Why (100) terraces make and break bonds

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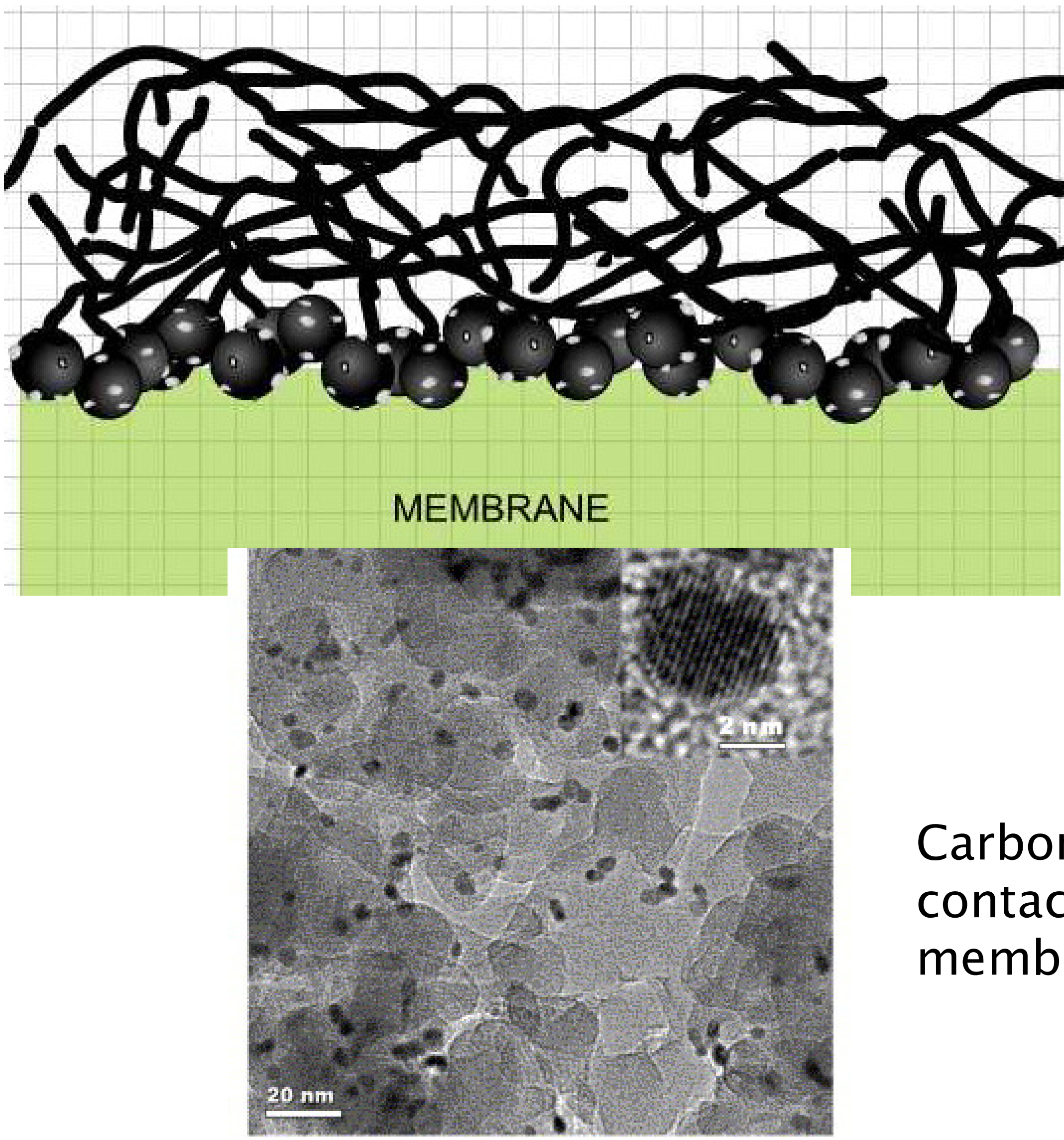
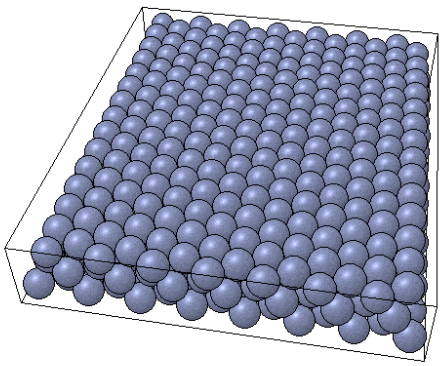
Real electrocatalysts

