**



CH_3CHO (3)

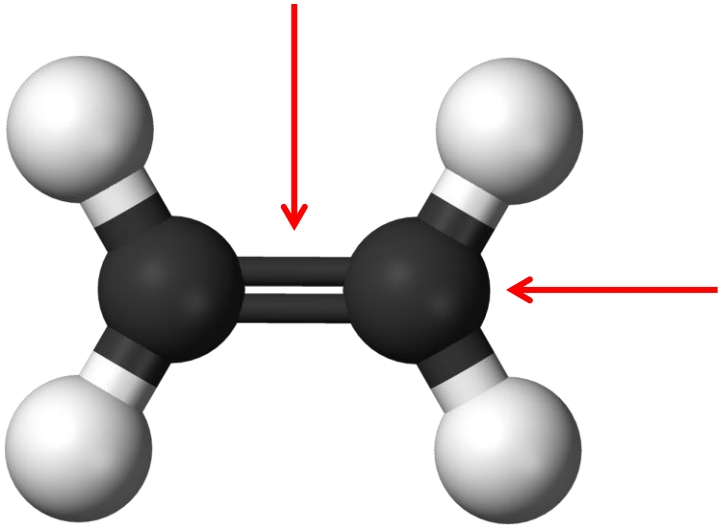
$CH_3CHO + 5/2 O_2 \longrightarrow 2CO_2 + 2H_2O$ (4)

ROBERT E. KENSON AND M. LAPKIN *Volume 74, Number 7 April 2, 1970*

Important applied methods

- **Desorption spectroscopy**
- **Raman and IR for the oxygen chemistry ($^{18}O_2$ isotope experiments), LEED**
- **XPS, EELS and XAS**
- **Electron microscopy**
- **Strong Theory support**

Activation of Ethylene



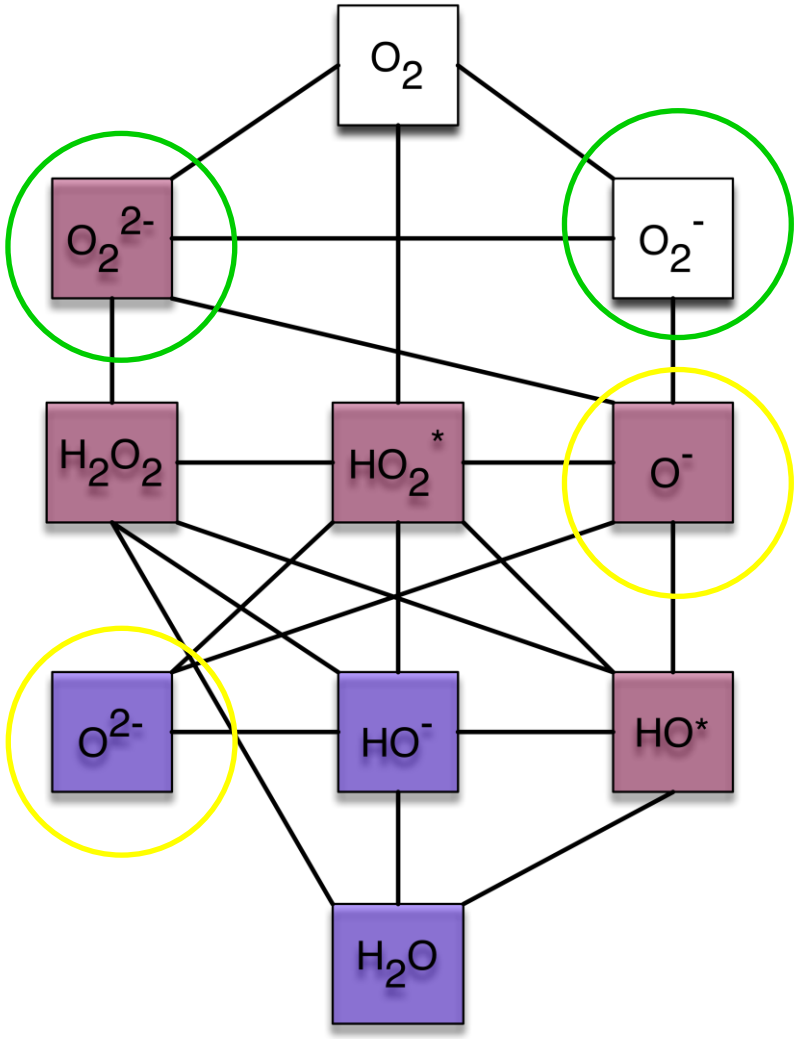
- fast adsoprtion /desorption

- low activation barrier (39-46 kJ/mol)

Ag or oxygen?

Increased 13 times on oxidised surfaces

Activation of Oxygen



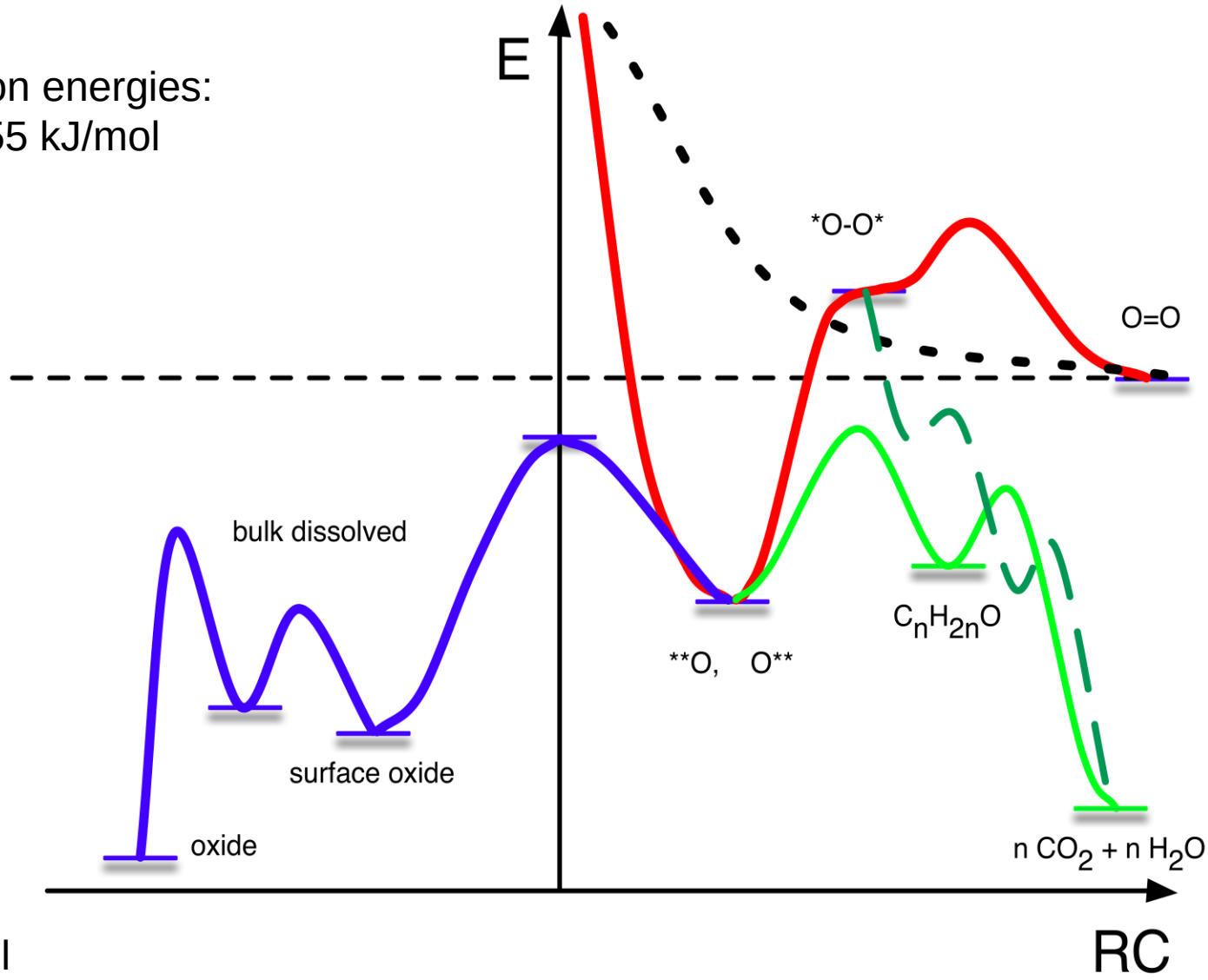
"A simple reaction network for the activation of oxygen.
Hydrogen and an unnamed electron donor are needed. Red denotes
the formal oxidation state -1 and blue the oxidation state -2"

Angew. Chem. Int. Ed. 2015, 54, 3465 – 3520

Angew. Chem. internat. Edit. Vol. 13 (1974), No.1

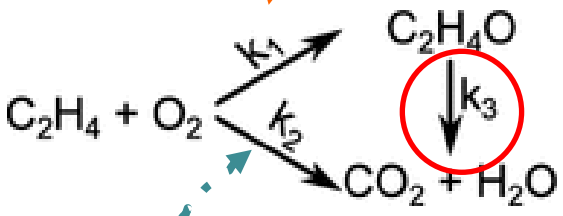
Activation of Oxygen: dissociative?

Desoption energies:
140 – 155 kJ/mol



Molecular or atomic oxygen for EO?

