Organische Adsorbate und Elektrokatalyse

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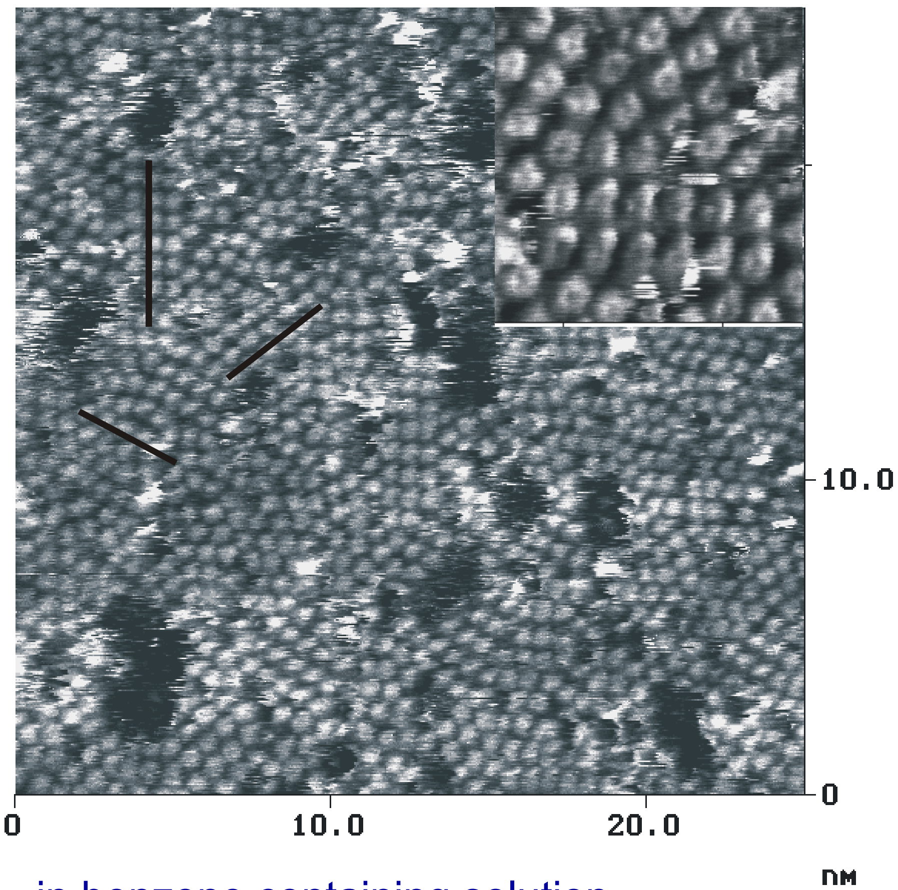
Motivation:

1. Vergleich zur fest/Gas Grenzfläche („akademisch“)
2. Bedeutung in Galvanik und Korrosion (Damaszen-Prozess)
3. Intermediate in Brennstoffzelle (Energie) etc.
4. Reibung

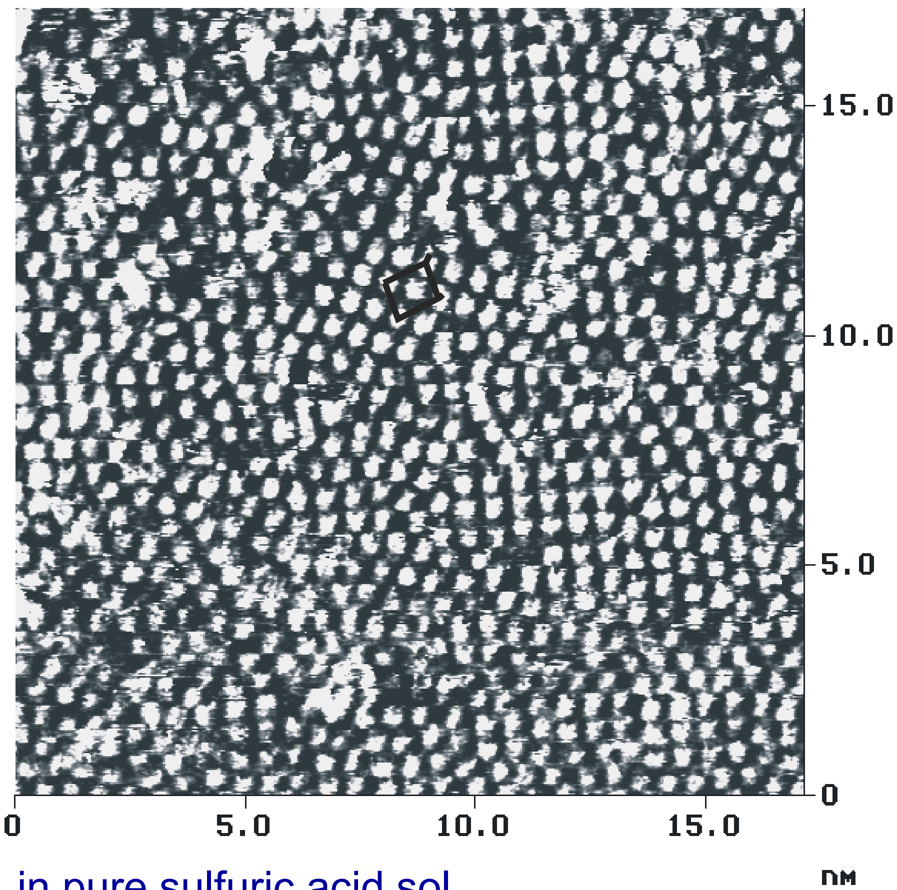
Grundlegende Fragen:

- assoziative oder dissoziative Adsorption
- Orientierung, atomare Zusammensetzung und Struktur des Adsorbatmoleküls
- Stabilität des Adsorbates, Reversibilität der Adsorption, Abhängigkeit von c und E
- Welches sind die Desorptionsreaktionen
- Welchen Einfluss hat die atomare Oberflächenstruktur?
- Welchen Einfluss hat eine zweite metallische Komponente im Substrat? (Kokatalysatoren, bimetallische Katalysatoren)

Benzene on Pt(111) in sulfuric acid: STM



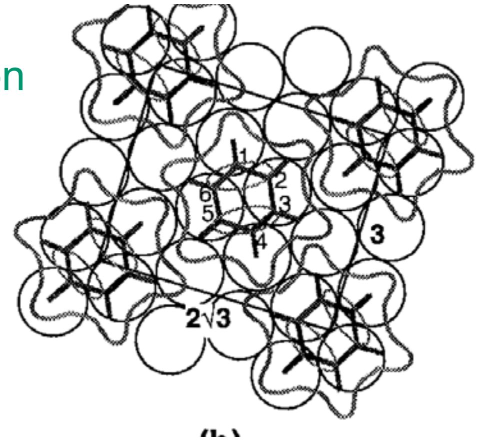
in benzene containing solution at 0.5 V vs RHE. Es, 0.5 V, E_b, 20 mV, I_t, 2 nA.



in pure sulfuric acid sol.

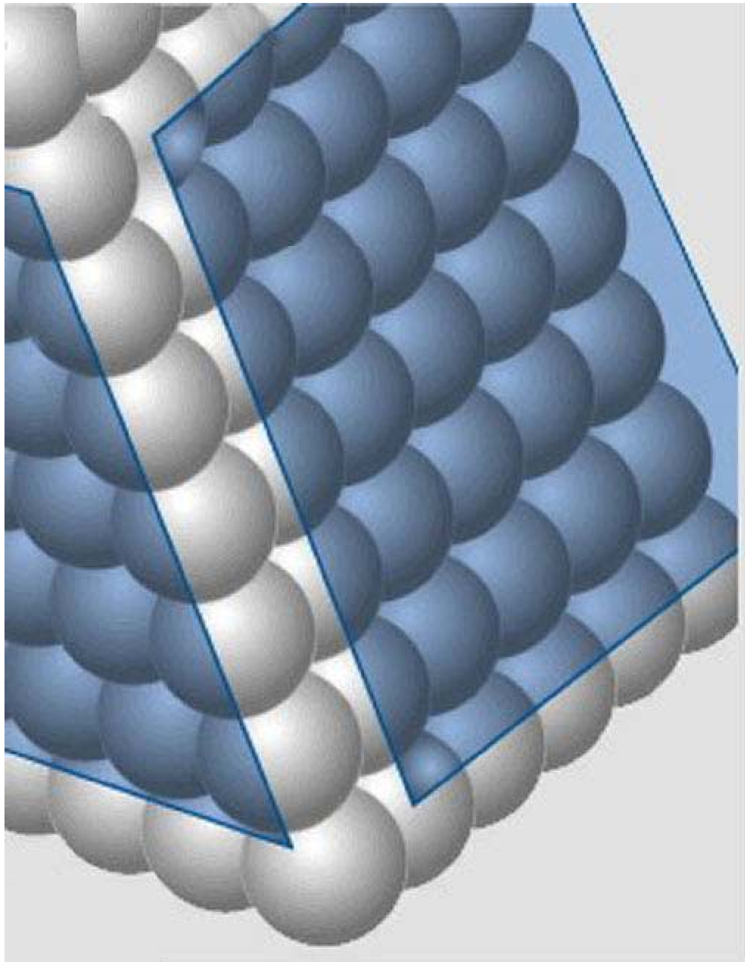
=> irreversible Adsorption

real space model for the (111)-*c*(2 √ 3 x 3)*rect* benzene adlattice on Rh(111),Pt(111) (ϑ = 0.17)



S. L. Yau, Y. G. Kim, K. Itaya, *JACS* **1996**, *118*, 7795.

Kristalle - Oberflächen



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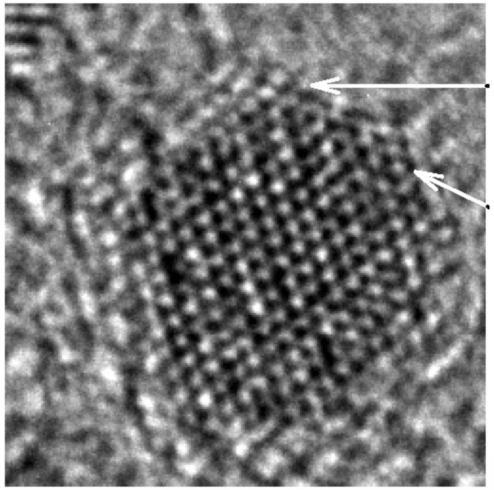
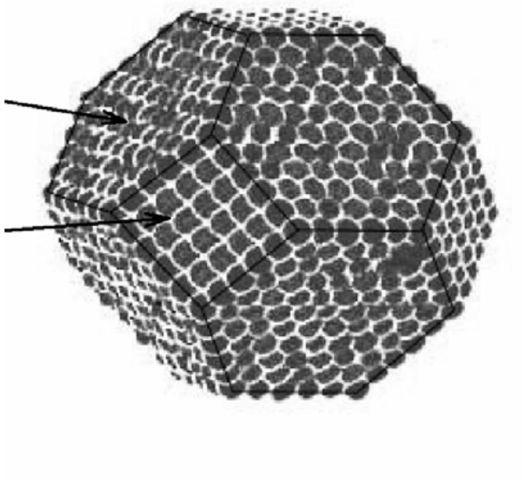
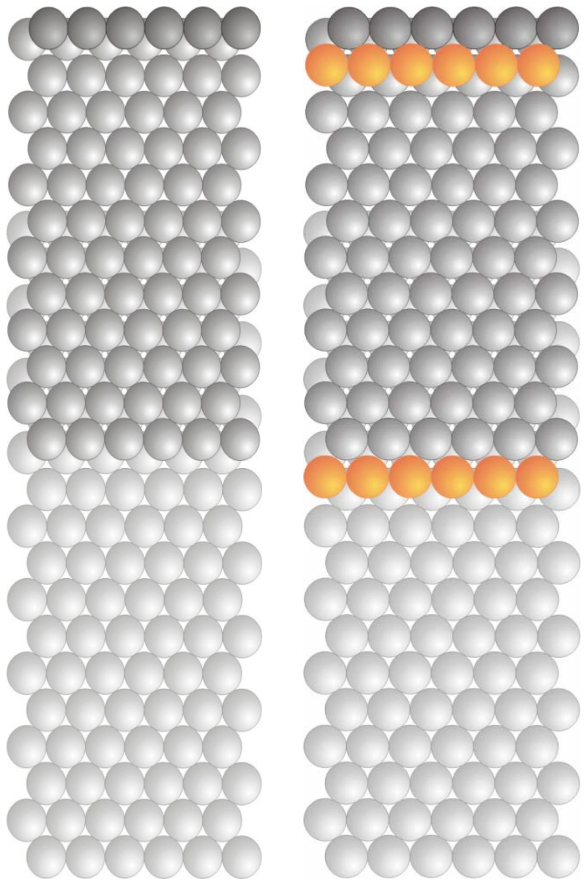
Stepped surfaces



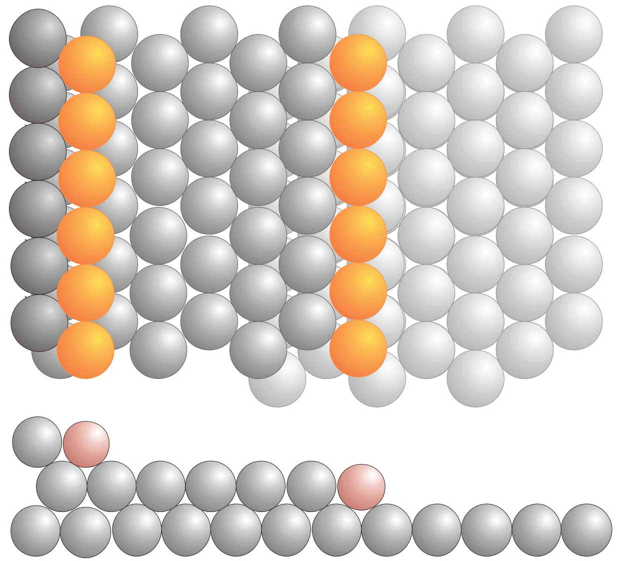


Markovic (Fuel cells)

Pt(665) = Pt[12(111)x(111)]



Pt(332) = Pt[6(111)x(111)]



step decoration on Pt by:

Cu, Ag, Sn, Ru, Mo, Bi, Ge,…….