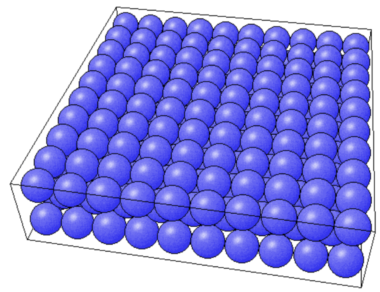


Carbon-supported nanoparticles in contact with a polymer electrolyte membrane

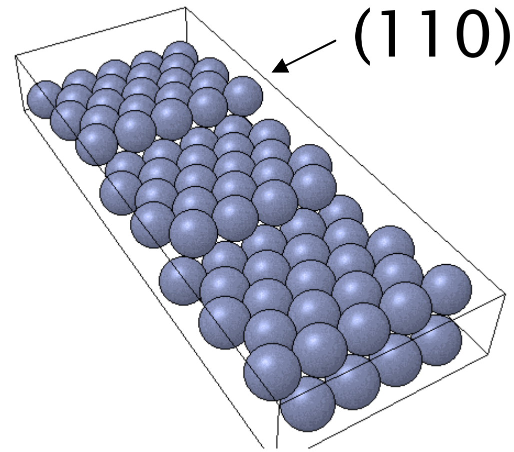
Well-defined surfaces

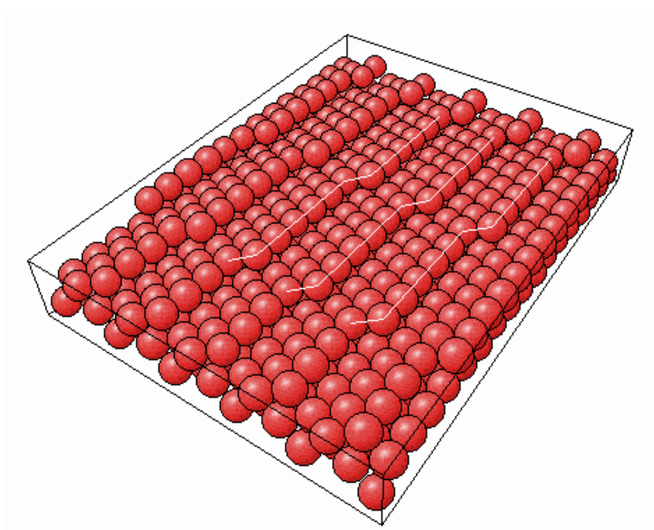
(111) or (100) terraces



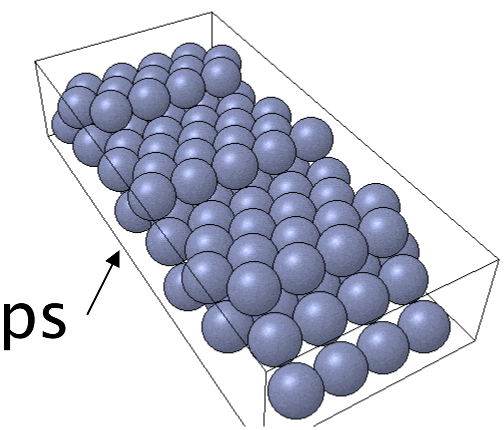


(110) steps





(100) steps



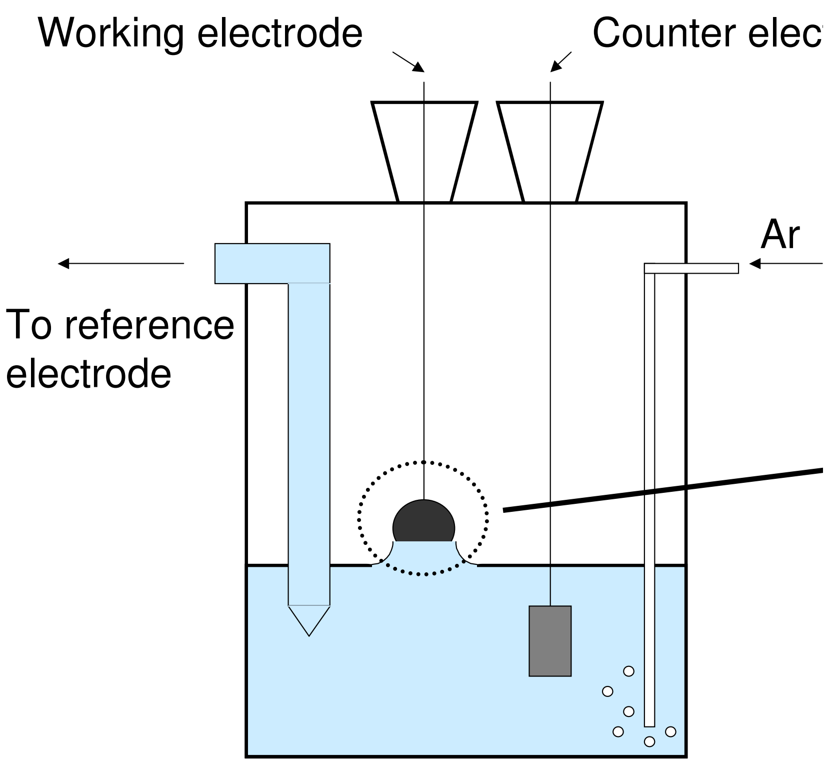
Structural models of nanoparticles

M.T.M.Koper, Nanoscale 3 (2011) 2054