Molecular oxygen: $O_{2,s}$

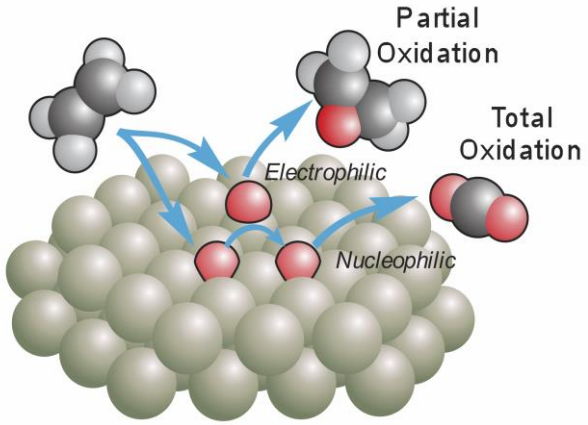


A similar conclusion regarding the nondissociative nature of oxygen on silver was reached by Herzog [98], who reacted ethylene with oxygen and nitrous oxide over silver catalysts. Although significant yields of ethylene oxide were obtained with oxygen, the use of nitrous oxide only produced CO_2 and H_2O, except at higher temperatures where molecular oxygen is known to be produced due to the catalytic decomposition of nitrous oxide [99]:

$$N_2O \longrightarrow N_2 + O(ads) \quad (5)$$

$$N_2O + O(ads) \longrightarrow N_2 + O_2 \quad (6)$$

atomic oxygen: O_s



Kilty PA, Sachtler WMH (1974) Catal Rev Sci Eng 10:1–16

Adsorption of EO on Ag? Isomerization!

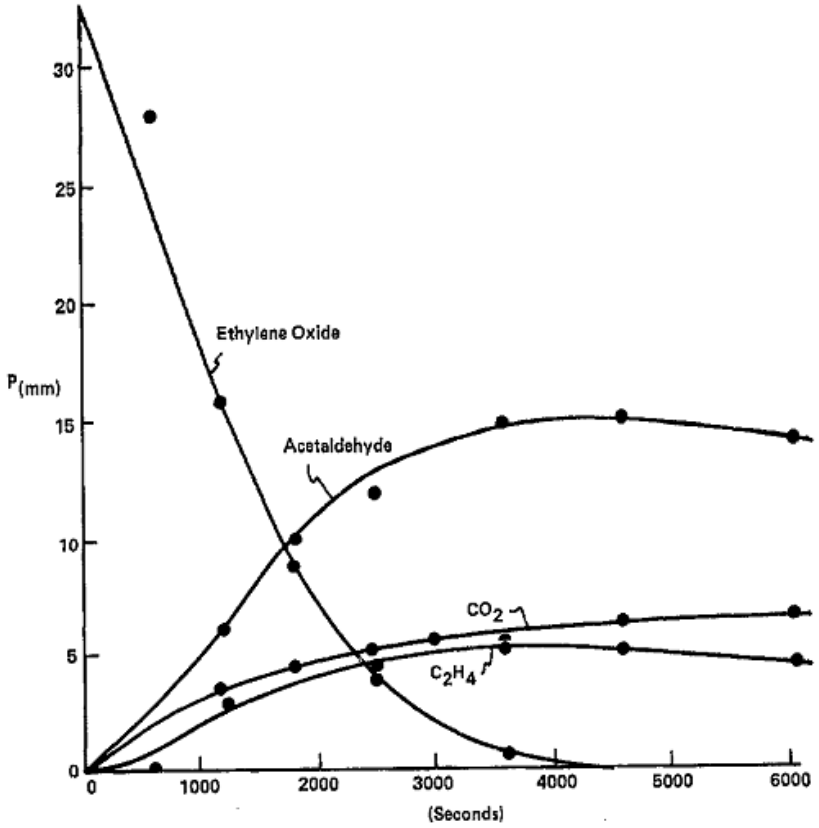
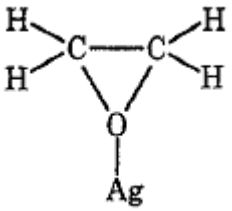
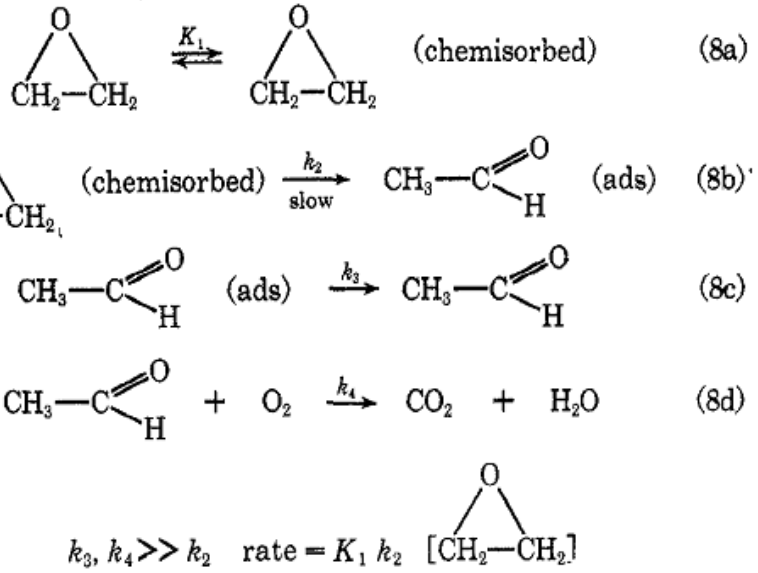


Figure 4. Plot of concentrations of reactants and products *vs.* time of kinetic run EO-1.





ROBERT E. KENSON AND M. LAPKIN *Volume 74, Number 7 April 2, 1970*

Molecular or atomic oxygen for EO?

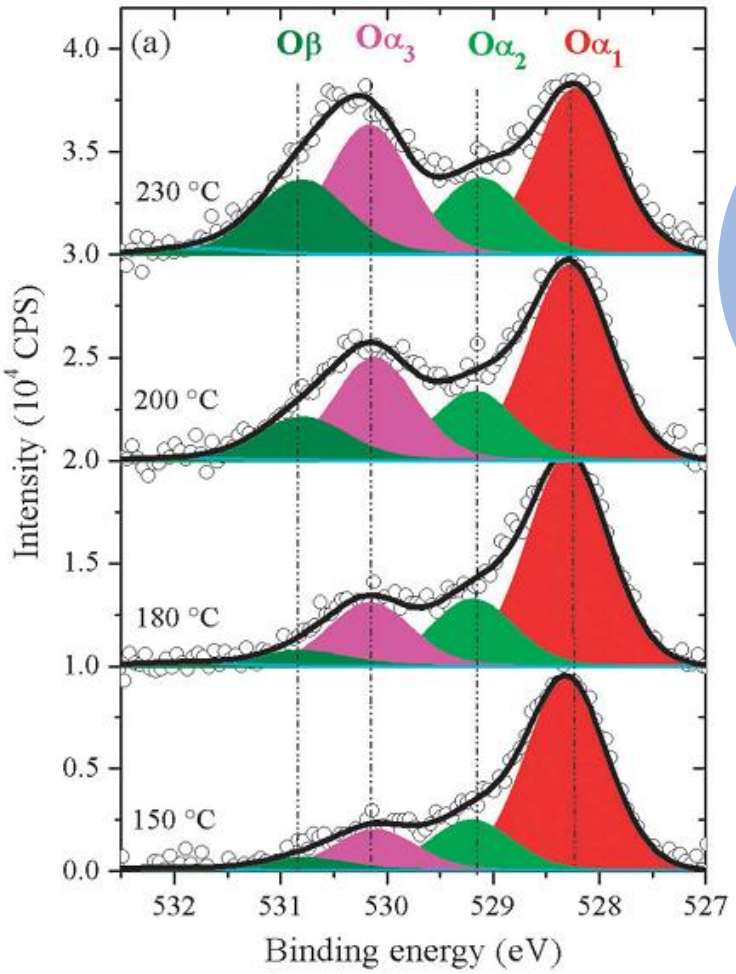
If only molecular oxygen,
selectivity limited to 87.5 % (6/7)!

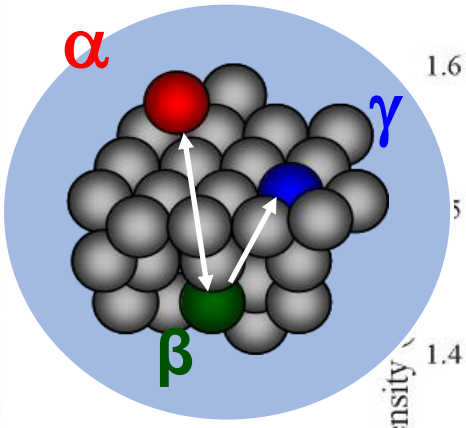
$$7C_2H_4+6O_2 \rightarrow 6(C_2H_4)O+2CO_2+2H_2O$$

Atomic oxygen is involved!