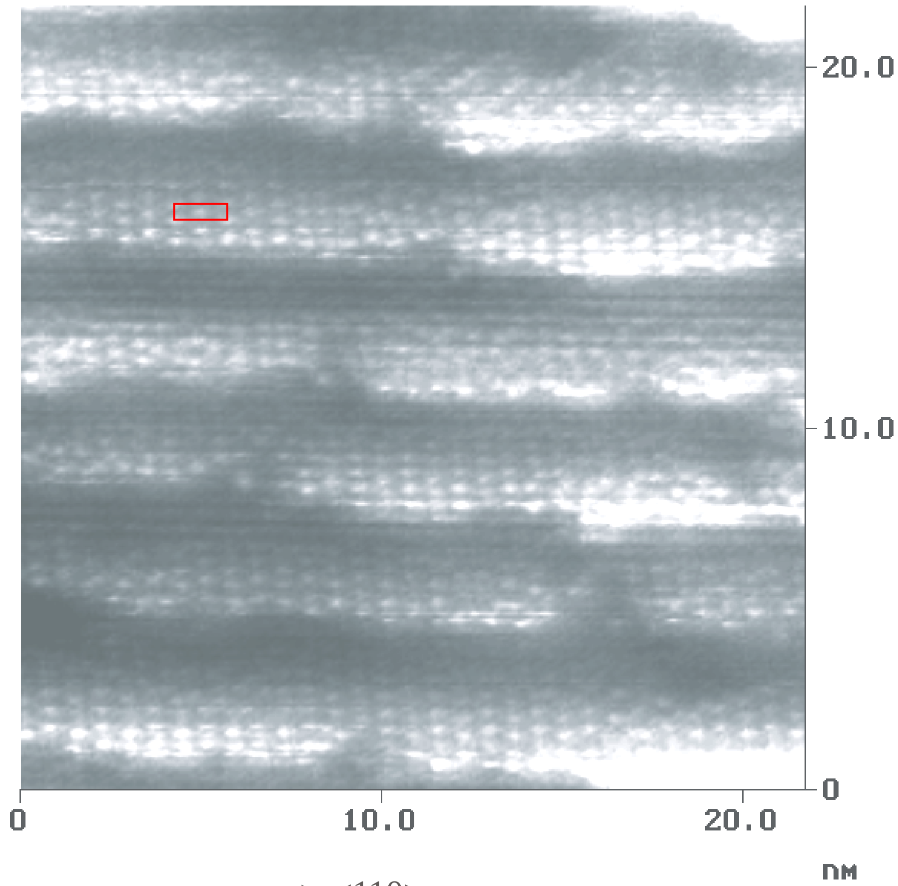
also: Au/Pd

ordered bimetalic surfaces: - help to undertand mechanism

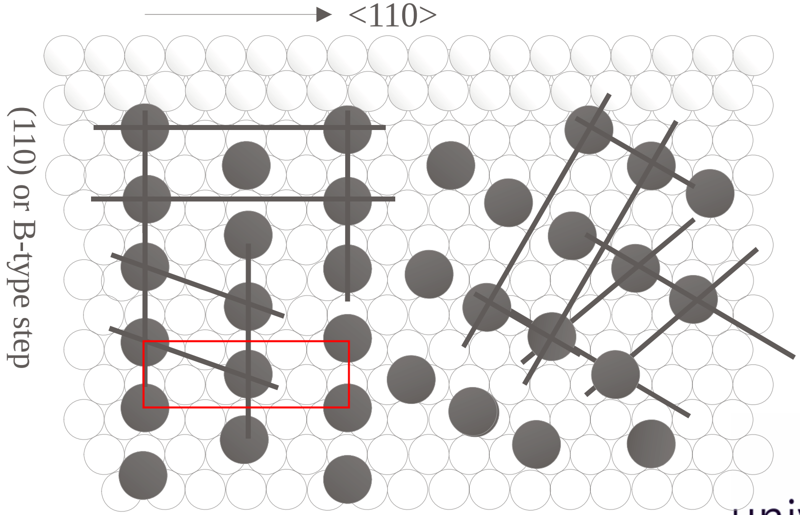
- benchmark for practical catalysts

Cu – UPD covered Pt(665).

0.05 M H_2SO_4 + $4x10^{-4}$ M $CuSO_4$,
at 0.15 V vs Cu/Cu^{2+}
E_t: 200 mV, I_t: 1 nA.

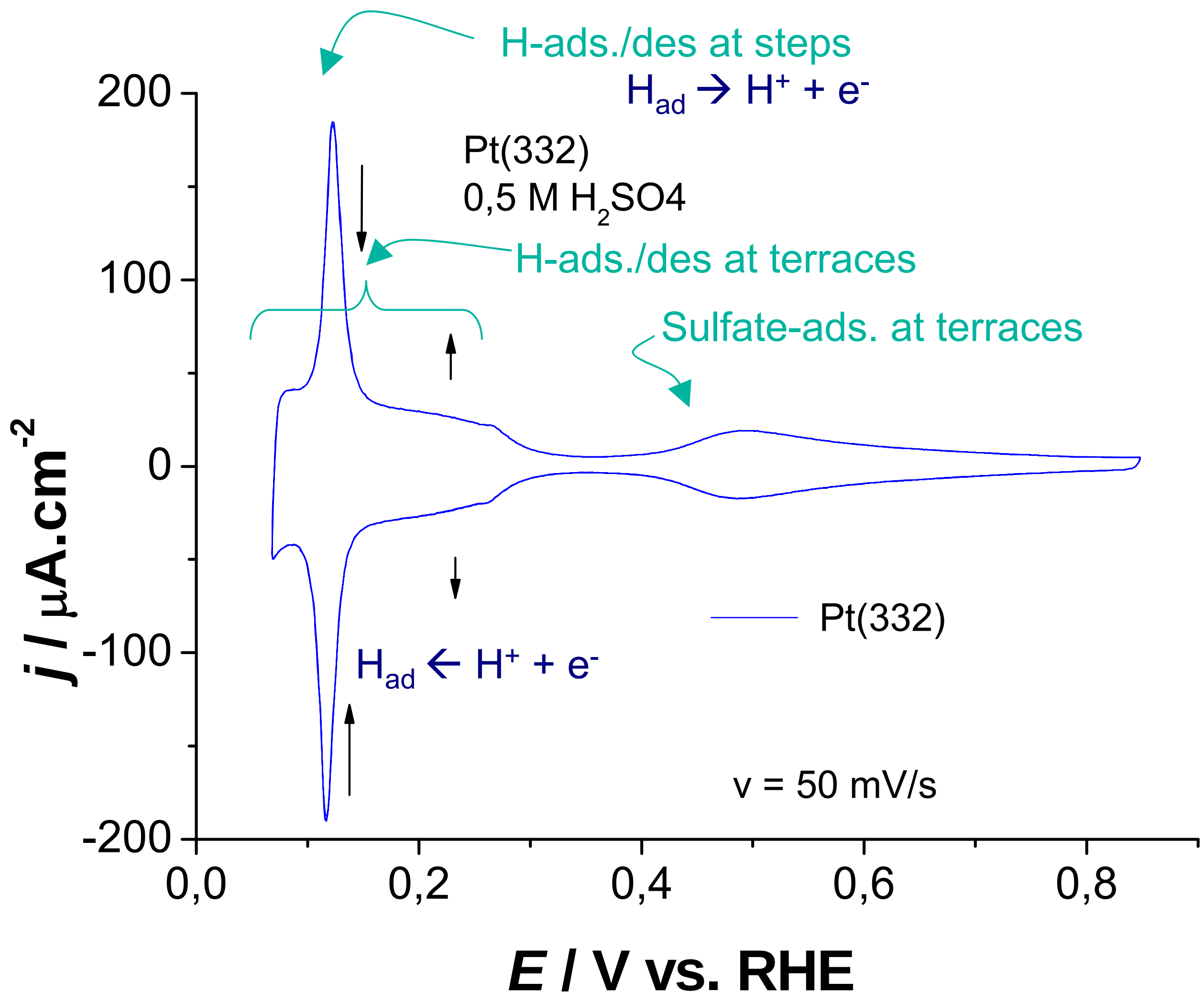


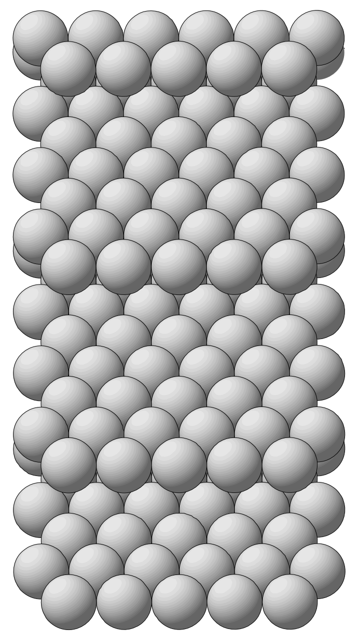
p(√3 x √7) = c(√3 x 5)rect
lattices of adsorbed sulfate



Charakterisierung

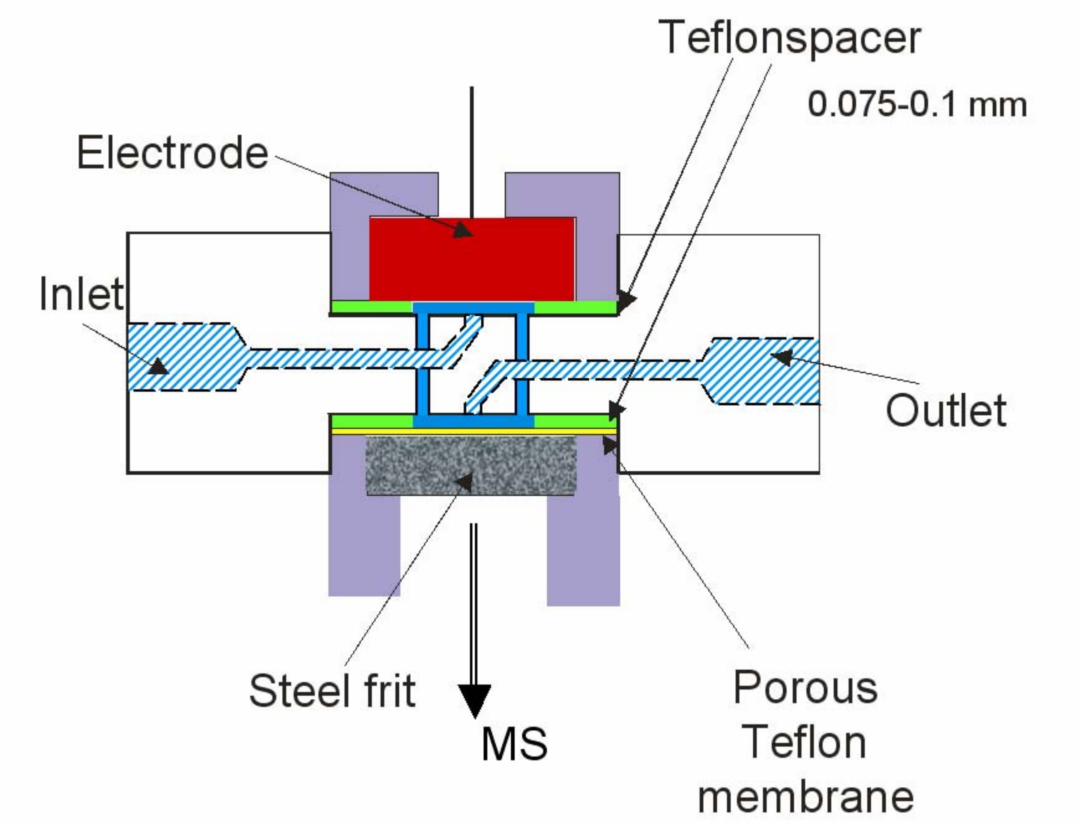
- Cyclische Voltammetrie
- STM, AFM
- XPS, LEED (nach Transfer ins UHV)
- Indirekt: elektrochemische Massenspektrometrie
- Oberflächen IR, surface enhanced Raman spectroscopy (SERS)





Pt(332) =
Pt(S)[6(111)x(111)]

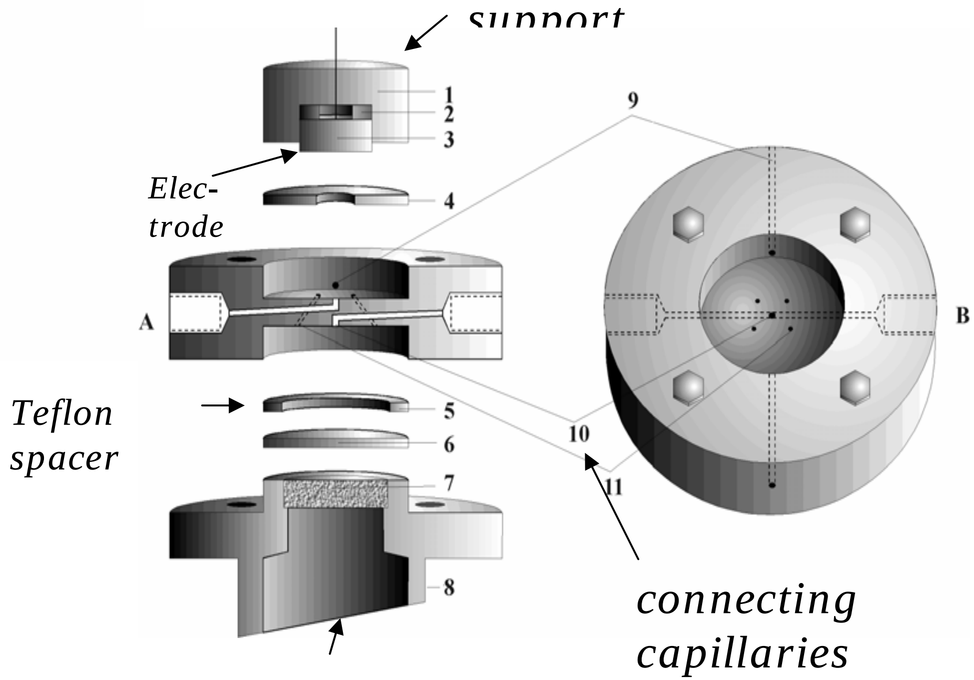
Products: flow through cell for DEMS



<u>D</u>ifferentielle <u>e</u>lektrochemische <u>M</u>assen<u>s</u>pektrometrie

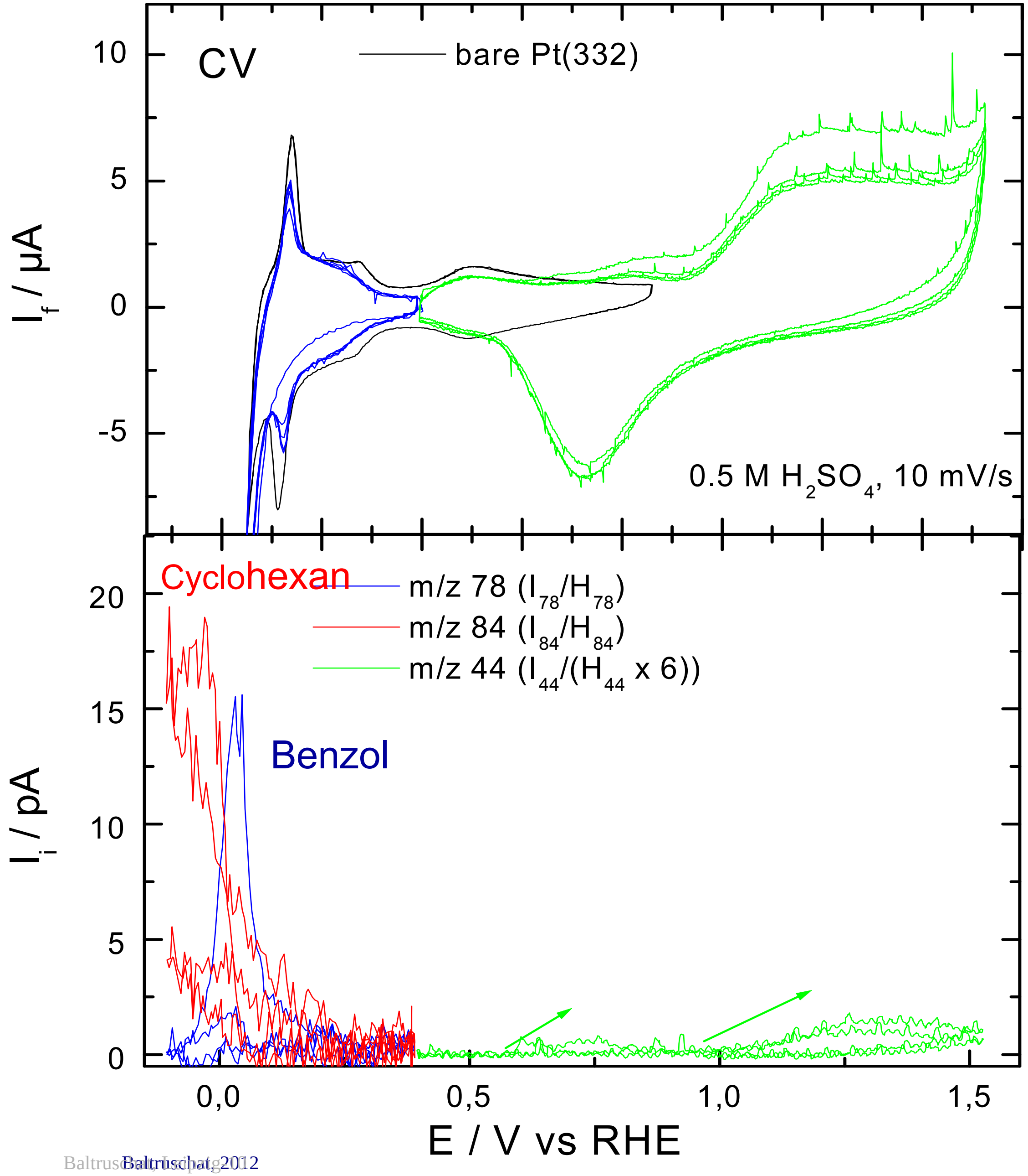
<u>d</u>ie <u>E</u>lektrochemie <u>m</u>acht <u>S</u>pass

- Best suited for continuous reactions
- Also suited for desorption reactions
- Defined convection and diffusion
- Detection limit: 0.1 ML ≅ 0,1 nmol



Jusys, Z., H. Massong, H. Baltruschat. (1999). <u>Journal of the Electrochemical Society</u> **146**: 1093..