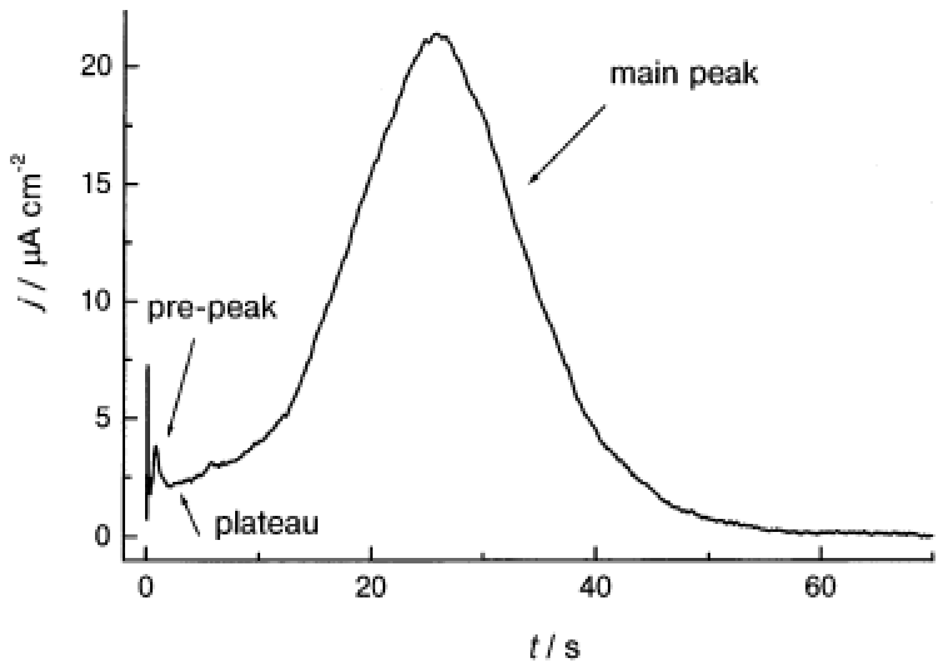
"Surface science under water"

$$CO_{ads} + H_2O \rightarrow CO_2 + 2\,H^+ + 2e^-$$

"CO stripping": oxidize CO from surface without CO in solution



Chronoamperometry: measure *j* after potential step



CO oxidation on Pt

Langmuir-Hinshelwood mechanism

$H_2O + * \leftrightarrows OH_{ads} + H^+ + e^-$

$CO_{ads} + OH_{ads} \rightarrow CO_2 + 2\ * + H^+ + e^-$

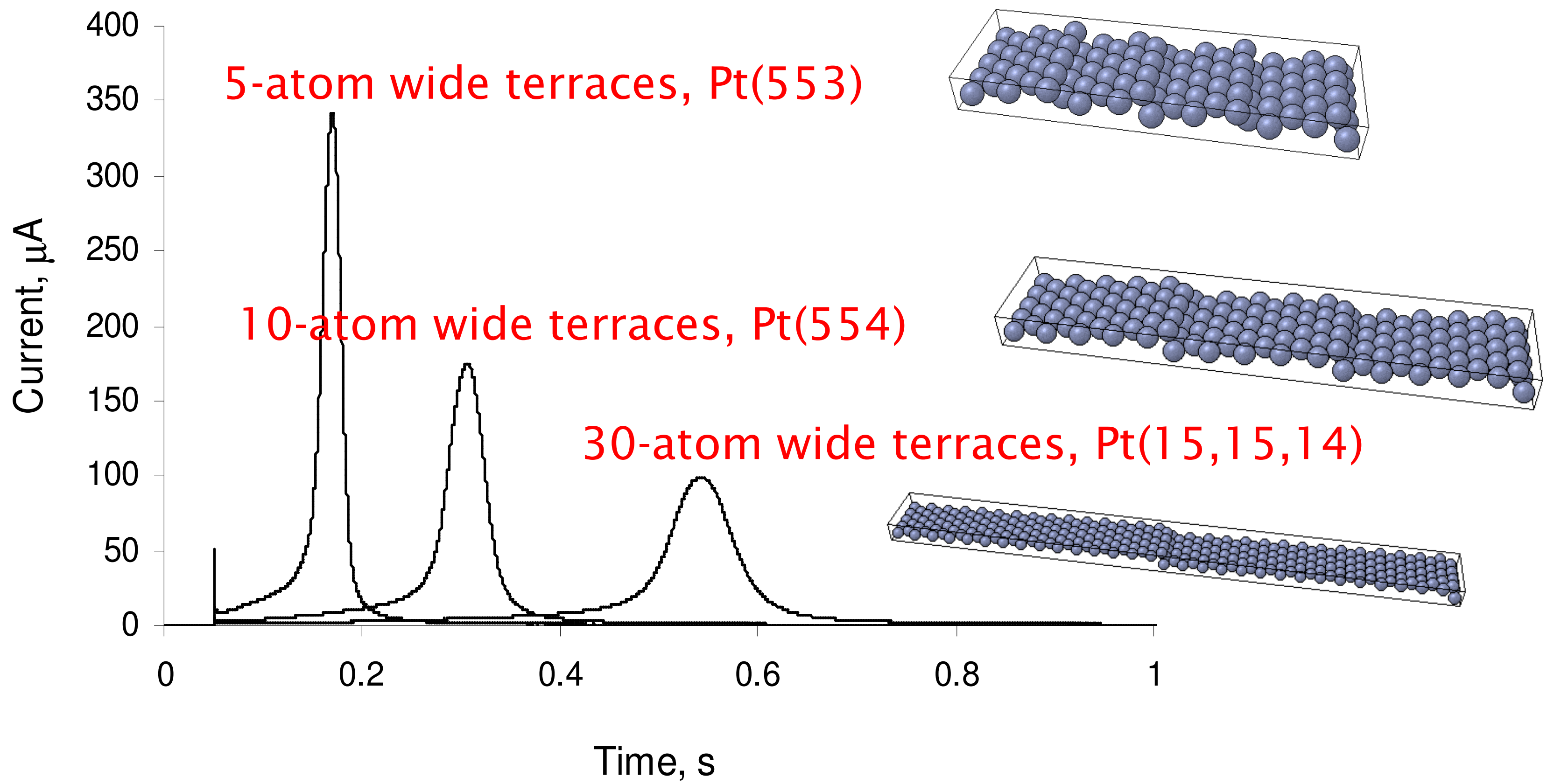
Mean-field kinetic modeling:

autocatalytic rate law: $$\frac{d\theta_{CO}}{dt} = -k(E)\theta_{CO}(1-\theta_{CO})$$

$$j(t) = \frac{Q(k/\Gamma_m)\exp(-k(t-t_{\max})/\Gamma_m)}{[1+\exp(-k(t-t_{\max})/\Gamma_m)]^2}$$

predicts a peaked current response as a function of time

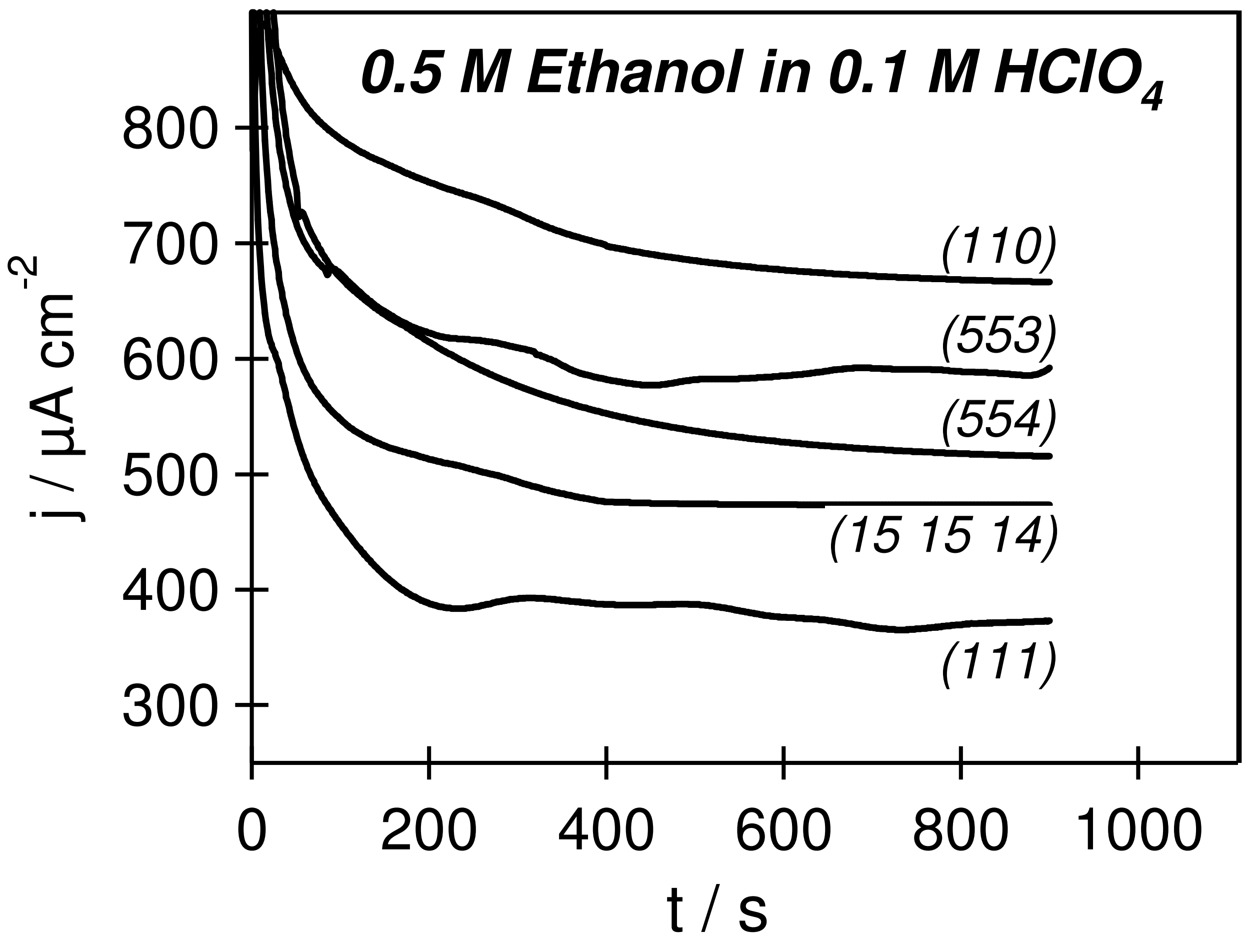
CO stripping on stepped Pt/acid



- rate constant varies linearly with step density:
  reaction takes place at steps through preferential formation of OH
- shape does not depend on terrace width: fast CO diffusion on terraces

N.P.Lebedeva, M.T.M.Koper, J.M.Feliu, R.A.v.Santen, J.Phys.Chem.B 106 (2002) 12938

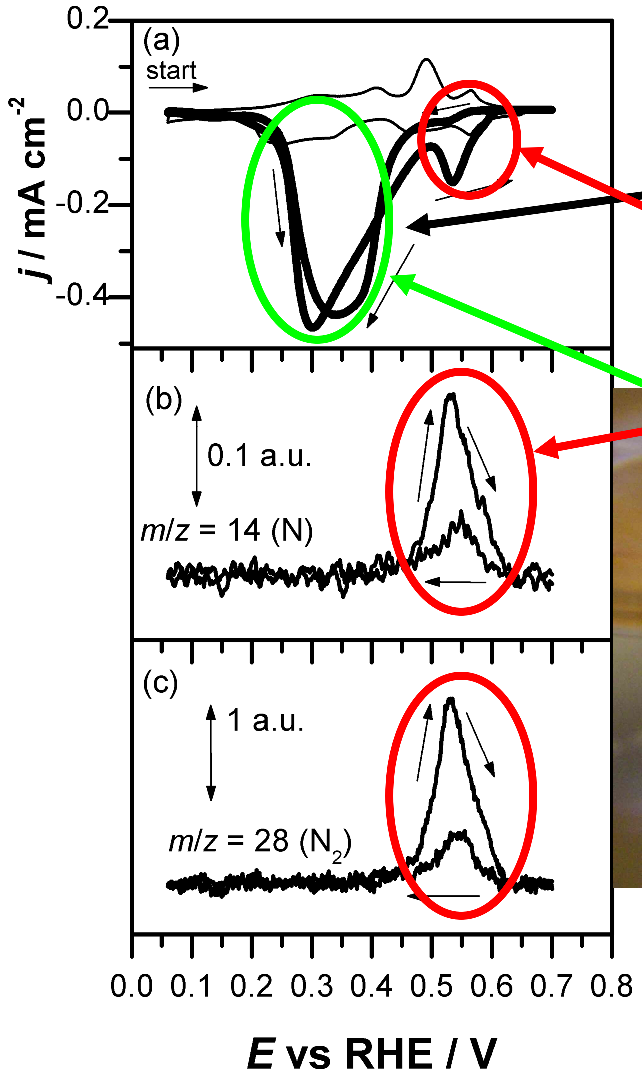
Ethanol oxidation

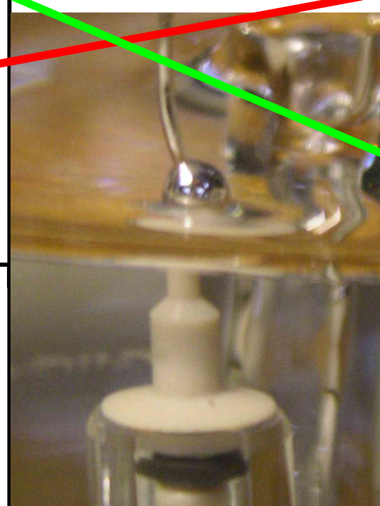


O-H bond breaking catalyzed by steps

S.C.S.Lai, M.T.M.Koper, Faraday Disc. 140 (2008) 399

NO_2^- reduction to N_2 on Pt(100)





Unique reactivity of nitrite on Pt(100) in 0.1 M NaOH

100% (?) selectivity to N_2!

Ammonia NH_3 formation

Mechanism?