JOURNAL OF CATALYSIS 98, 530-539 (1986)

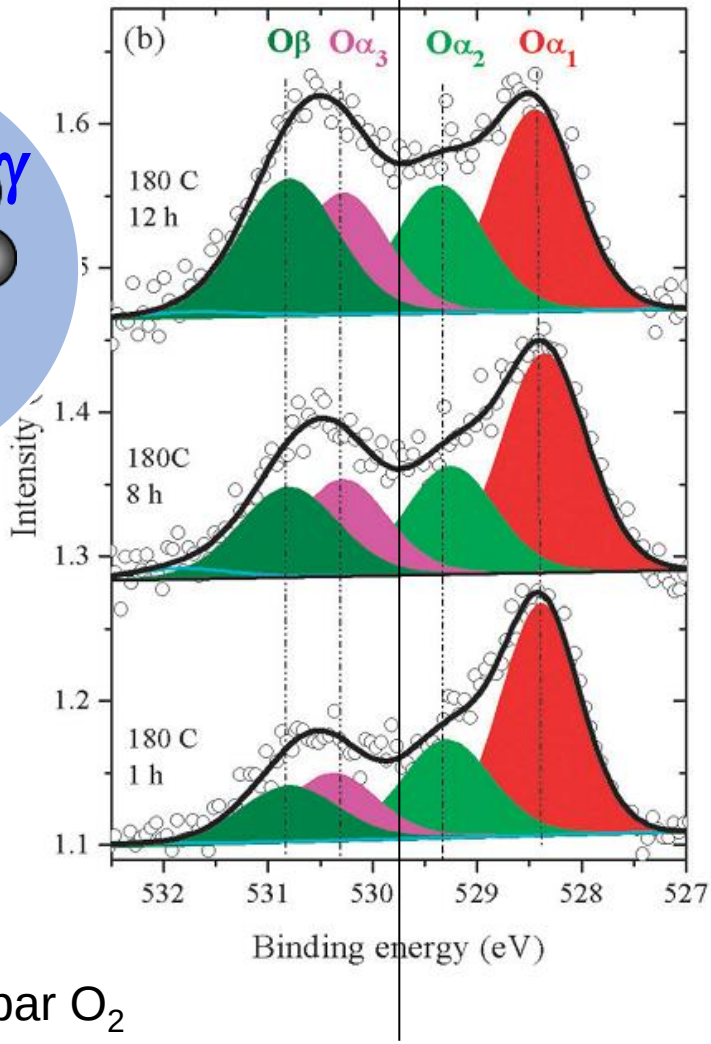
Which kind of oxygen species exist?





3 diffferent on the surface + subsurface

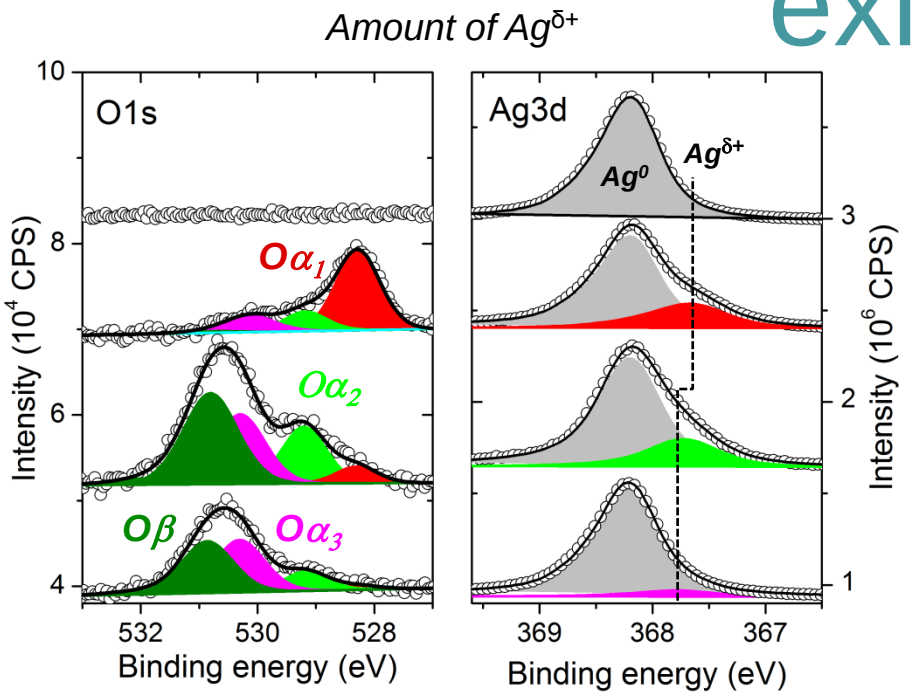
electr. nucl.



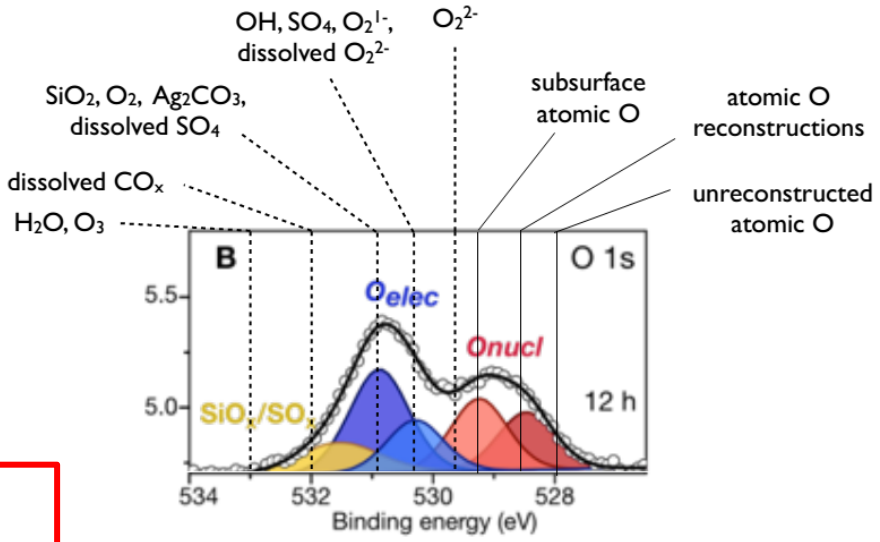
NAP-XPS: 0.25 mbar O_2

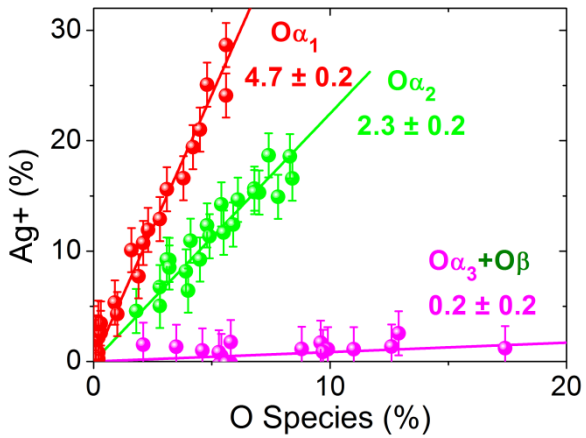
Phys.Chem.Chem.Phys.,2012,14, 4554–4564

Which kind of oxygen species exist?



From Theory (T. Jones FHI-AC)





Ag-O
charge transfer

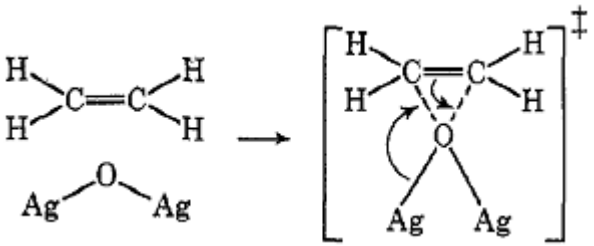
- Electrophilic O is "covalent O" : O_2, SiO_x, SO_x, OH, CO_x, ...
- Nucleophilic O is "ionic O": atomic O
- What about dynamics?

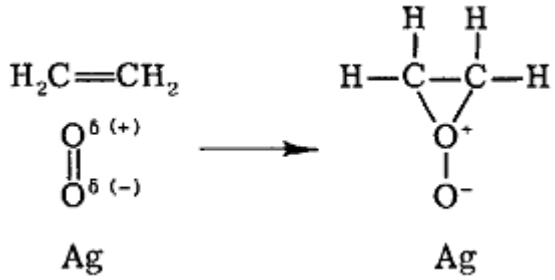
Let`s conclude: A complex situation?

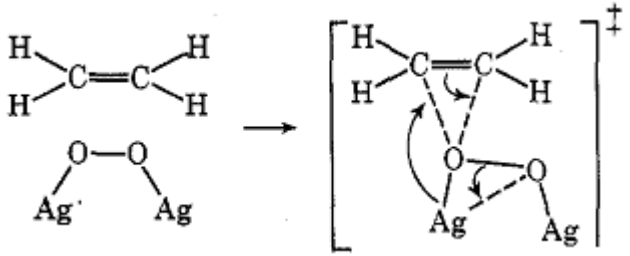
- **Atomic and molacular oxygen is involved**
- **4 to 5 different oxygen species which co-exist:**
  nucleophlic + electrophilic
- **Competing product formation:**
  Acetaldehyde or EO / Isomerization
- **Surface dynamic**
- **No uniform mechanism**

Let`s conclude: A complex situation?