Pt(332): cathodic desorption of adsorbed benzene

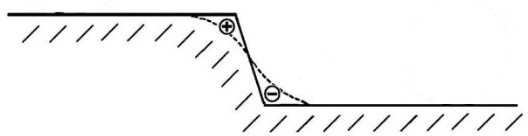


Pt(111): no hydrogenation
Pt(110): complete hydrogenation

Pt(332): 80% hydrogenation

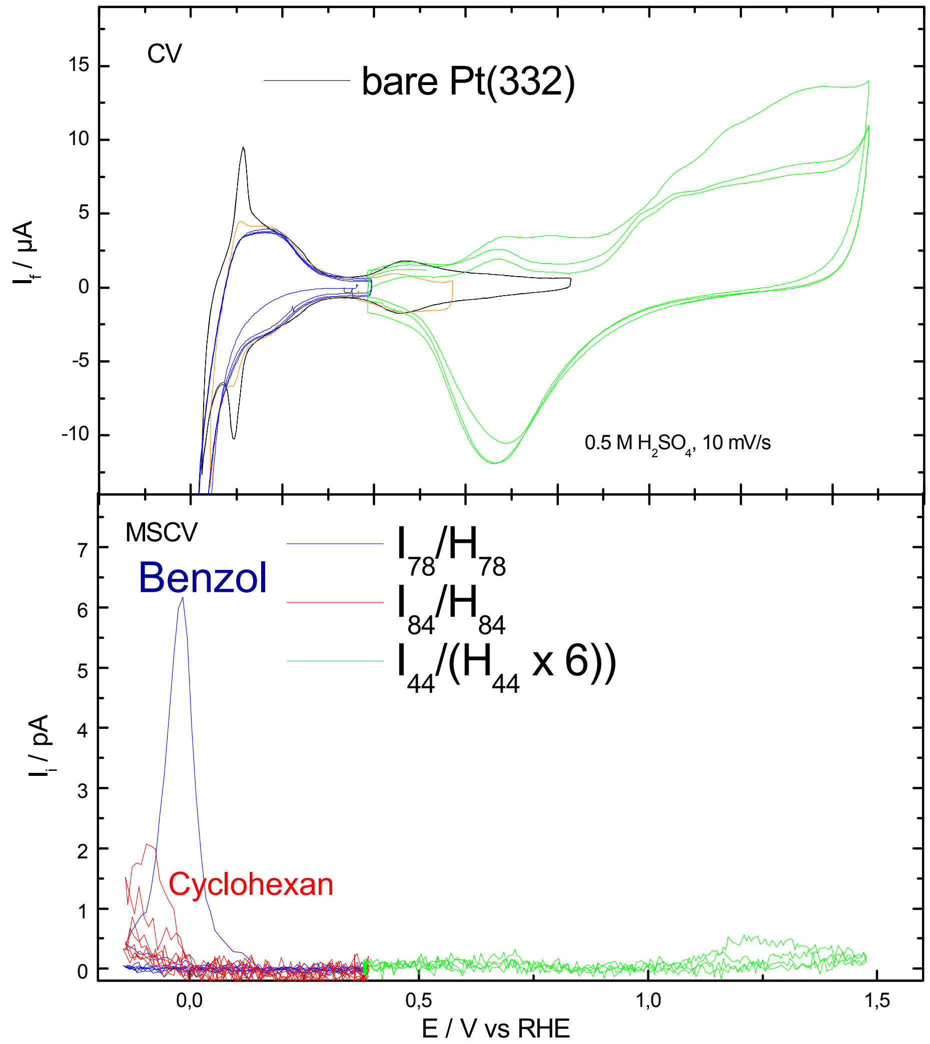
geometric – steric effects
electronic effects

steps are the reactive sites!

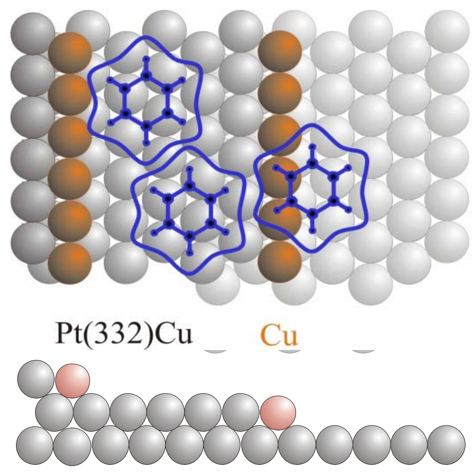


Smolouchowski-effect

Pt(332)/Cu : cathodic desorption of adsorbed benzene



Pt(332) = Pt[6(111)x(111)]



suppression of hydrogenation by step decoration

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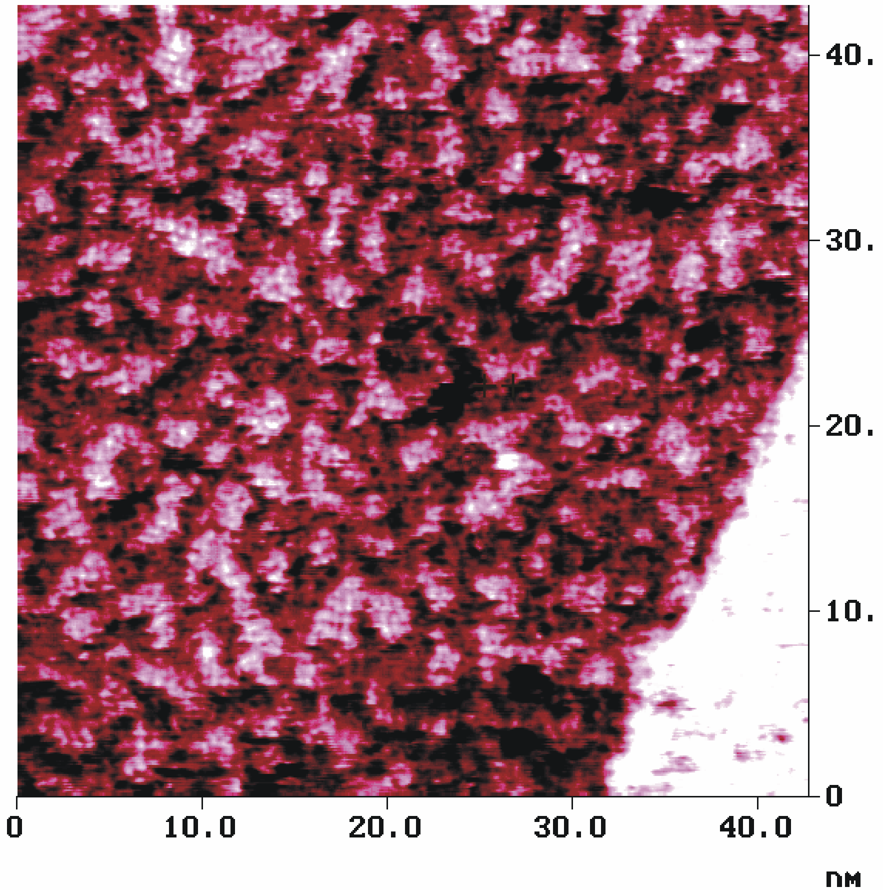
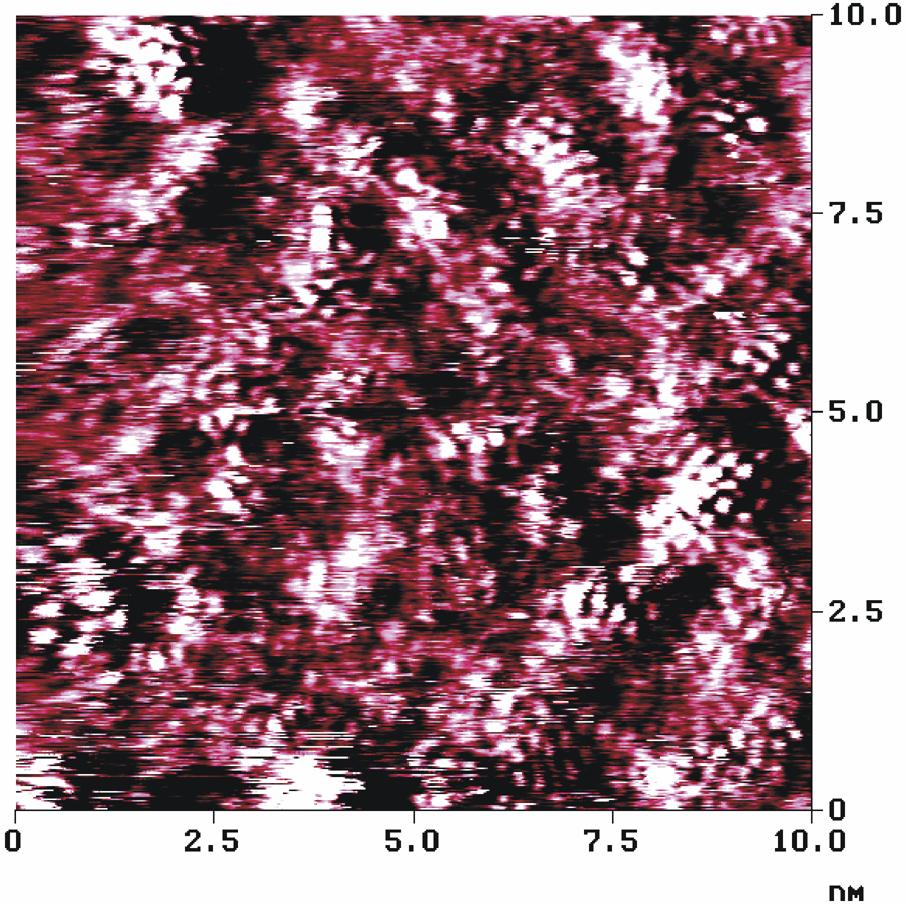
Structure of adsorded ethene on Pt(111):





In sulphuric acid solution
Ads. potential:
~0.3 V vs Cu / Cu

very small ordered domains
with distance between
maxima: ~0.3 nm

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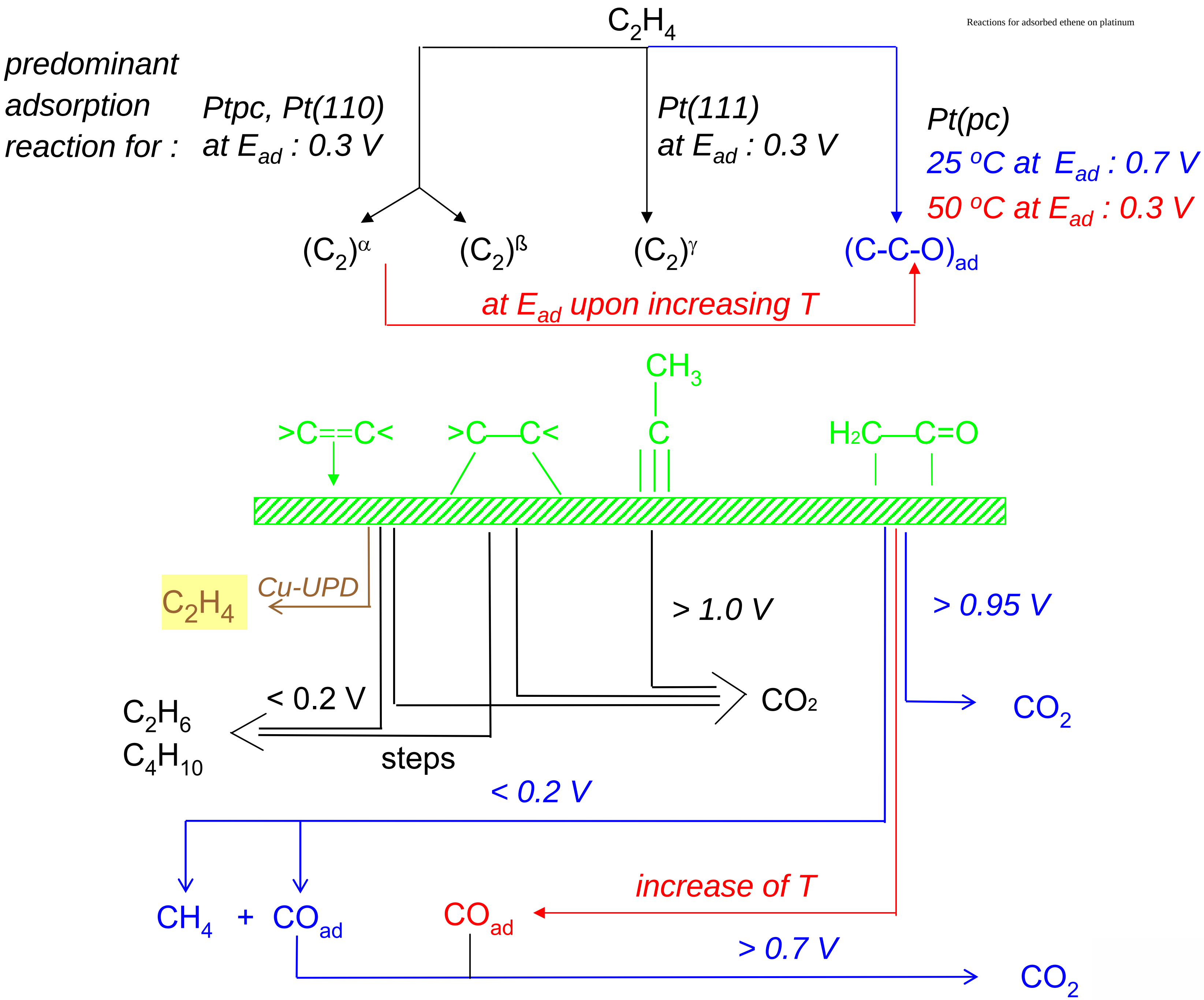
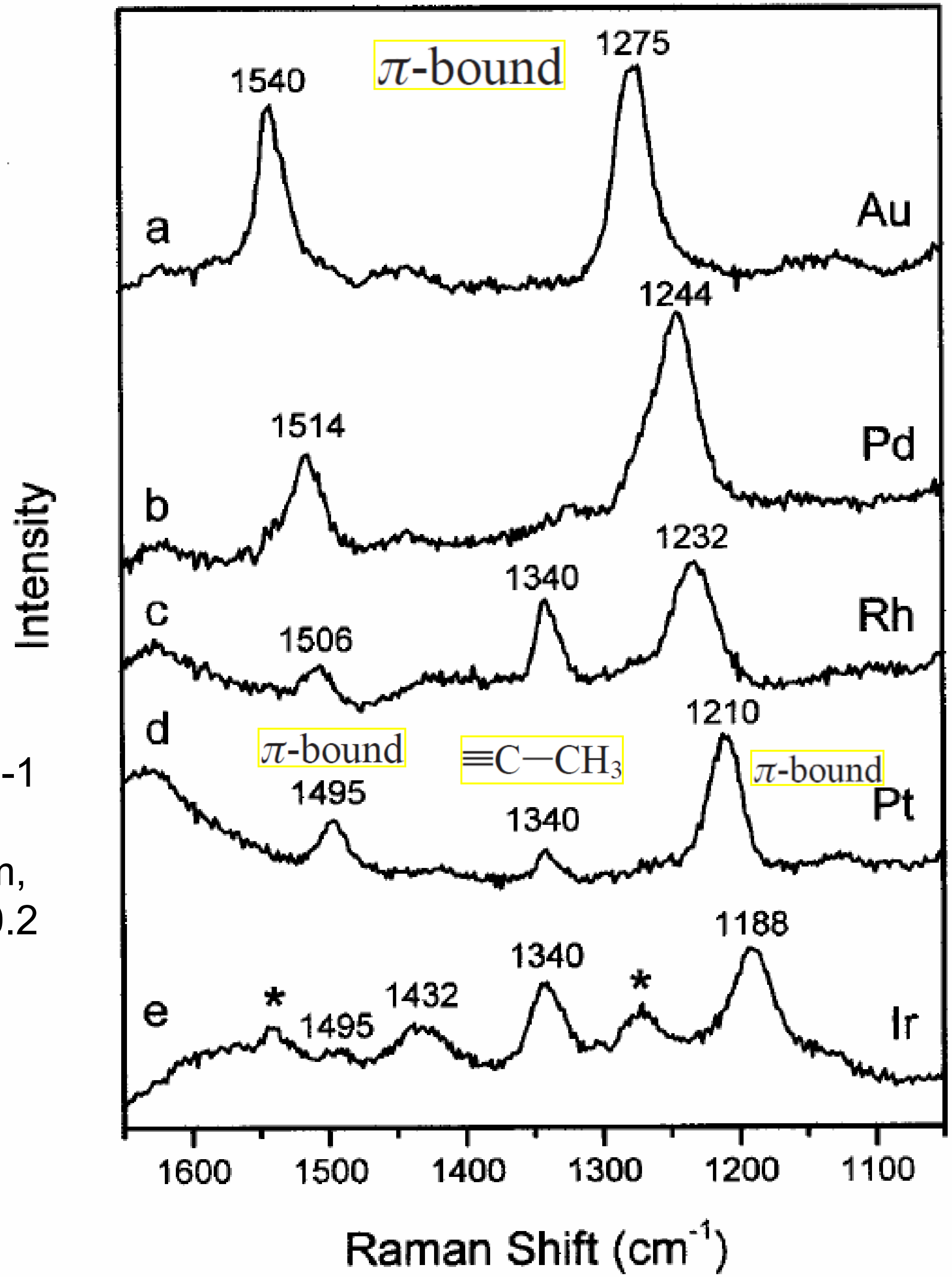
Reactions for adsorbed ethene on platinum