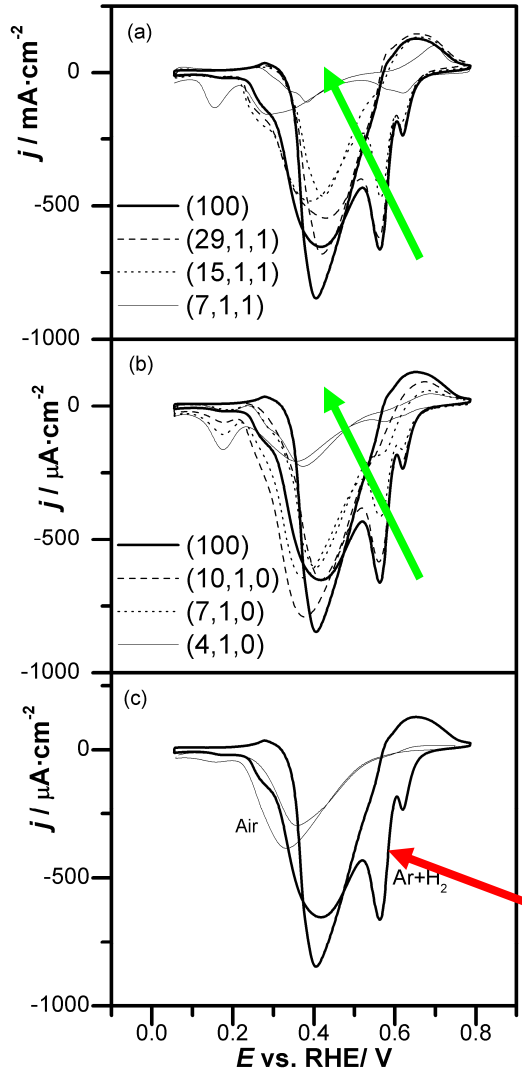
No N_2O involved;