To cite this article: P. A. Kilty & W. M. H. Sachtler (1974) THE MECHANISM OF THE SELECTIVE OXIDATION OF ETHYLENE TO ETHYLENE OXIDE, Catalysis Reviews, 10:1, 1-16, DOI: 10.1080/01614947408079624

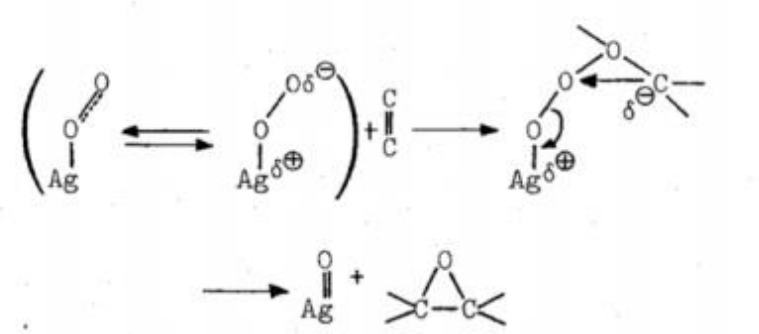






ROBERT E. KENSON AND M. LAPKIN

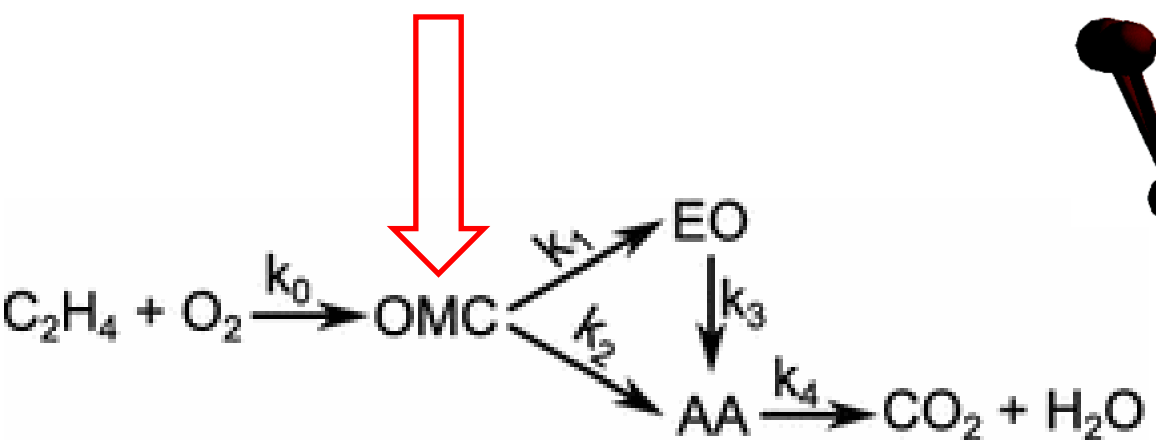
Volume 74, Number 7 April 2, 1970

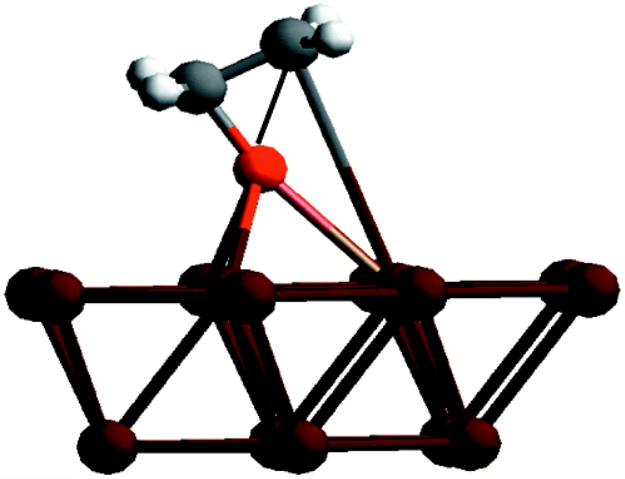


CATAL. REV.—SCI. ENG., 23(1&2), 127-149 (1981)

A common stable intermediat: Oxametallacycle!

common intermediat





Stacchiola D, Wu G, Kaltchev M, Tysoe WT (2001) Surf Sci 486:9–23

Linic S, Medlin JW, Barteau MA (2002) Langmuir 18:5197–5204

Linic S, Barteau MA (2001) J Am Chem Soc 124:310–317

Oxametallacycle: What experimental evidence?

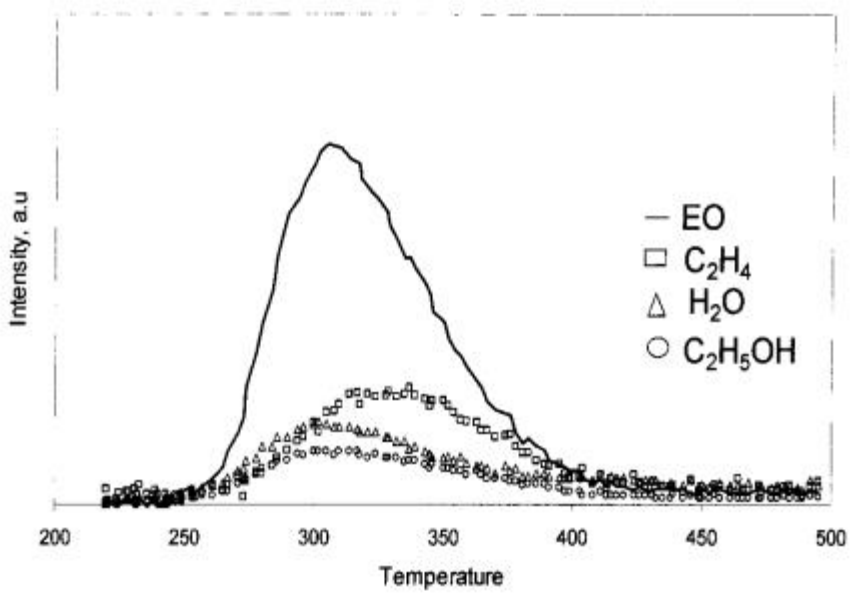


Figure 2. TPD spectra following a 250 K dose of EO on Ag(111).

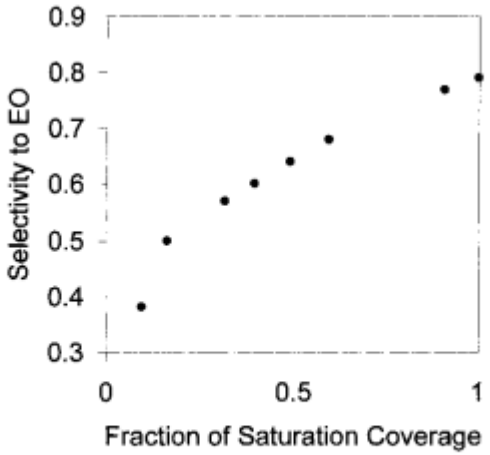


Figure 3. Selectivity to EO during TPD as a function of coverage of strongly bound intermediate, after 250 K dose.

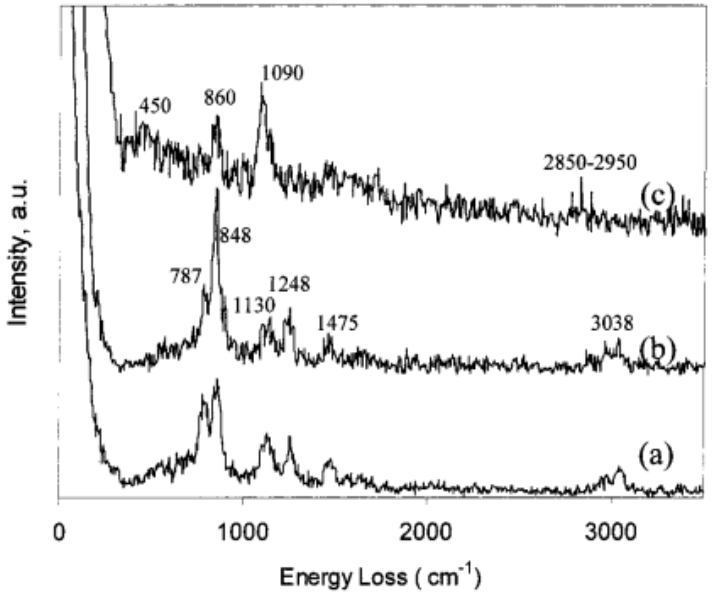
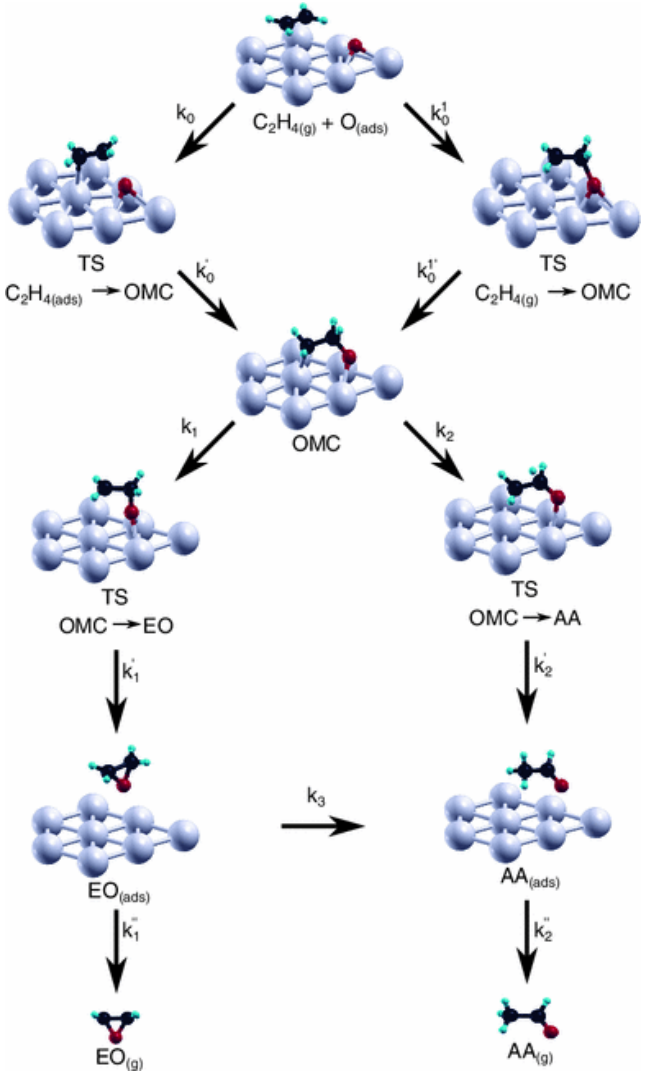