Pt

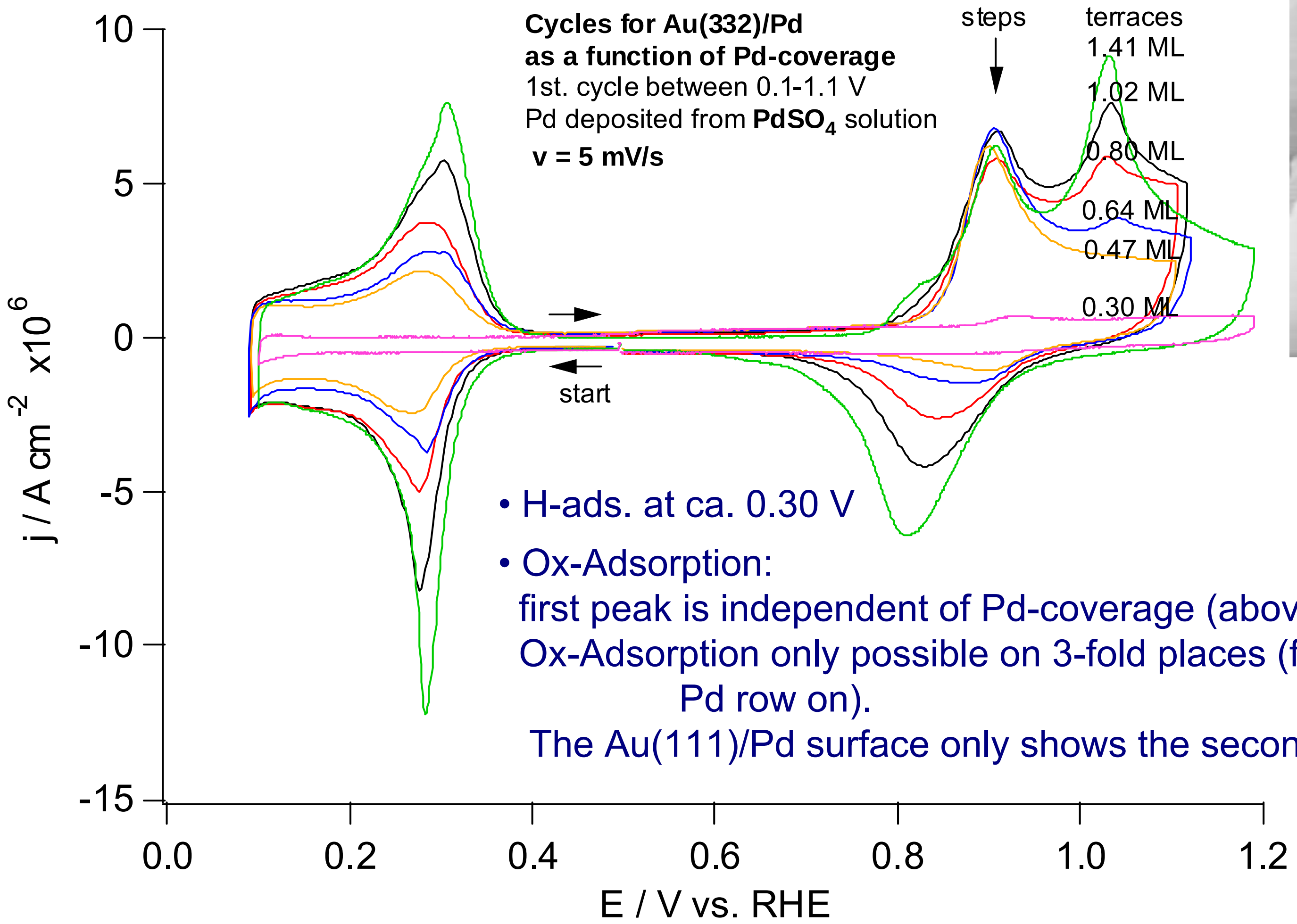




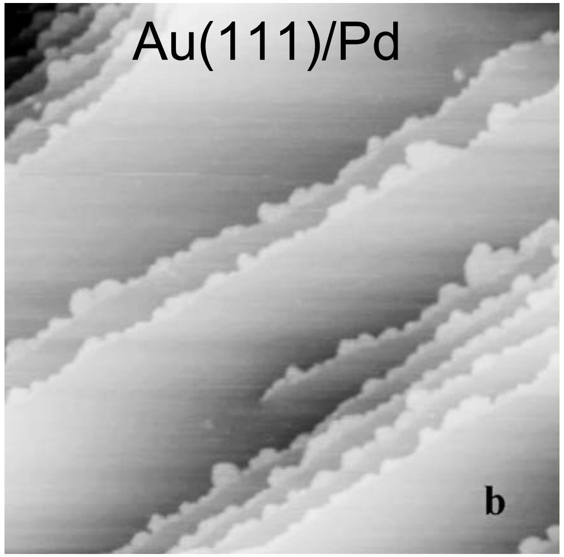
Representative SER spectra in 1050-1650 cm-1 region for ethylene chemisorption on (a) unmodified gold and (b) palladium, (c) rhodium, (d) platinum, and (e) iridium films on gold at -0.2 V vs SCE in C2H4-saturated 0.1 M HClO4.

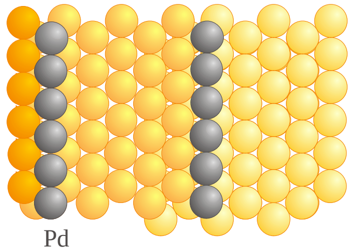
M. F. Mrozek and M. J. Weaver, Journal of Physical Chemistry B 105:8931 (2001).

Au(332)/Pd



- H-ads. at ca. 0.30 V
- Ox-Adsorption:
  first peak is independent of Pd-coverage (above 0.4);
  Ox-Adsorption only possible on 3-fold places (from the 2nd Pd row on).
  The Au(111)/Pd surface only shows the second peak.



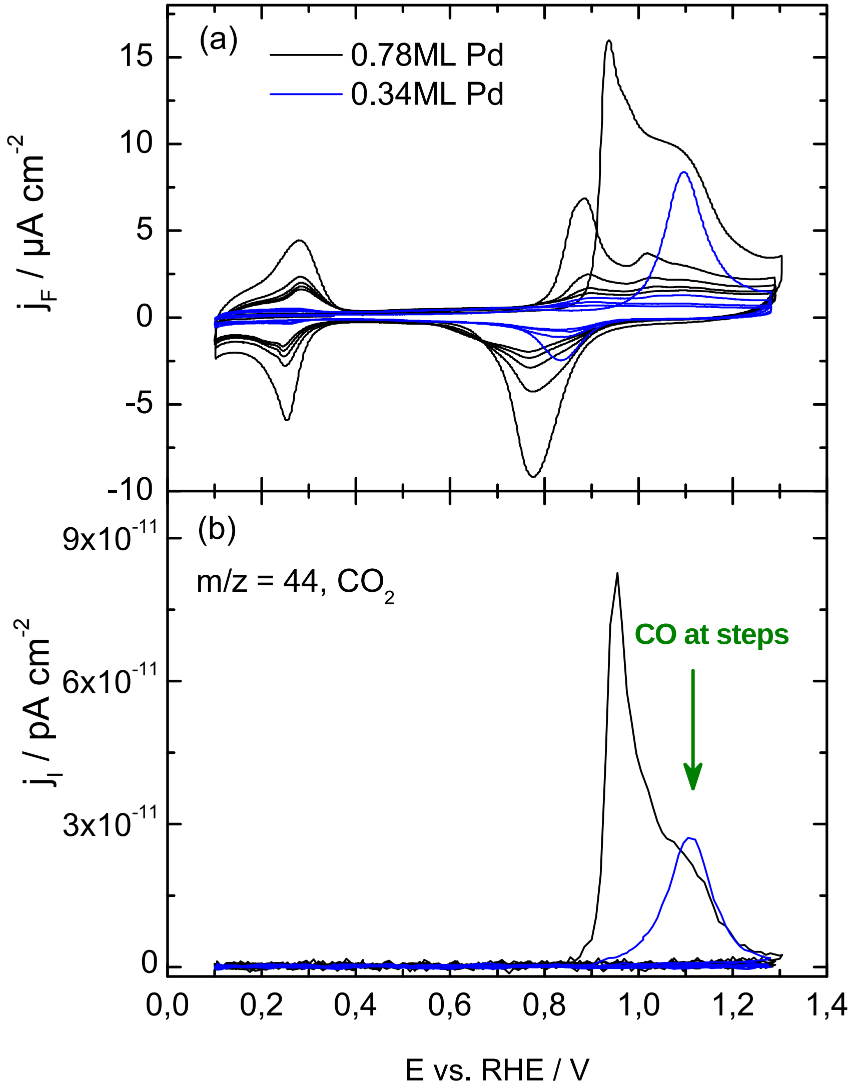


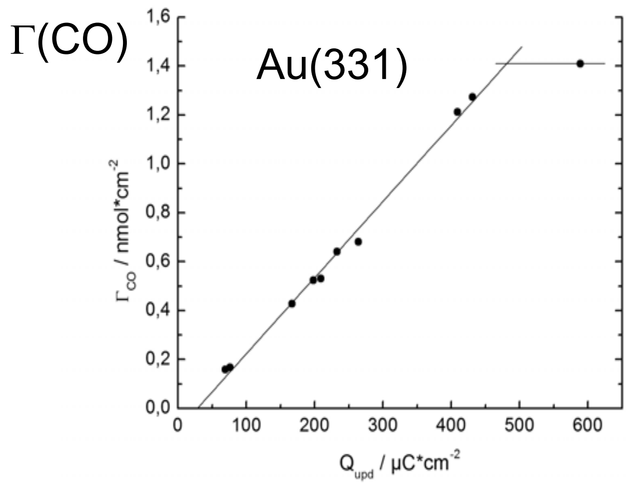
Model of step decoration for Au(332)/Pd

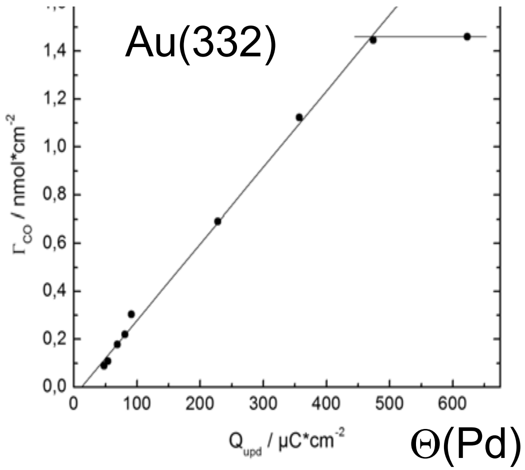
O-ads. at Pd(hkl): Hoshi, Makiko Kuroda, Ogawa, Koga, Hori *Langmuir* **2004,** *20,* 5066

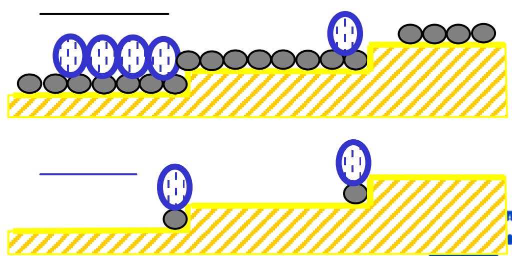
F. Hernandez and H. Baltruschat, Langmuir, 22 (2006) 4877.