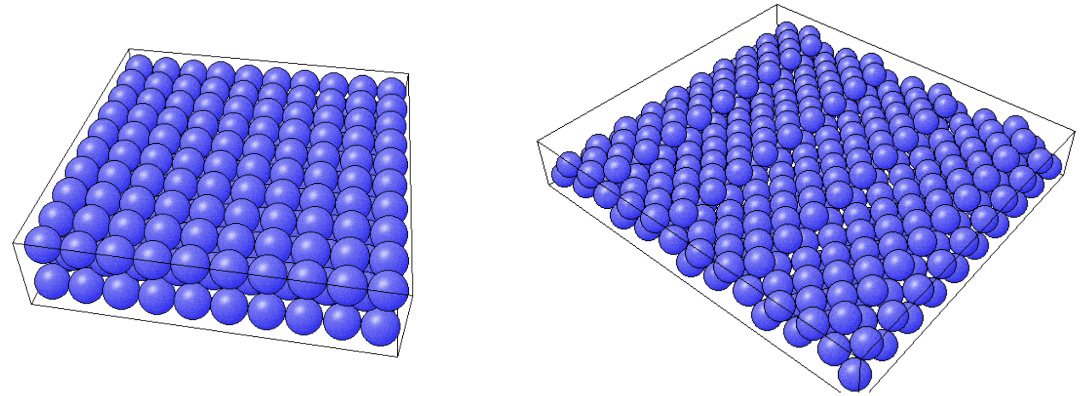
$NH_{2,ads} + NO_{ads} \rightarrow N_2$

$$2\ NO_2^- + 8\ H^+ + 7\ e^- \rightarrow N_2 + 4\ H_2O$$

M.Duca, M.Oroval, P.Rodriguez, M.T.M.Koper, J.Am.Chem.Soc. 132 (2010) 18042

Steps are not good…

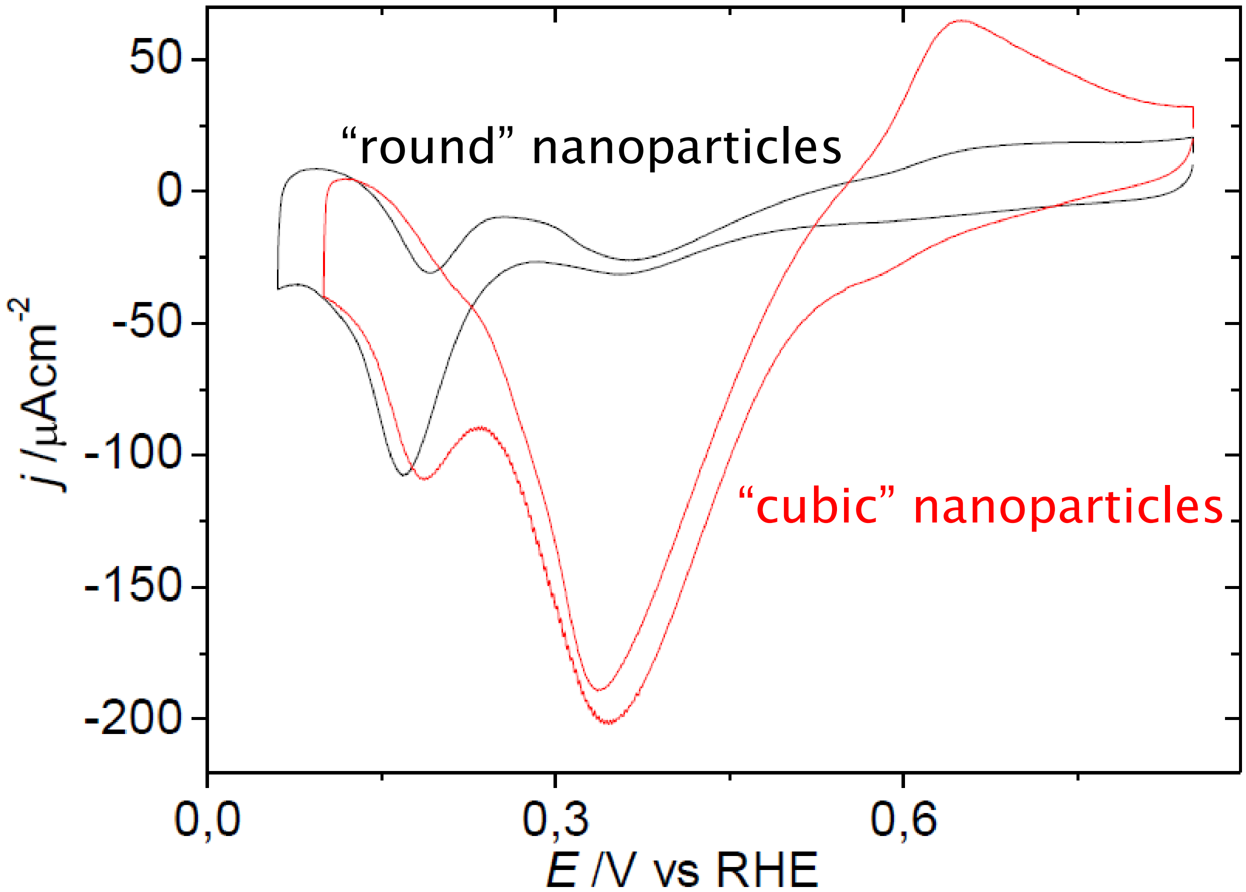




- N_2 producing peak disappears with increasing step density
- Properly annealed Pt(100) is better than Pt(100) annealed in air