Figure 4. HREEL spectra collected after exposing EO to Ag(111) at varying dose temperatures. (a) 110 K; (b) 140 K; (c) 250 K.

b) molecularly adsorbed EO
c) Ring closure to OMC
in line with DFT prediction

Linic S, Barteau MA (2001) J Am Chem Soc 124:310–317

Oxametallacycle: Langmuir-Hinshelwood mechanism



O_{ads} + Ethylene$_{ads}$

⇩ transition state

common intermediate

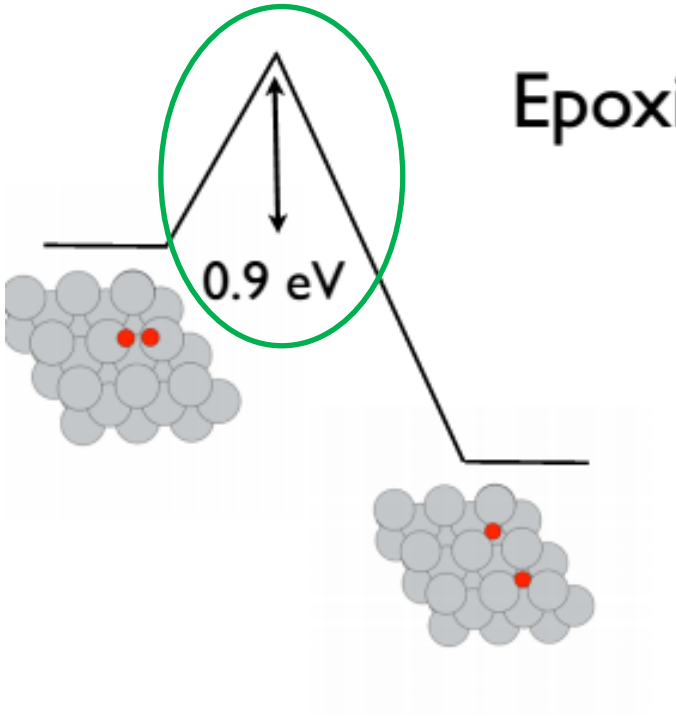
Product selectivity depends on the relative barriers:

$$E_{a,EO} \text{ vs. } E_{a,AA}$$

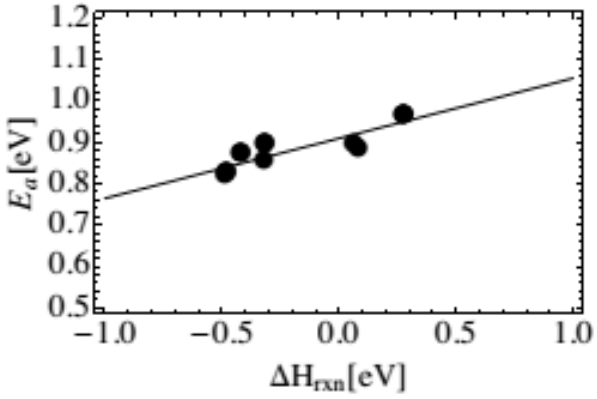
Ozbek MO, Onal I, Santen RA (2012) Top Catal 55:710–717

Let`s discuss the barriers

Atomic or moleular oxygen: dissociation barrier coverage dependend!



Epoxidation route I



coverage

$O_{2ads} \longrightarrow 2O_{ads}$

$0.125\ ML \leq \Theta \leq 0.5\ ML$

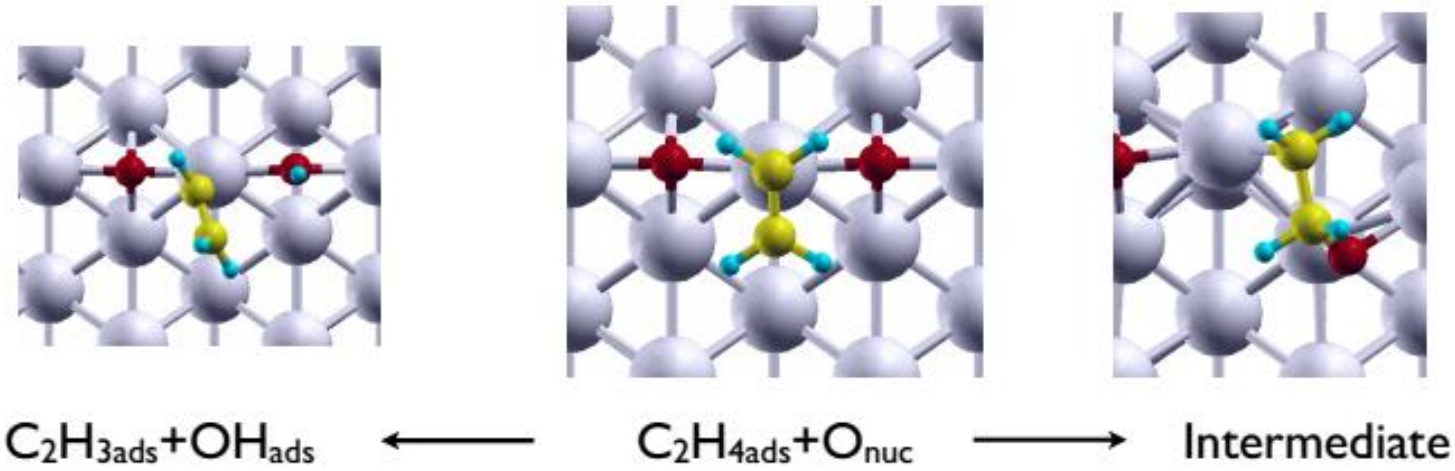
Ethylene pre-adsorbed reduces the barrier to 0.5 eV!

Results by T. Jones AC-FHI, in parts unpublished

Let`s discuss the barriers

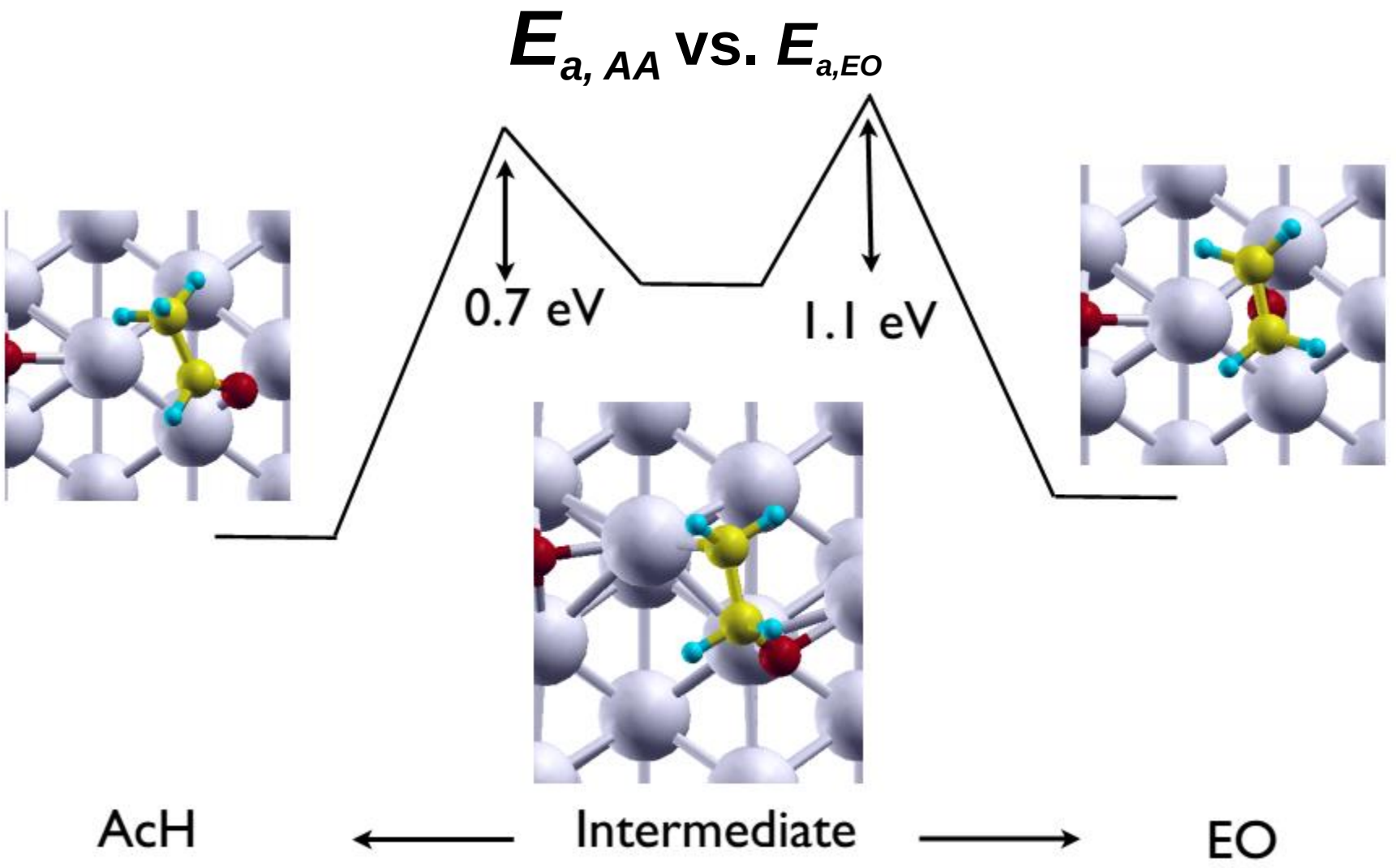
With nucleophilic oxygen direct combustion?