CO oxidation on Pd/Au(332): DEMS









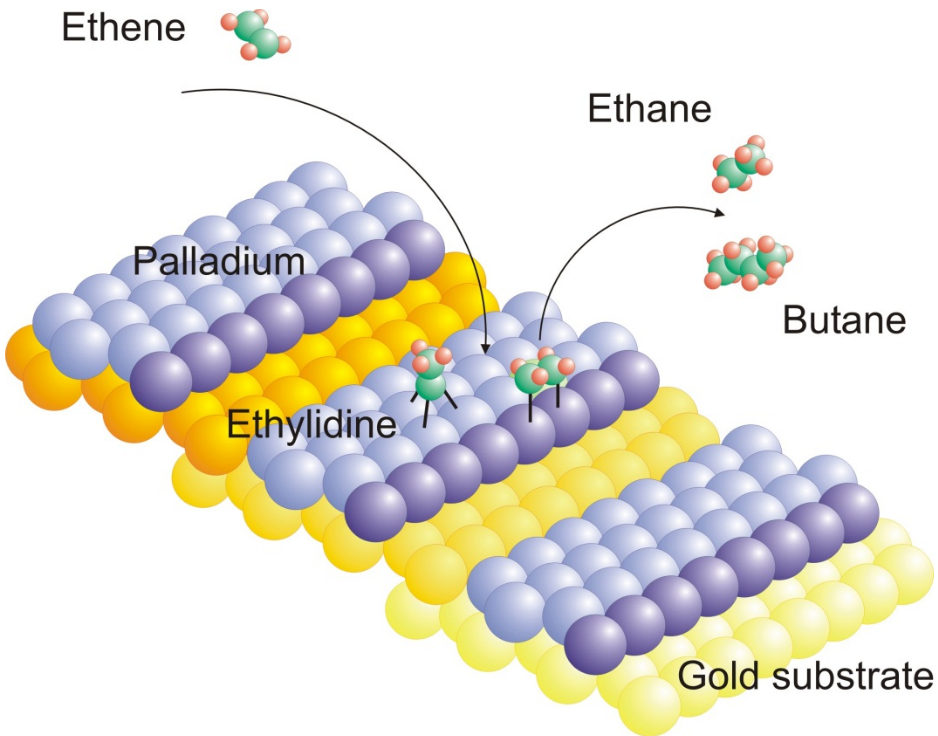
•CO at steps (Pd/Au) oxidised in the 2nd peak ⇒ higher stability

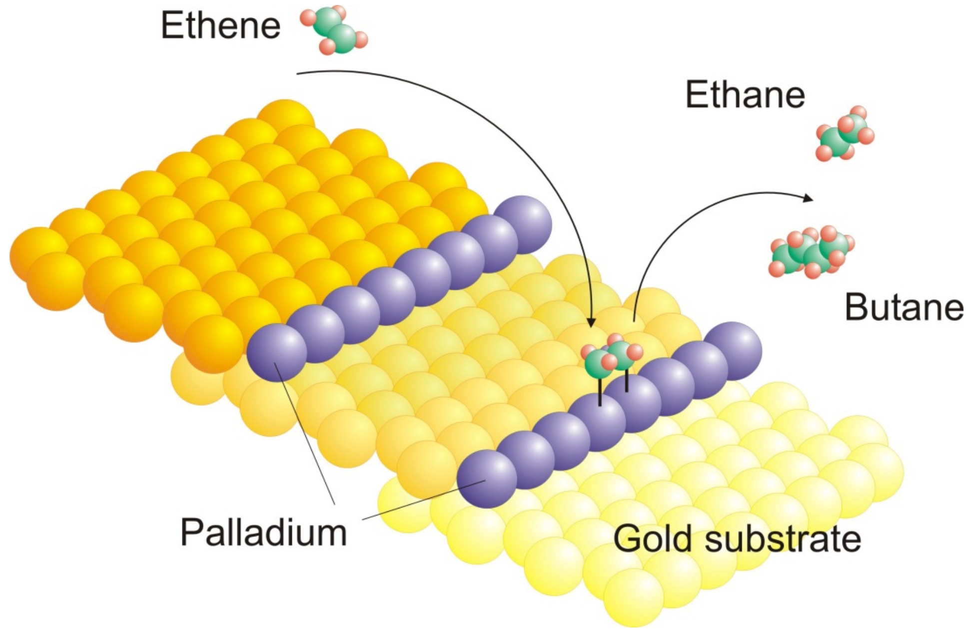
•but: steps necessary for the 1st peak to appear ⇒ CO diffuses to steps

Steidtner, J.; Hernandez, F.; Baltruschat, H. *J. Phys. Chem. C* **2007** *111*, 12320

cf. Au(111) 'miscut'/ Pd: El-Aziz, L.A. Kibler, J. Electroanal. Chem. 534 (2002) 107

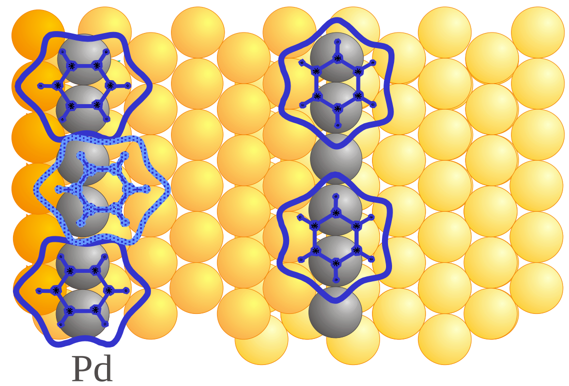
Cathodic desorption of ethene and ethine





Pd step sites are responsable for hydrogenation of the adsorbate

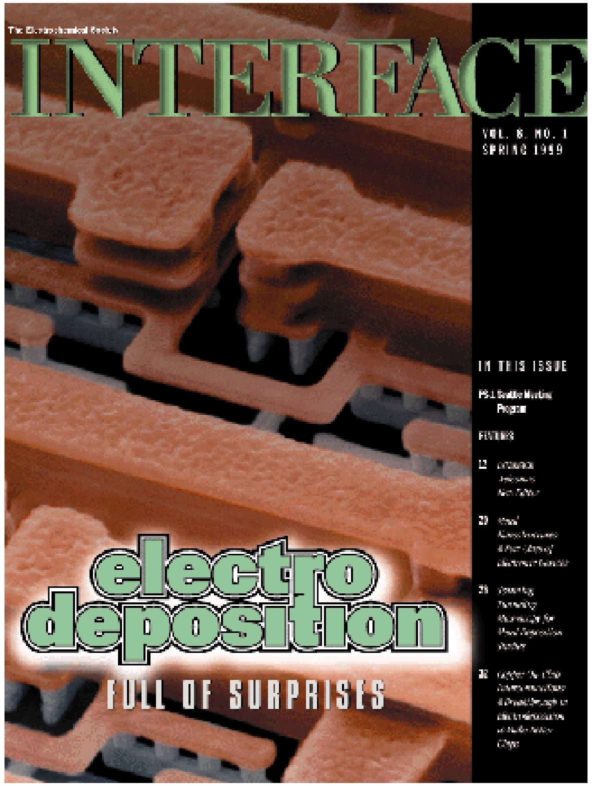
At room temperature ethene and ethine are adsorbed on terraces as immobile ethylidine

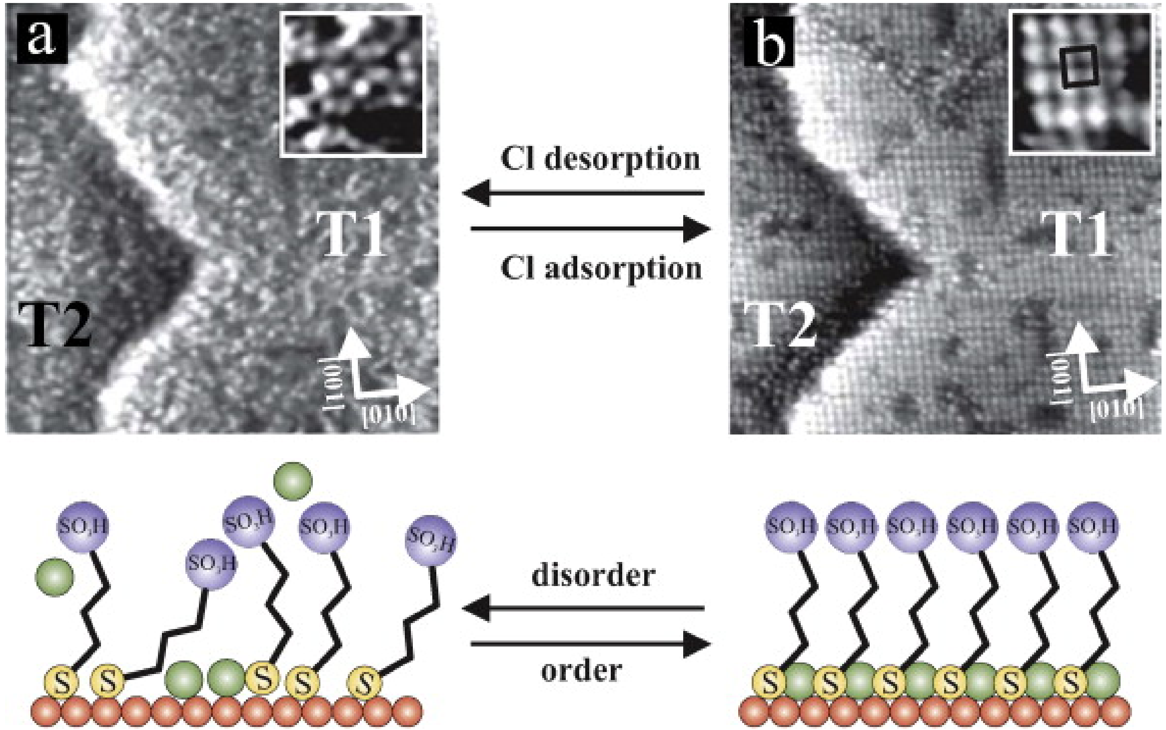


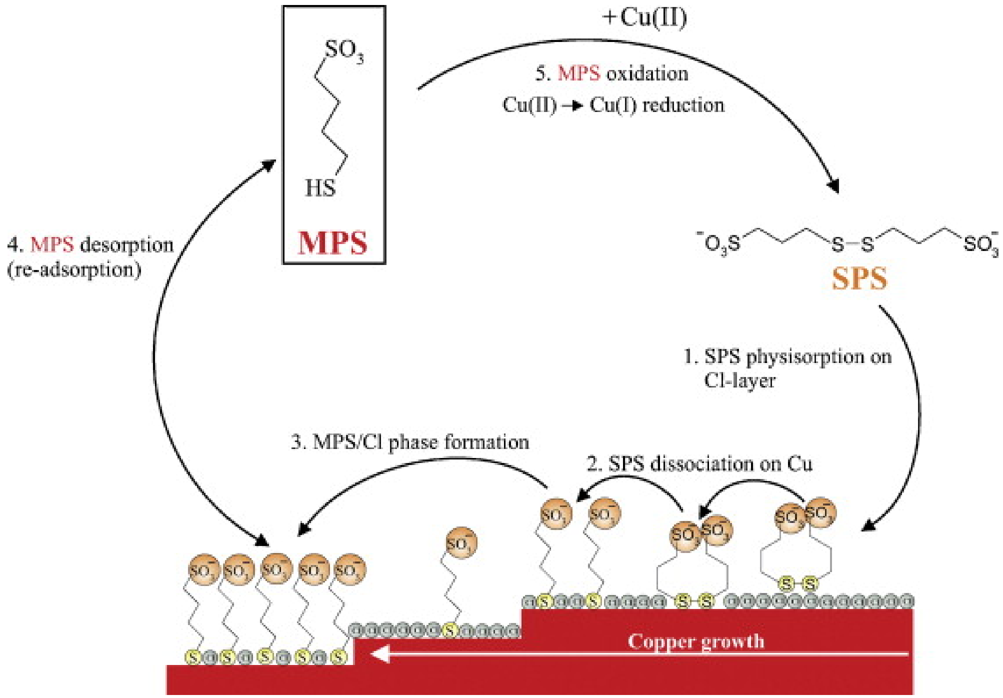
sehr effiziente Katalyse der H_2 Ox.

Steidtner, J.; Hernandez, F.; Baltruschat, H. *J. of Physical Chemistry C* **2007,** *111*, 12320

ad 2. e.g.: Damascene process





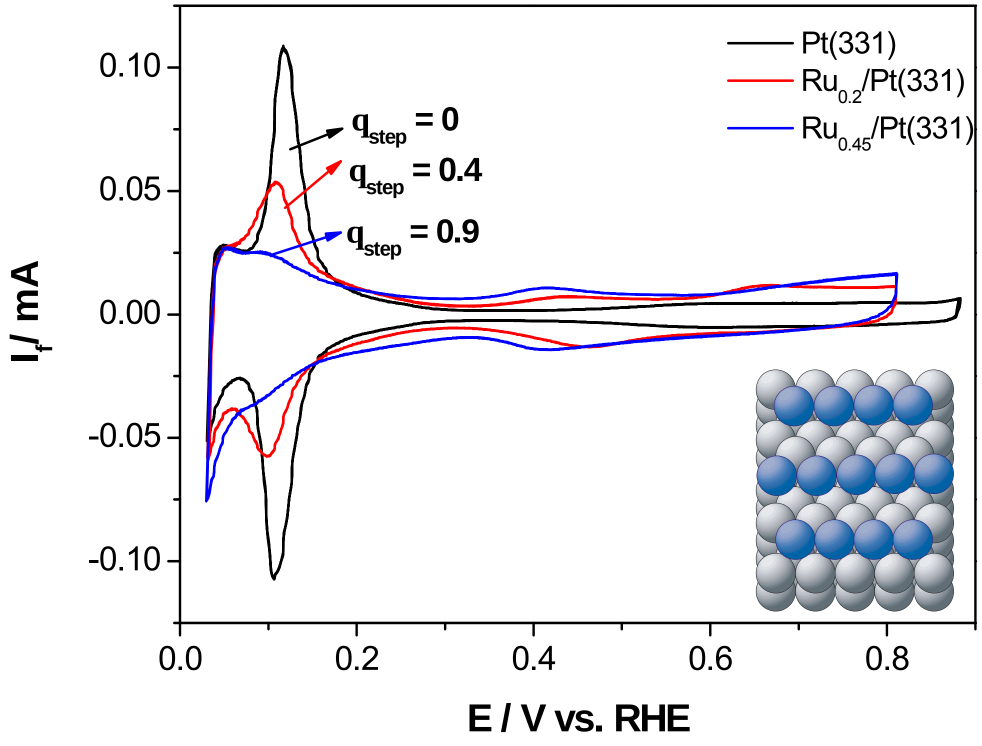


SPS: sodiumsulfopropyl)disulfide
MPS: mercaptopropane sulfonic acid

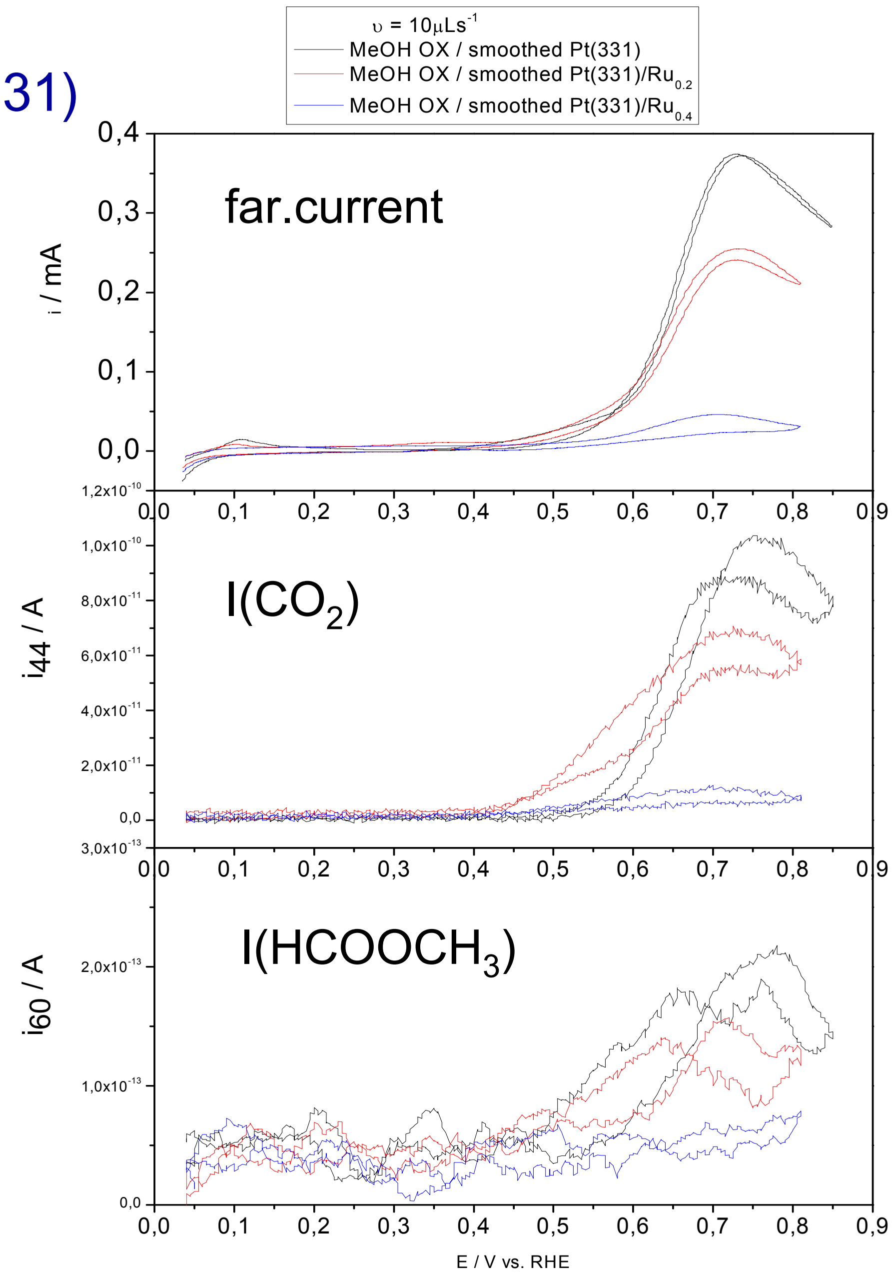
N.T.M. Haia, …. T. Bredow, P. Broekmann, Electrochim. Acta 70 (2012) 286– 295

ad 3: Elektrokatalyse

Electrooxidation of methanol on Ru/Pt(331)