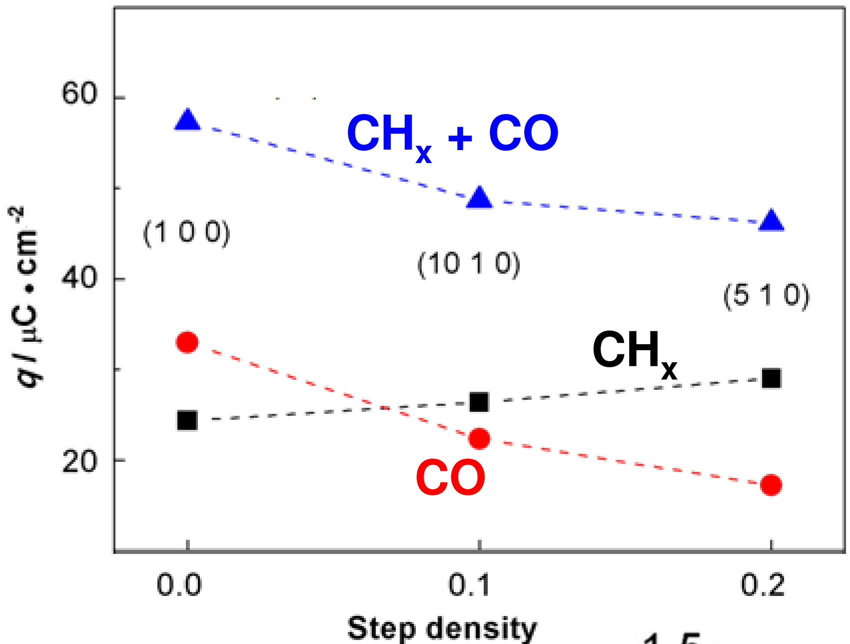
M.Duca, M.C.Figueiredo, V.Climent, P.Rodriguez, J.M.Feliu, M.T.M.Koper, J.Am.Chem.Soc. 133 (2011) 10928

NO_2^- reduction on Pt nanoparticles

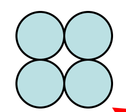


A.I.Yanson, P.Rodriguez, N.Garcia-Araez, R.V.Mom, F.D.Tichelaar, M.T.M.Koper, Angew.Chem.Int.Ed. 50 (2011) 6346
M.Duca, P.Rodriguez, A.I.Yanson, M.T.M.Koper, Top. Catal. (2013)