Epoxidation by O_{nuc}



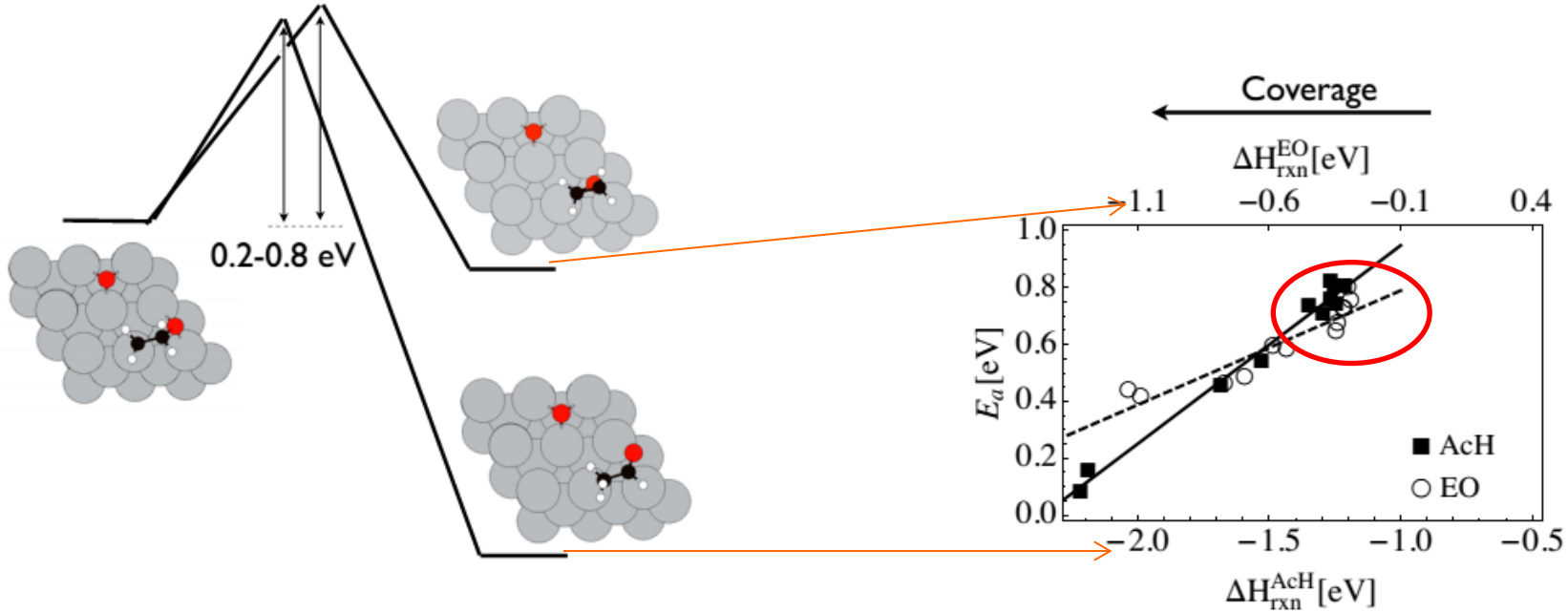
Results by T. Jones AC-FHI, in parts unpublished

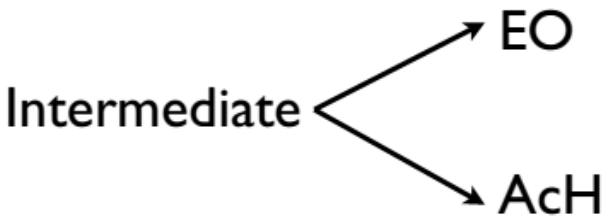
Let`s discuss the barriers



Results by T. Jones AC-FHI, in parts unpublished

Let`s discuss the barriers

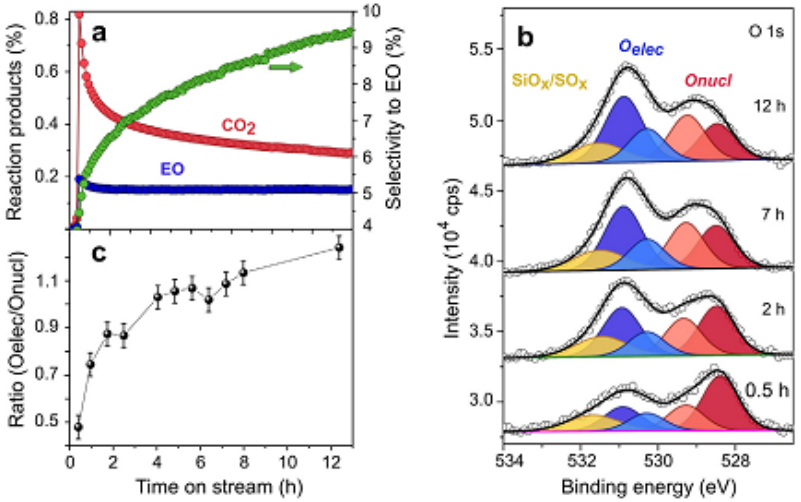




At low coverages of oxygen is a high EO selectivty possible!

Results by T. Jones AC-FHI, in parts unpublished

Co-feed with ethylene chloride: promtor and/or co-catalyst

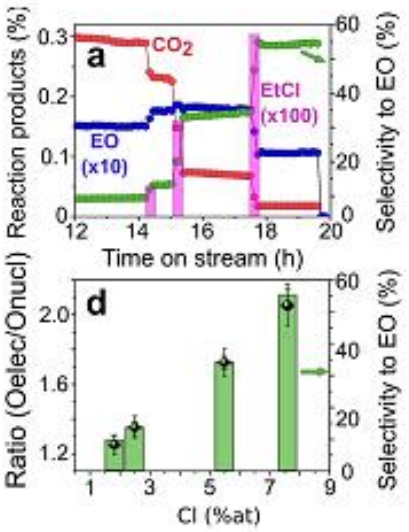


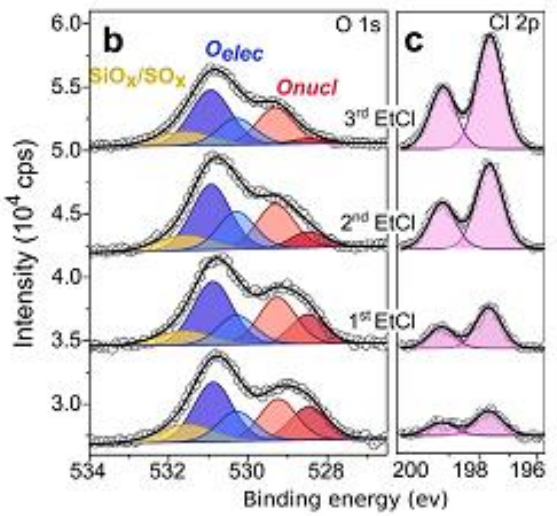
0.3 mbar, 230 °C, C_2H_4:O_2= 1:2

EC:

- **oxygen management**
- **blocks active/unselectice Ag-sites**
- **too much EC: Poisening!**