Pt(331) in 0.1M H_2SO_4 + 0.5M $HClO_4$
50 mV/s before and after Ru deposition



10^{-2} M methanol in 0.1 M H_2SO_4 + 0.5 M $HClO_4$ at 10 mV/s and flow rate 10 µL/s

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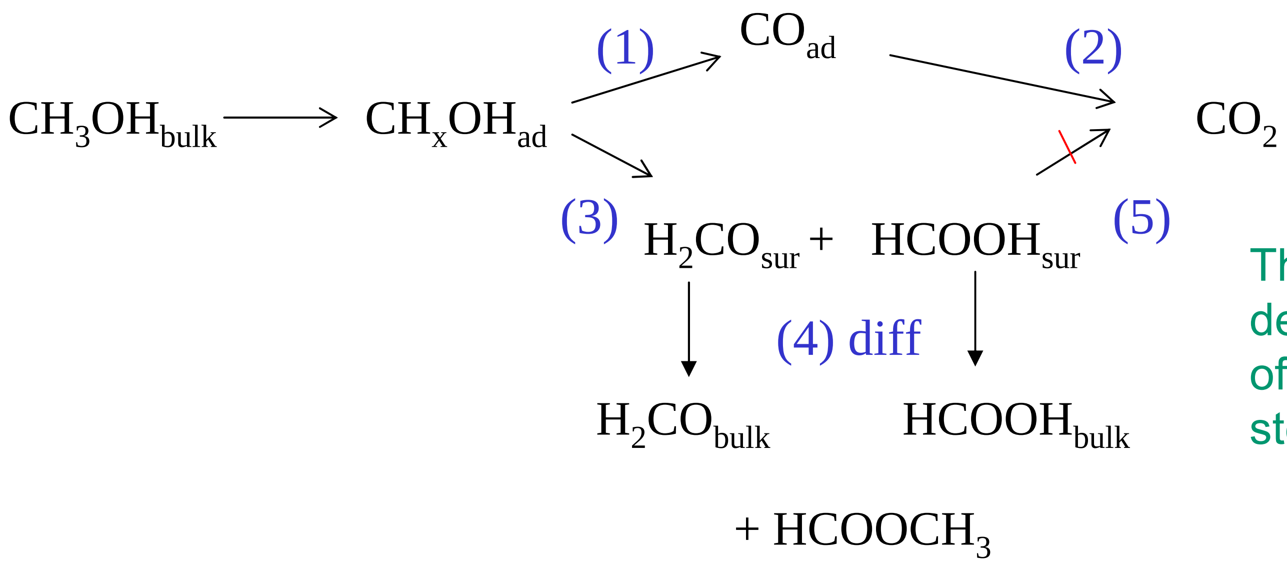
ad 3: Elektrokatalyse

Reaction paths for methanol oxidation



The current efficiency is determined by the ratio of the reaction rates via step (1) and (3).

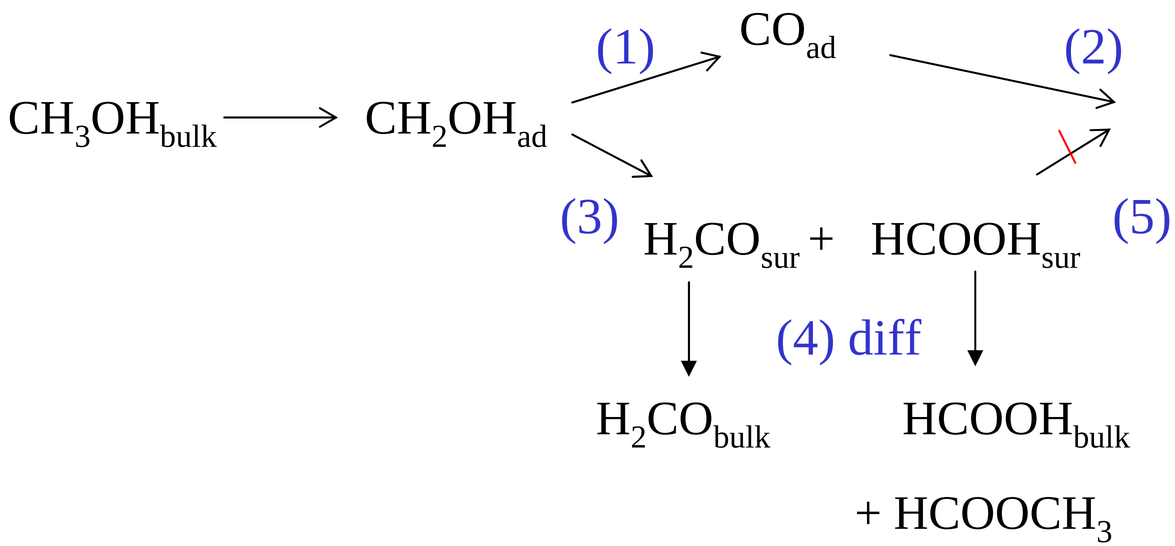
No formation of methylformate on the timescale of the experiment
==> direct formation of methylformate at the surface

R = H:
formic acid
R = Me:
Methylformate

Higher nucleophilic power of methanol

Abd-El-Latif, A. A., H. Baltruschat (2011). J. Electroanal. Chem. **662**(1): 204

Reaction paths for methanol oxidation



The current efficiency is determined by the ratio of the reaction rates via step (1) and (3).

Influence of <u>catalyst layer thickness</u>
(for 0.1 M CH_3OH)
on <u>current efficiency</u> A for CO_2:

Smooth Pt: A = 20 % (independent of flow rate)

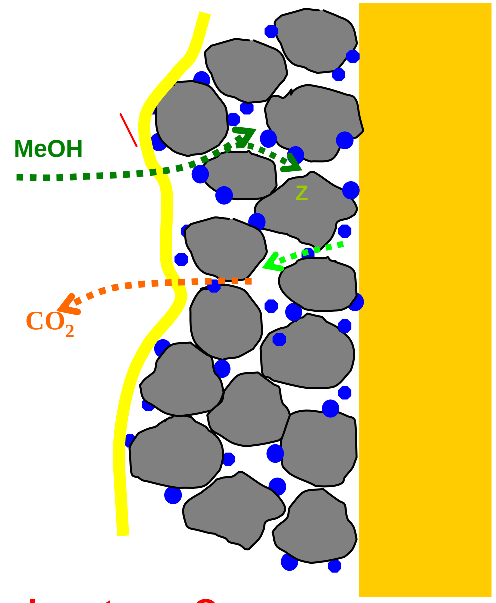
XC 72:

10 μg Pt cm^{-2}: A = 30 - 50%

0.6 mg Pt cm^{-2}: A ≈ 95%

⇒ Minimal catalyst layer thickness needed

⇒ Parallel path mechanism



rates of single steps?

H. Wang, T. Löffler, H. Baltruschat, *J. Appl. Electrochem.* **2001**, *31*, 759 .
H. Wang, C. Wingender, H. Baltruschat, M. Lopez, M. T. Reetz, *J. Electroanal. Chem.* **2001**, *509*, 163 .

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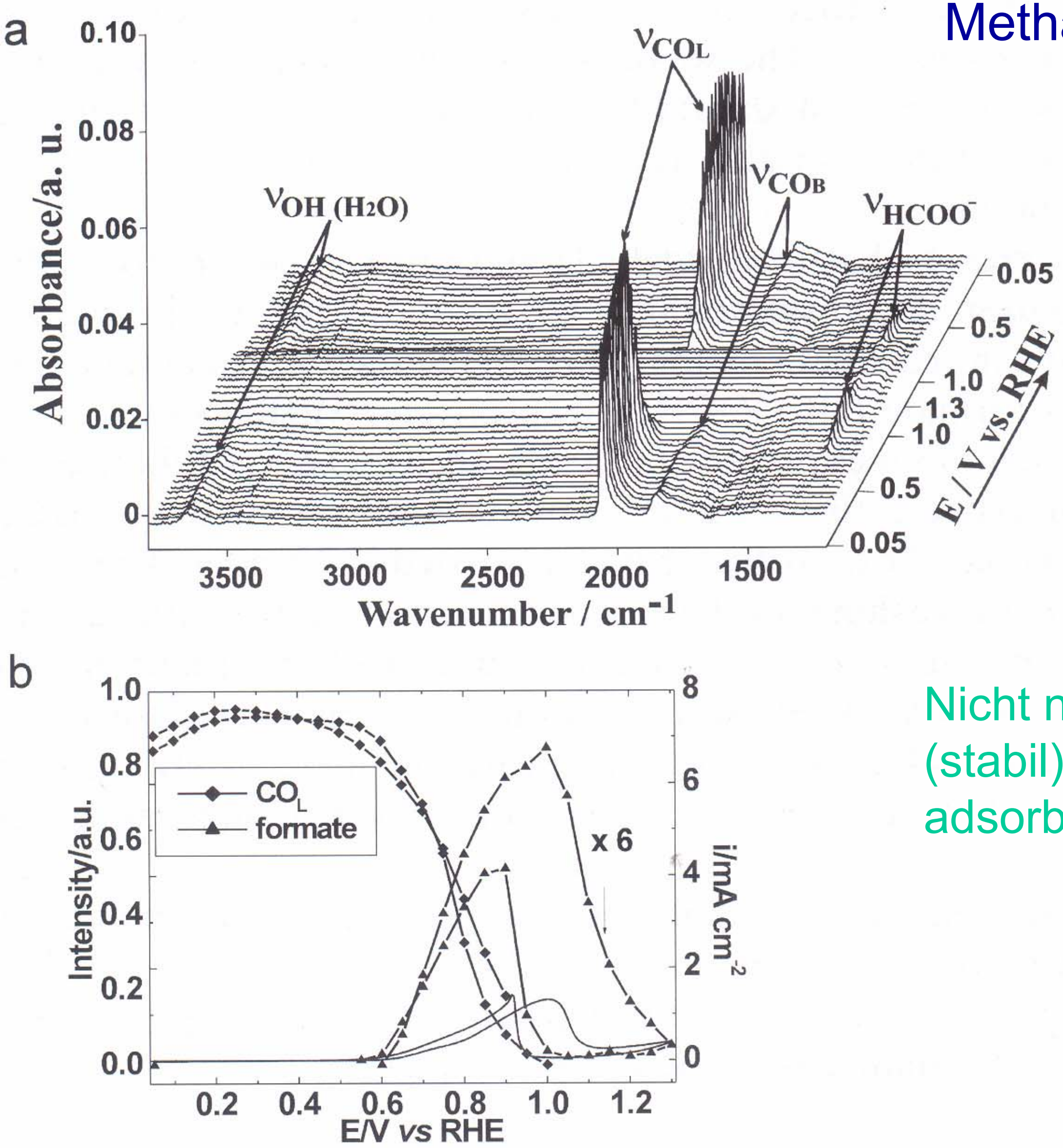
Methanoloxidation