Oxidation of dimethylether CH_3OCH_3

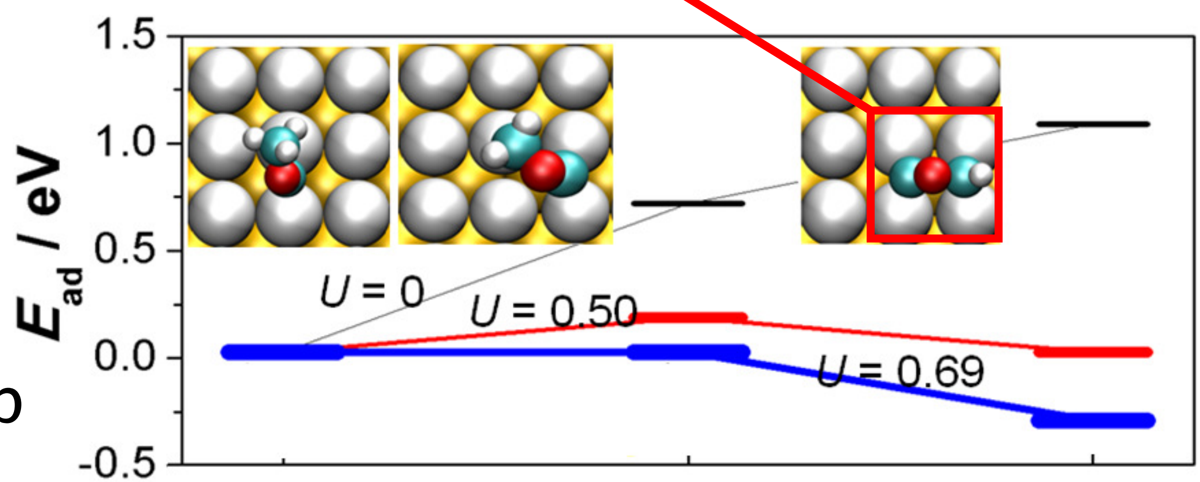


Experiment:
Steps inhibit C-O bond breaking



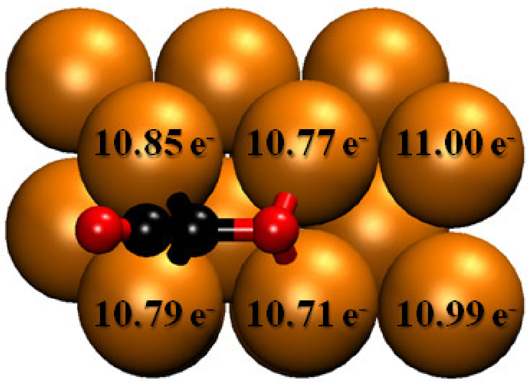
Density of active sites:
$(1-2/n)*N_{as}[Pt(100)]$

DFT calculation:
COCH → CO + CH
is the most likely bond breaking step

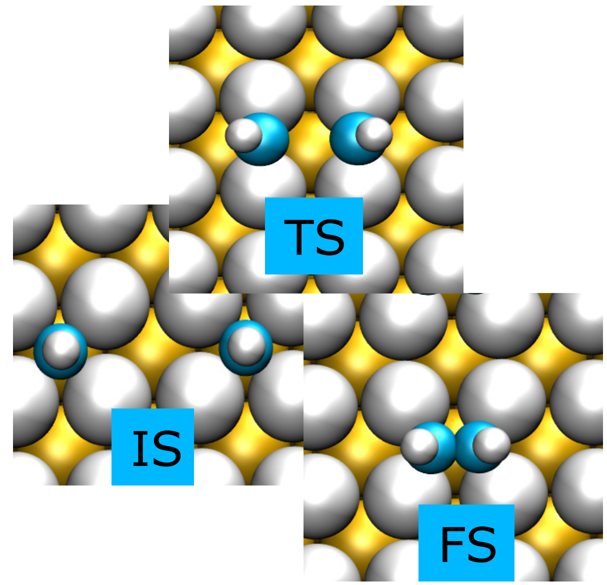


H.Li, F.Calle-Vallejo, M.J.Kolb, Y.Kwon, Y.Li, M.T.M.Koper, submitted

Active sites on (100)



Active site for C-C bond formation in CO reduction on Cu(100)



Active site for N-N bond formation in ammonia oxidation on Pt(100)

Reactive sites on electrode surfaces

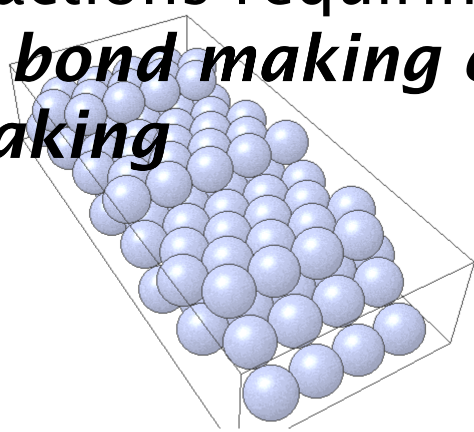
Reactions on steps and defects in (111) facets:

- CO oxidation, through water activation
- Methanol and ethanol oxidation, through initial deprotonation

O-H bond breaking

- Reactions requiring

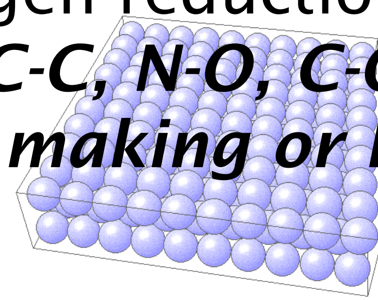
C-H bond making or breaking



Reactions on (100) facets:

- Nitrite to N_2 reduction on platinum
- CO to C_2H_4 reduction on copper
- NH_3 to N_2 oxidation on platinum
- H_3COCH_3 (dimethylether) to CO_2 oxidation on Pt
- Oxygen reduction on gold

N-N, C-C, N-O, C-O, O-O bond making or breaking



M.T.M.Koper, Nanoscale 3 (2011) 2054