0.3 mbar, 230 °C, C_2H_4:O_2= 1:2
+ pulsing with EC





T.C.R. Rocha et al./Journal of Catalysis 312 (2014) 12–16

Co-feed with ethylene chloride: promtor and/or co-catalyst

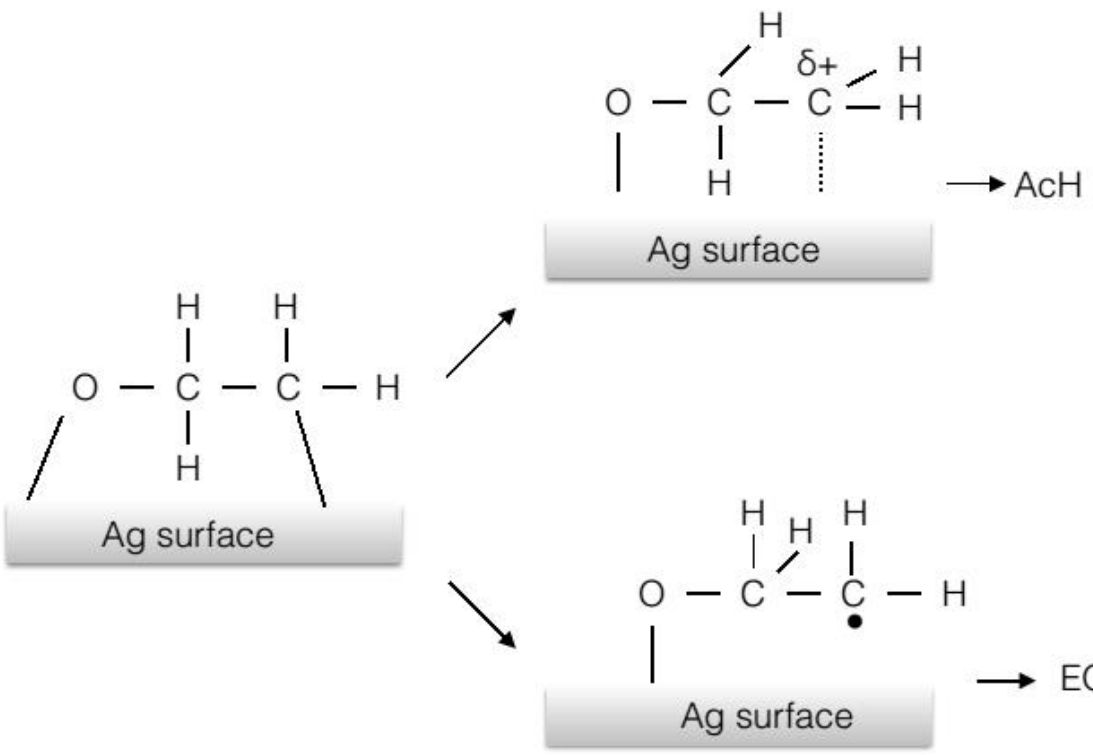
Ethylene chloride effects:

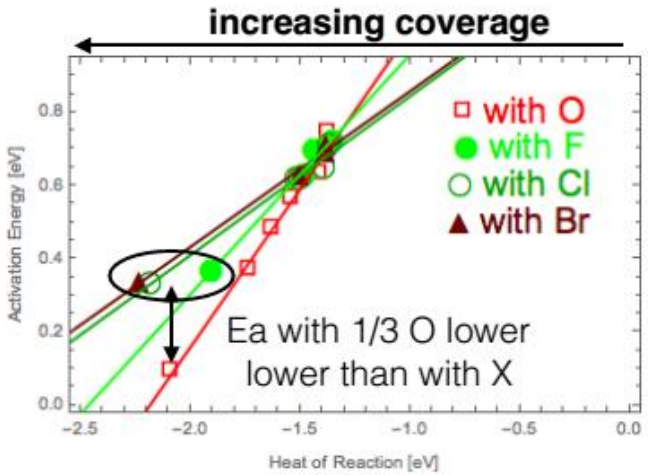
- **oxygen management on the surface + in the bulk!**
- **blocks active/unselectice Ag-sites**
- **prevents surface from reconstruction**
- **weakens the Ag-O bond, easier oxygen-transfer**
- **EC dosing + promoters has a strong impact on S(EO)**
- **too much EC: Poisening!**

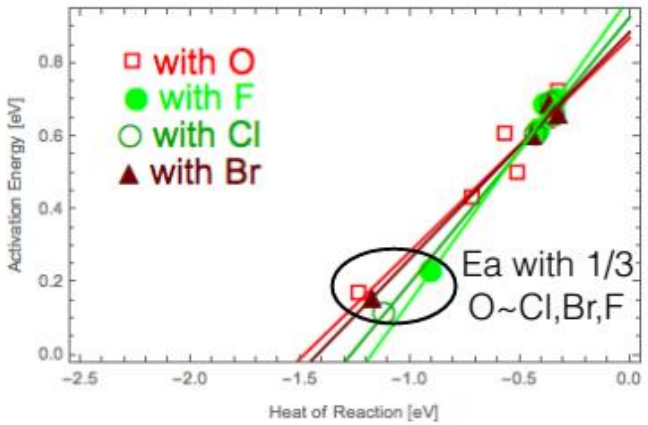
Ozbek MO, Onal I, Santen RAV (2011) J Phys Condens Matter 23:404202

Campbell CT (1986) J Catal 99:28–38

Co-feed with ethylene chloride: promtor and/or co-catalyst





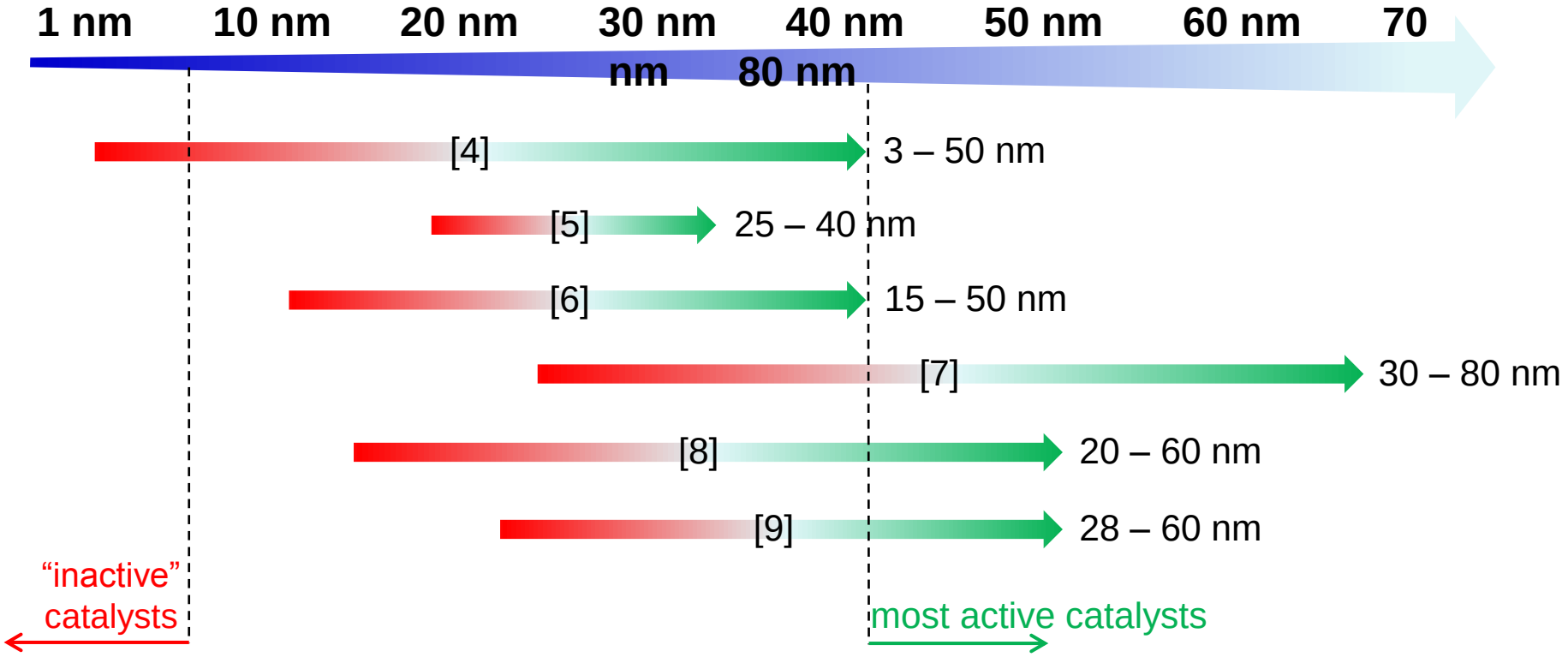


Results by T. Jones AC-FHI, in parts unpublished

The EO catalyst: Support + particle size

Ag particle size on supported catalysts

Arrows show increase in catalyst productivity with Ag particle size until a maximum is reached.



PhD-Proposal: M. Lamoth

- Almost no selectivity observed for particles < 2nm[4]
- Particles < **10 nm** are “known to exhibit no catalytic acitivty”[8]

[4] Wu and Harriott, *J. Catal.* **1975**, *39*, 395-402 **[5]** Verykios *et al.*, *J. Catal.* **1980**, *66*, 368-382 **[6]** Lee *et al.*, *Appl. Catal.* **1989**, *50*, 17 **[7]** Tsybulya *et al.*, *J. Catal.* **1995**, *154*, 194-200 **[8]** Goncharova *et al.*, *Appl. Catal. A* **1995**, *126*, 67-84 **[9]** Bukhtiyarov *et al.*, *J. Chem. Faraday Trans.* **1997**, *93*, 2323-2329

The EO catalyst: Support + particle size

Carbides (SiC, TiC, ZrC, WC,)
Nitrides (TiN, ZrN, Si_3N_4, Zr_3N_4, Mg_3N_2)
Silicides (Fe_3Si, Ca_2Si, $CaSi_2$, $TiSi_2$, WSi_2)
Oxides (**α-Al_2O_3**, BeO, CeO_2, ZrO_2, MgO)
Borides (SiB_3, SiB_6, TiB_2, ZrB_2, FeB)
Spinels ($MgAl_2O_4$)
Silicates ($MgSiO_3$)