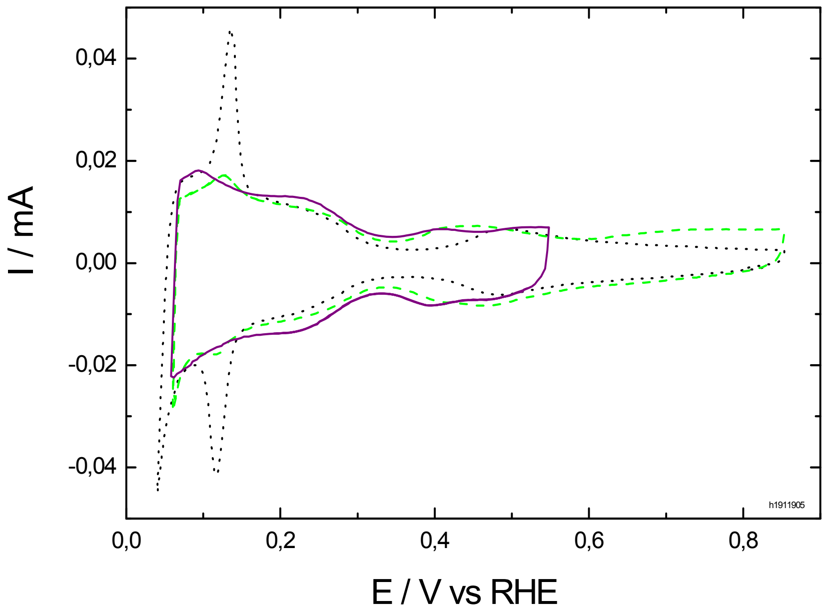


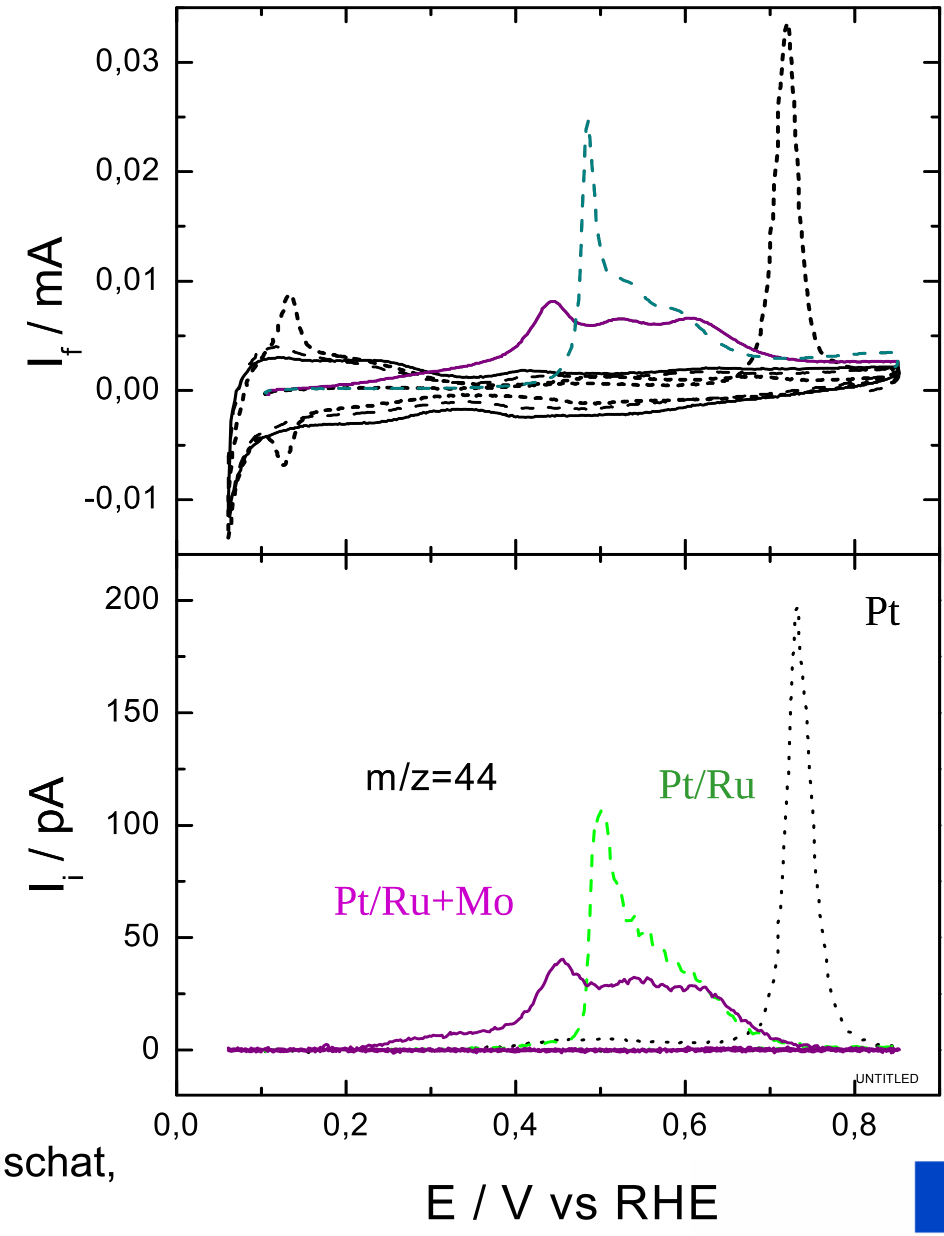
Nicht nur adsorbiertes CO (stabil), sondern auch adsorbiertes Formiat

Fig. 19. (a) A series of SEIRA spectra of a Pt electrode in 0.1 M $HClO_4$ + 0.5 M methanol solution collected during a potential sweep from 0.05 to 1.3 V and back to 0.05 V (vs. RHE) at a scan rate of 5 mV s^{-1}. (b) Potential dependence of the band intensities of CO_L around 2060 cm^{-1} and the ν_s(OCO) of formate at 1320 cm^{-1} taken from (a). The smooth trace is the CV recorded simultaneously with the spectra [101].

Chen, Y. X.; …..; Osawa, M. *JACS* **2003**, 125, 3680.

Pt(332) / Ru + Mo





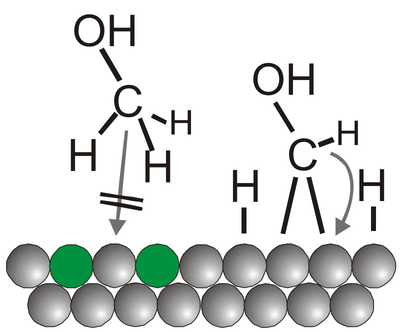
Synergistic effect of Mo and Ru!

G. Samjeské, H. Wang, T. Löffler, H. Baltruschat, *Electrochimica Acta* **2002**, *47*, 3681

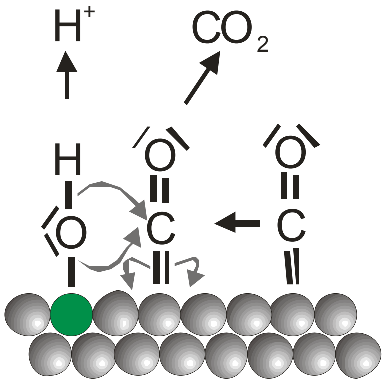
Effect of co-catalysts

geometric effect

(ensemble effect)

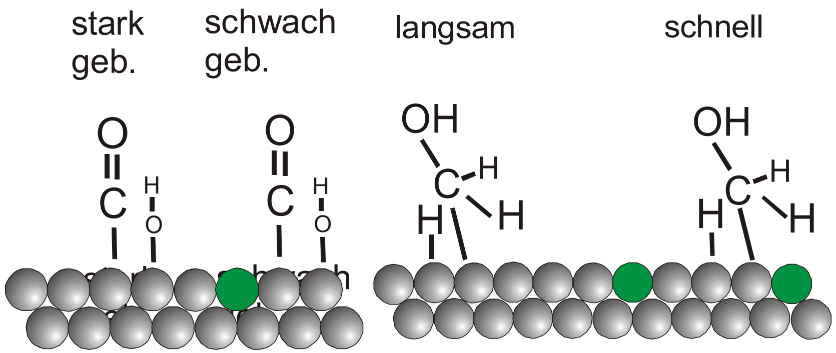


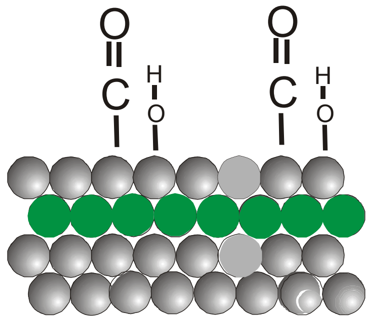
bifunctional mechanism



ligand - effect

(electronic effect)





ligand effect:

1) stress or strain
2) pure electronic

Understand how to influence catalyst surfaces

➔ learn how to optimize catalysts

model catalysts as benchmark

Ru: electronic + bifunctional

Sn: only electronic

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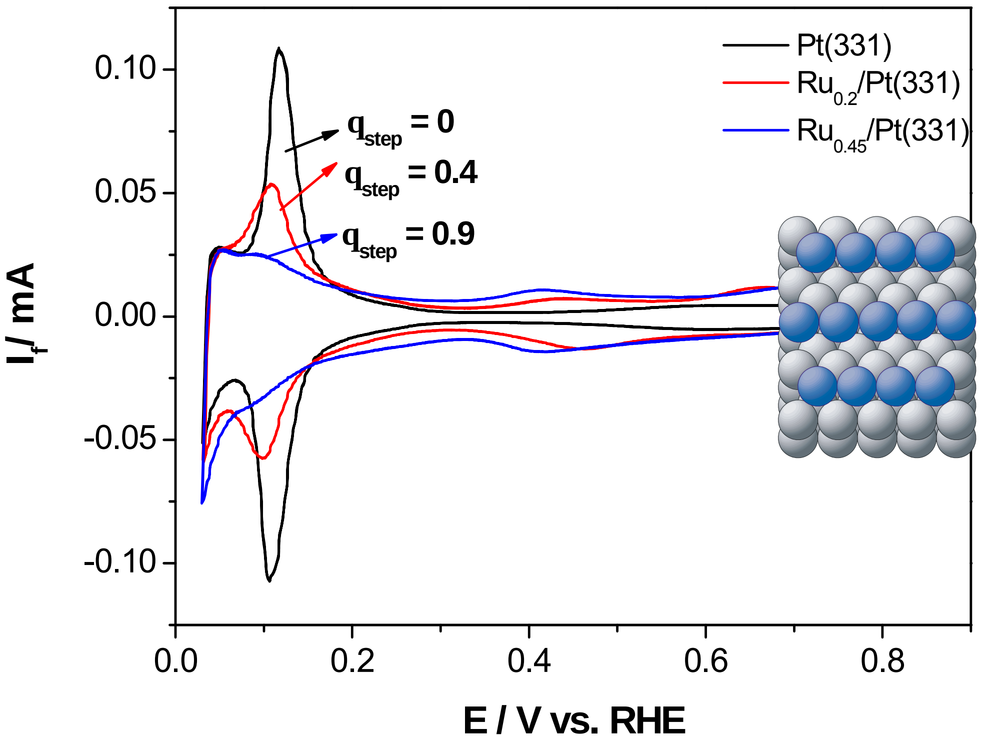
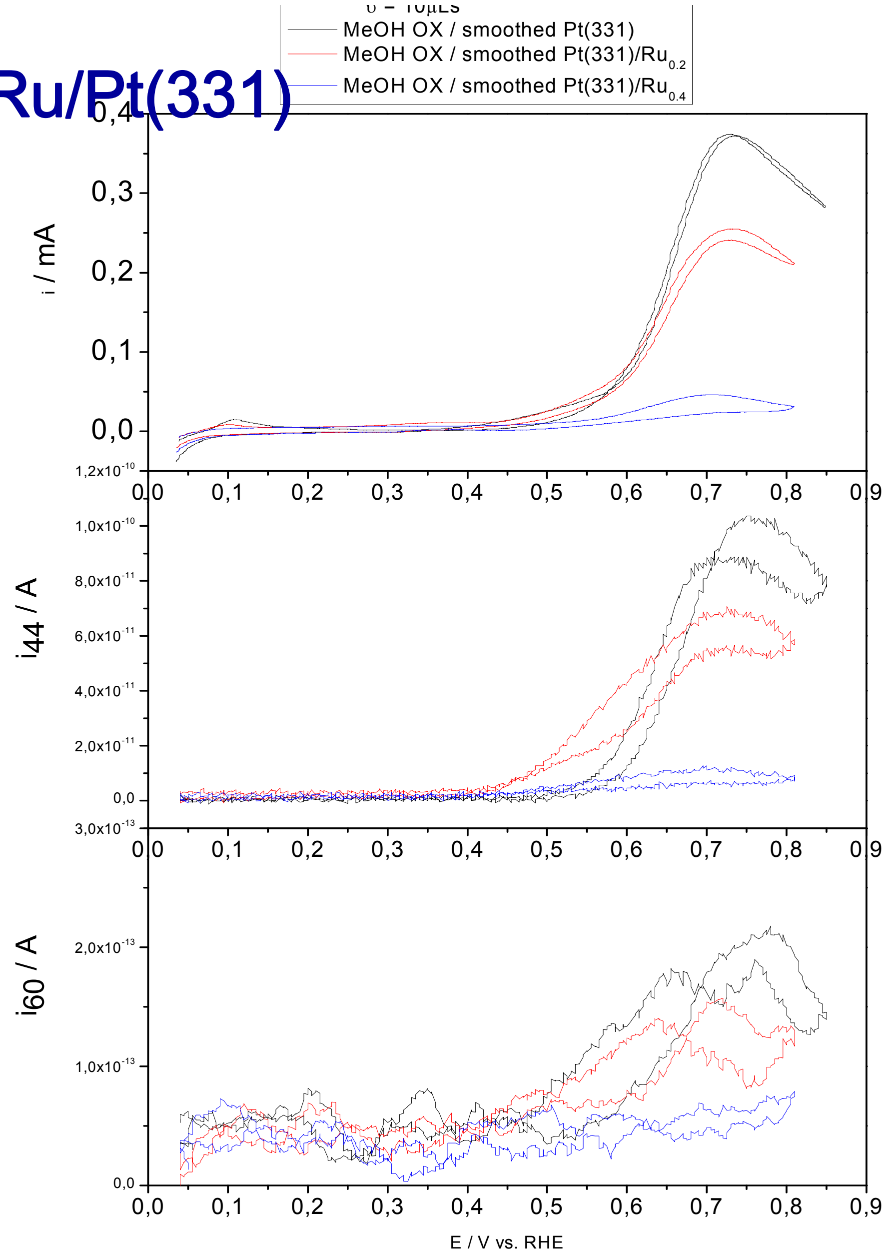
Electrooxidation of methanol on Ru/Pt(331)



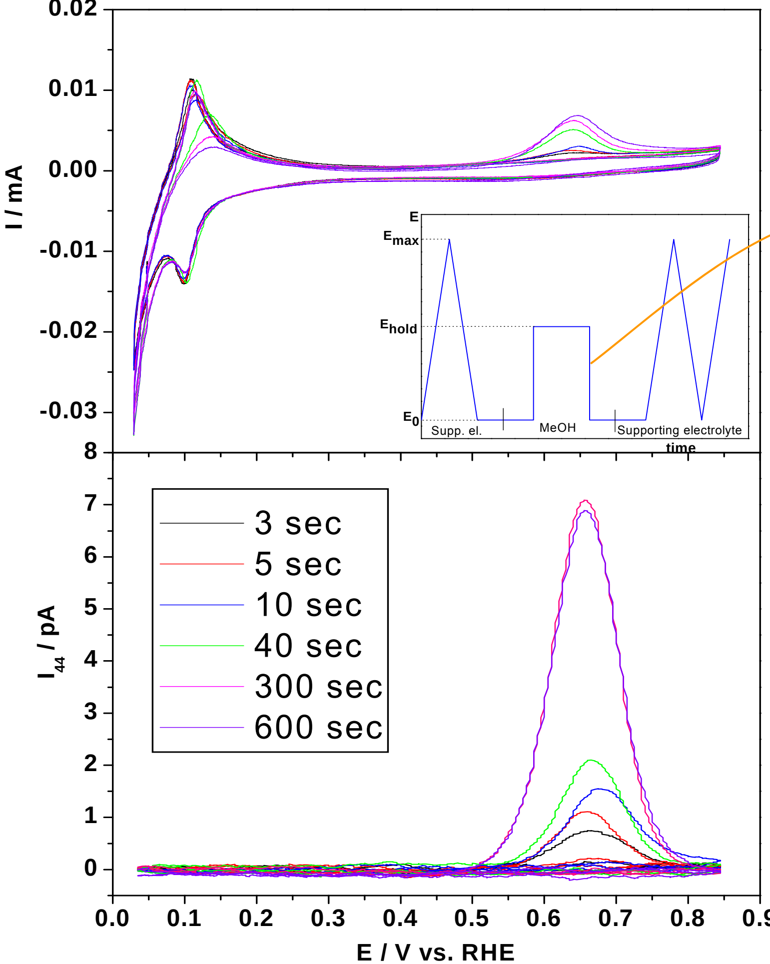
Pt(331) in 0.1M H_2SO_4 + 0.5M $HClO_4$
50 mV/s before and after Ru deposition

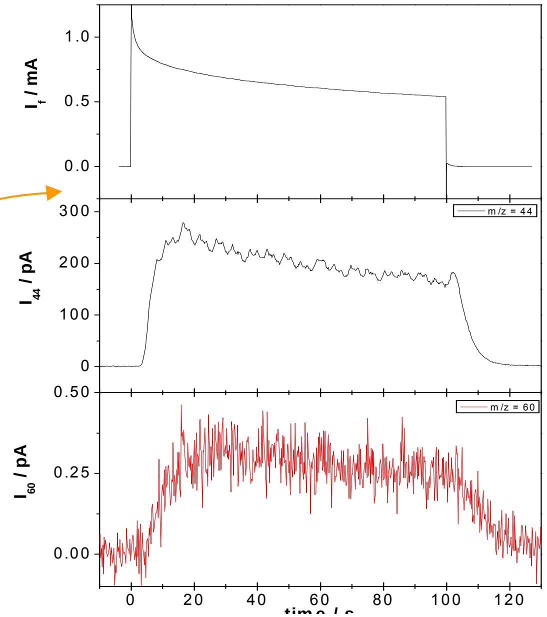


- The electrocatalytic activity for Pt(331) towards ethanol and methanol oxidation has a maximum for small Ru coverage <== Pt-step sites necessary