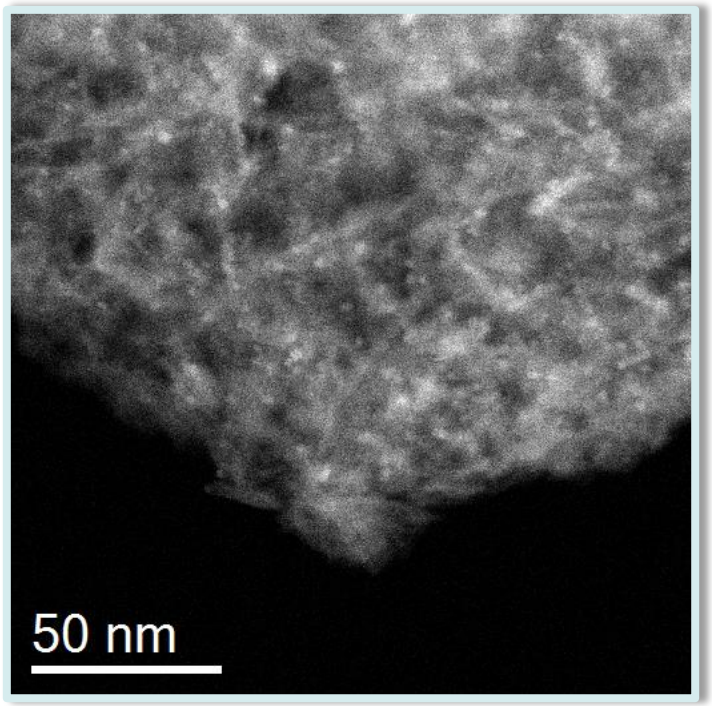
Inert supports

Active supports

Oxides (TiO_2, Fe_2O_3, MgO, ZrO_2, $FeTiO_3$, $CaTiO_3$, $SrTiO_3$)
Zeolites (alumosilicates)
Transition-aluminas
Silicas
Silica-mixed oxides
(-titania, -alumina)
Carbonates ($CaCO_3$)

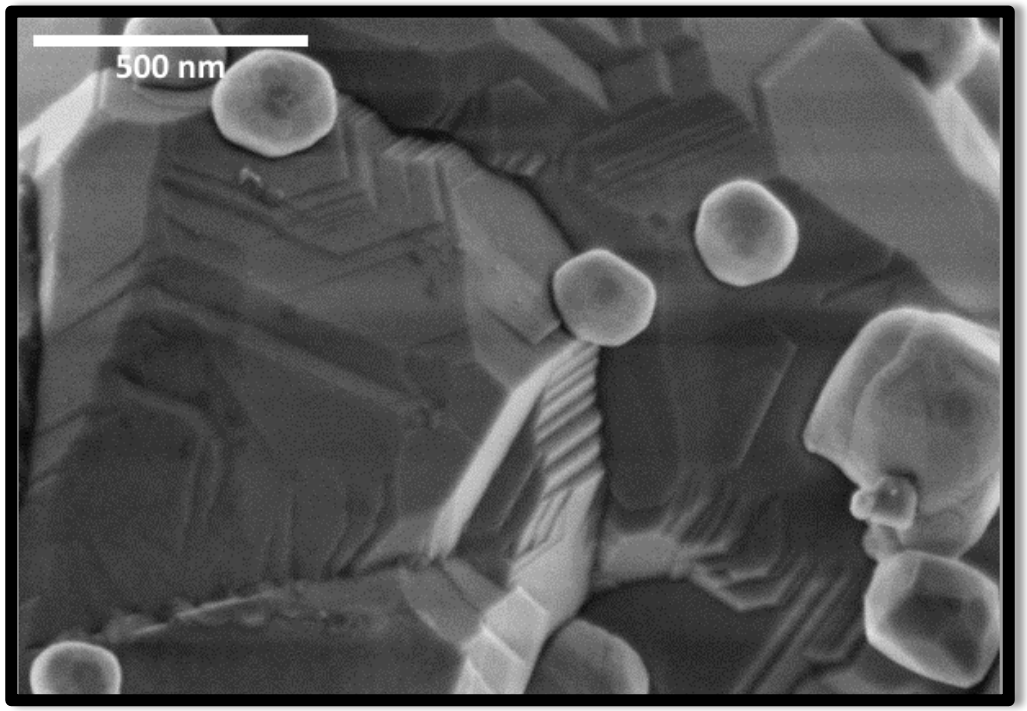
The EO catalyst: Support + particle size

Active supports



Siral 20 / 5 wt. Ag / calcined @ 500 °C

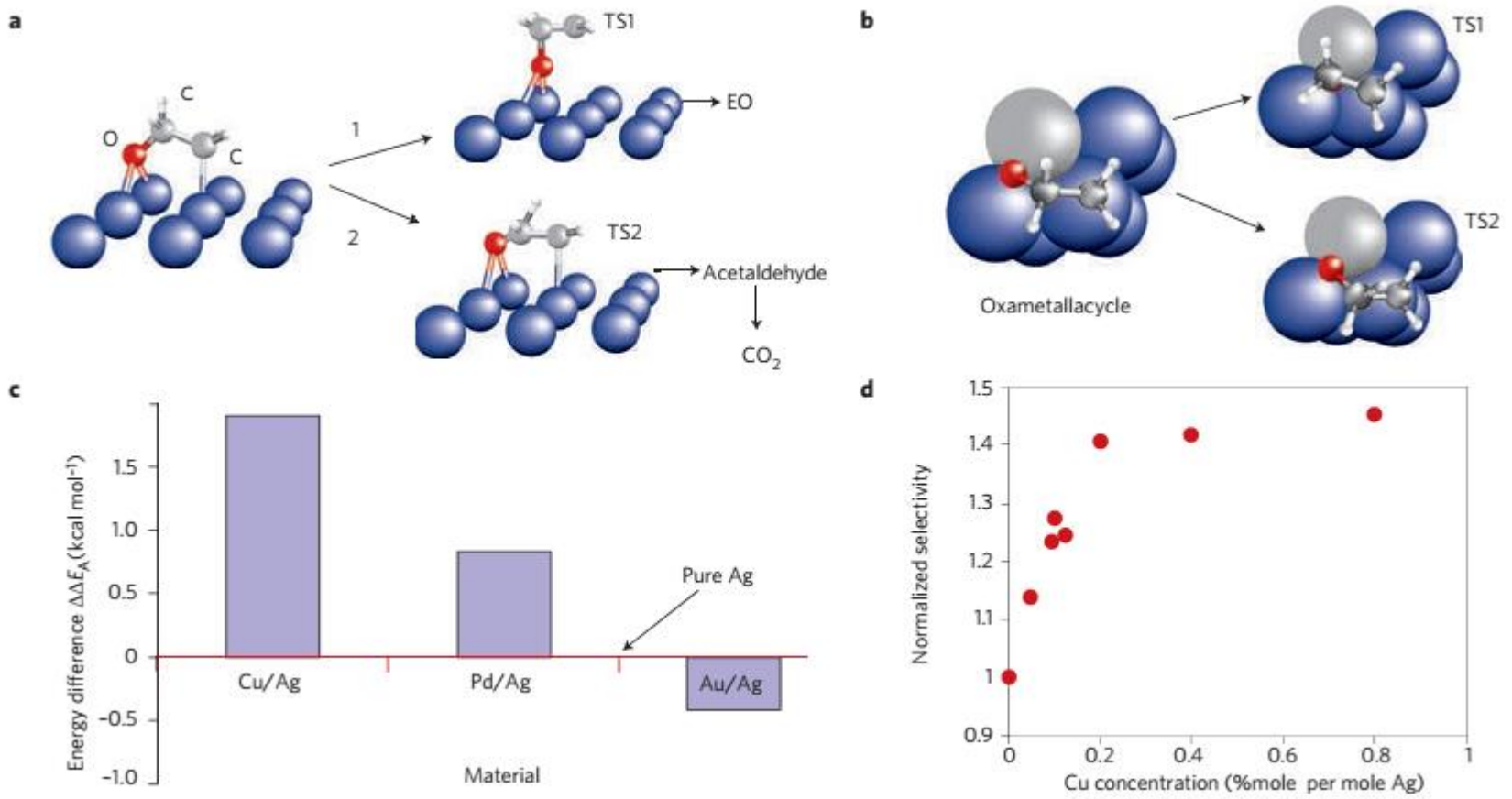
Inert supports



α-Al_2O_3 / 5 wt. Ag / calcined @ 500 °C

Masterthesis M. Lamoth

The EO catalyst: Perspectives!



$\Delta\Delta EA = (\Delta E_{TS2}(alloy) - \Delta E_{TS1}(alloy)) - (\Delta E_{TS2}(Ag)\ \Delta E_{TS1}(Ag))$

nature chemistry| VOL 1 | APRIL 2009 | www.nature.com/naturechemistry

Linic, S., Jankowiak, J. & Barteau, M. A. Selectivity driven design of bimetallic ethylene epoxidation catalysts from first principles.J. Catal. 224,489–493 (2004).

Conclusion

- **The ethylene epoxidation is an important industrial process via direct ox.**
- **The industrial catalysts is a Ag@α-Al_2O_3+promoters: Li, Cs, W, S, Re**
- **The O_2-Ag chemistry is challenging and dynamic: nucl./electr./sub-surf.**
- **Molecular and atomic oxygen form EO**
- **The OMC is the most probable common intermediat + LH-mechanism**
- **The selectivity is strongly T and coverage dependent**
- **EC is an important co-feed and co-catalyst for the industrial process:**

electronic + structural impact

Not discussed: Carbon (sub-surface), sulfur/sulfate promotion, Catalyst synthesis etc.