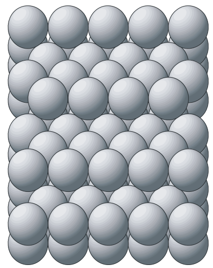
10^{-2} M methanol in 0.1 M H_2SO_4 + 0.5 M $HClO_4$ at 10 mV/s and flow rate 10 µL/s

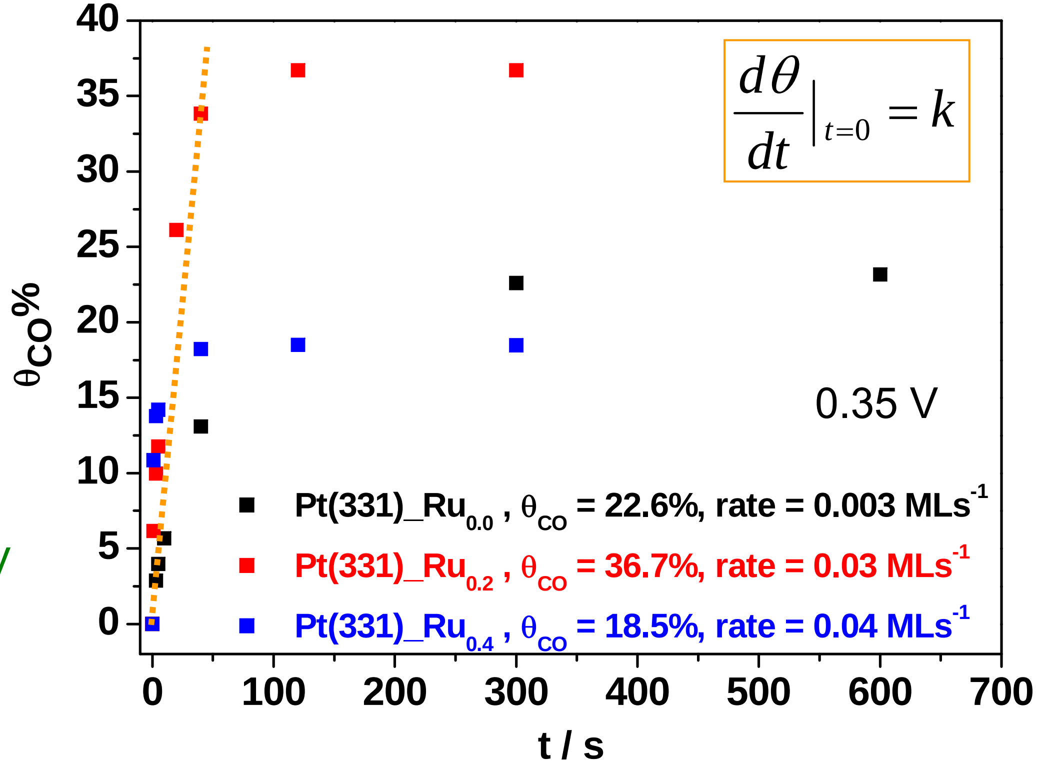
MeOH adsorption rate





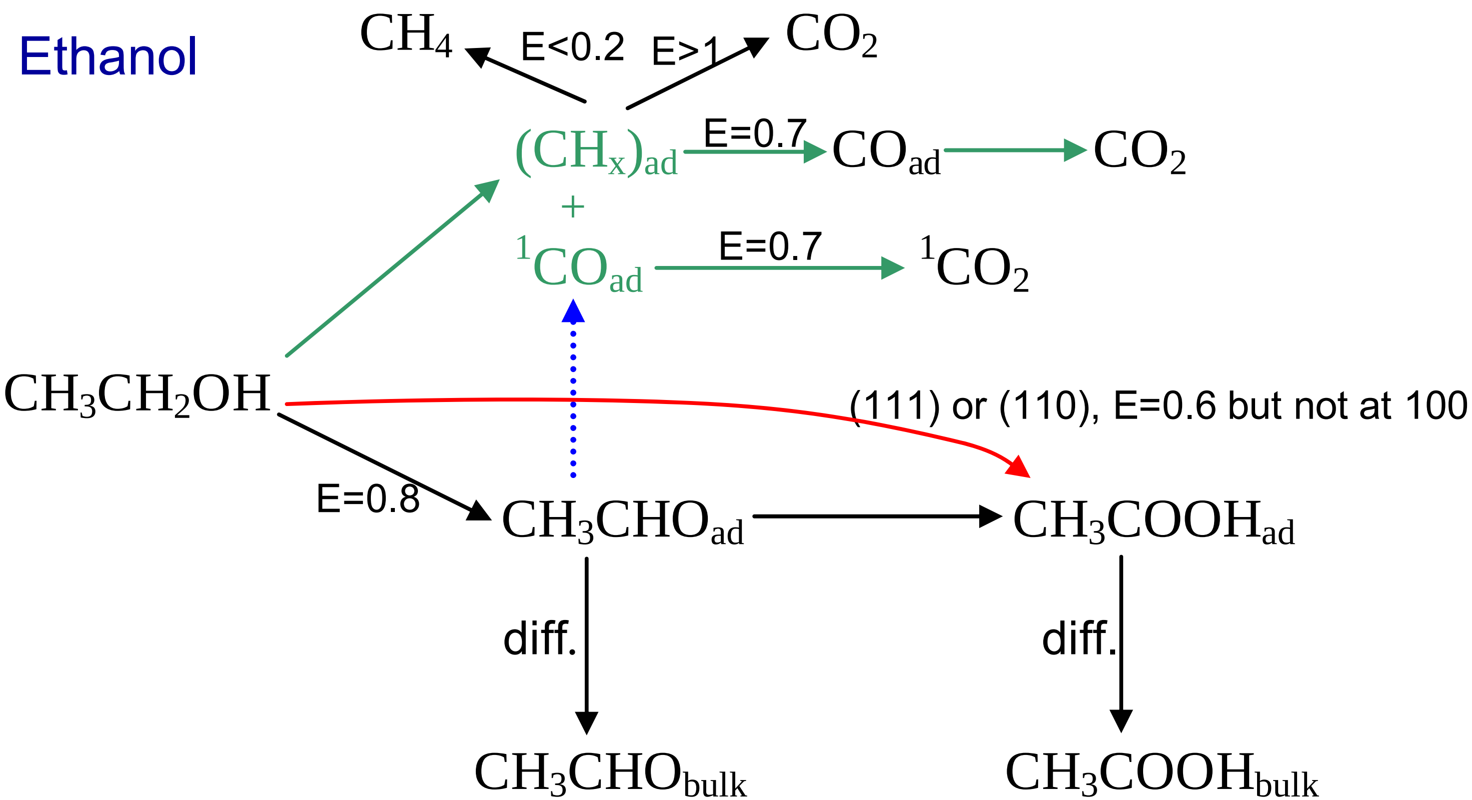
Pt(3,3,1)

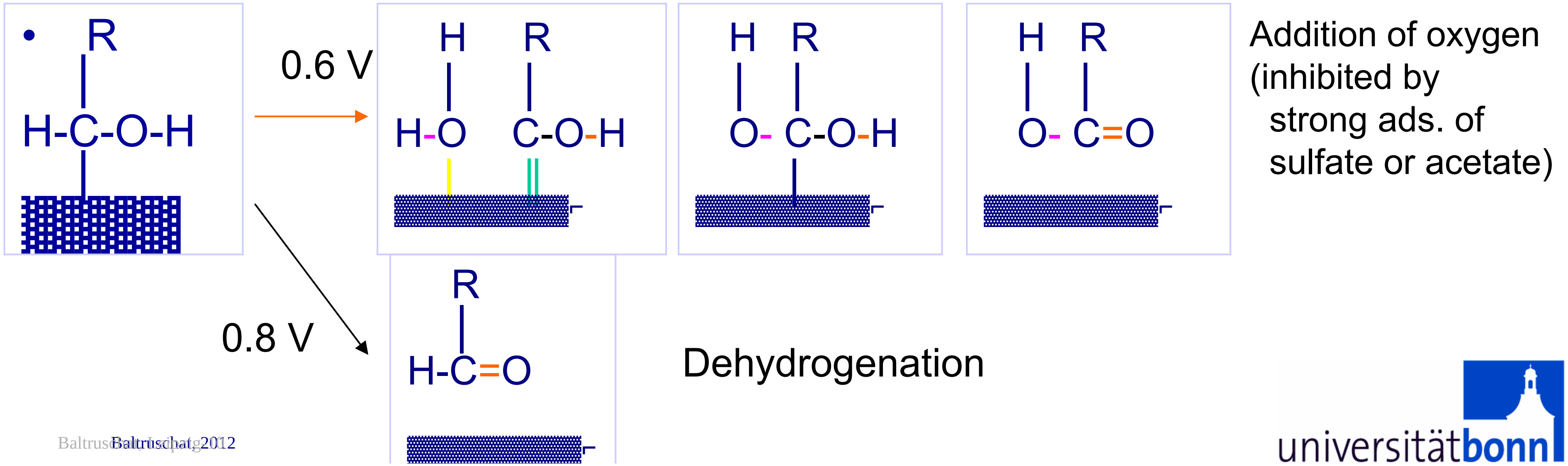




- With Ru: higher adsorption rate
- The rate of methanol adsorption is doubled with doubled step density
- Potential dependence: factor 10 per 100 mV ==>1st charge transfer is rds
- rate increases with increasing step density

Ethanol





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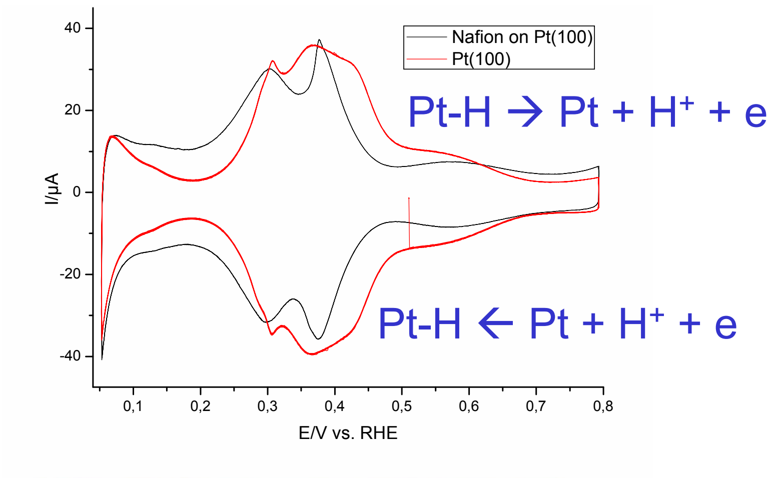
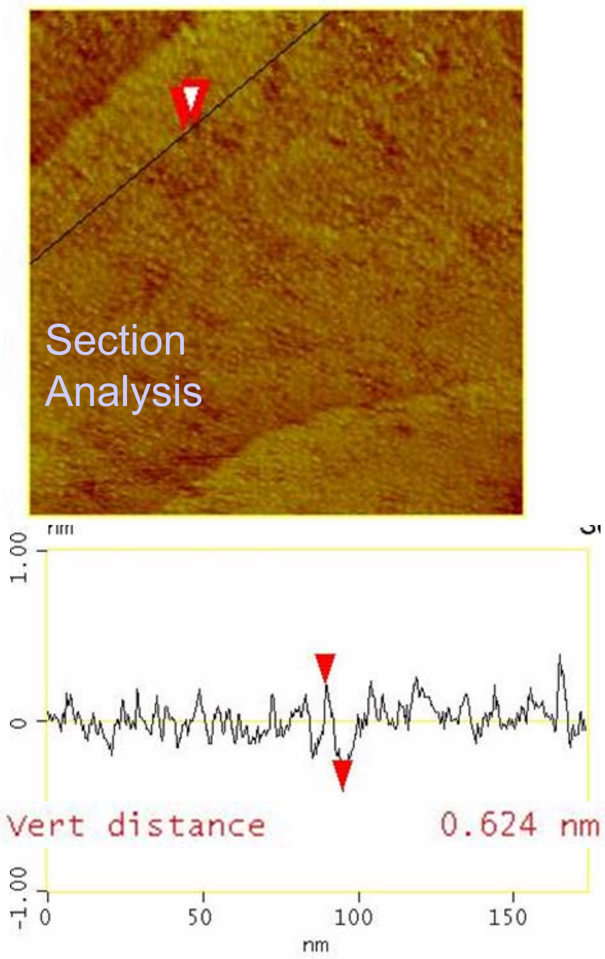
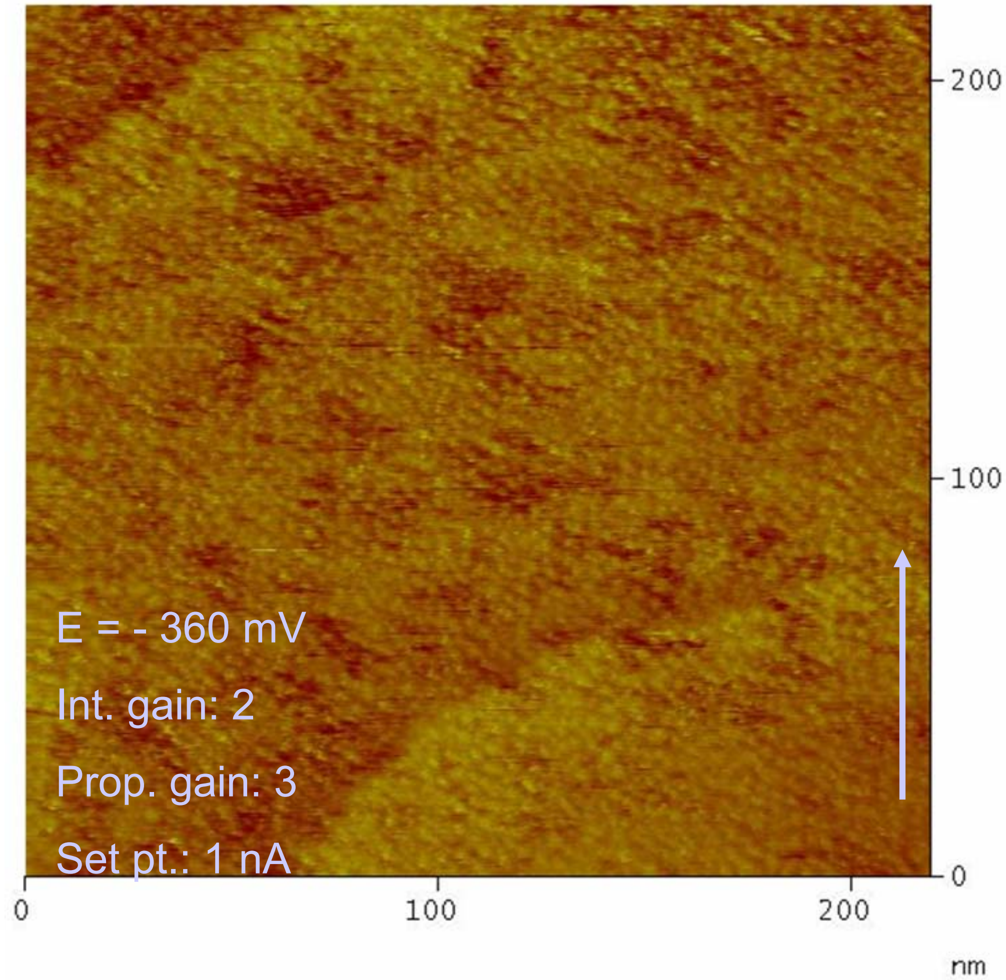
STM: Nafion auf Pt(100)



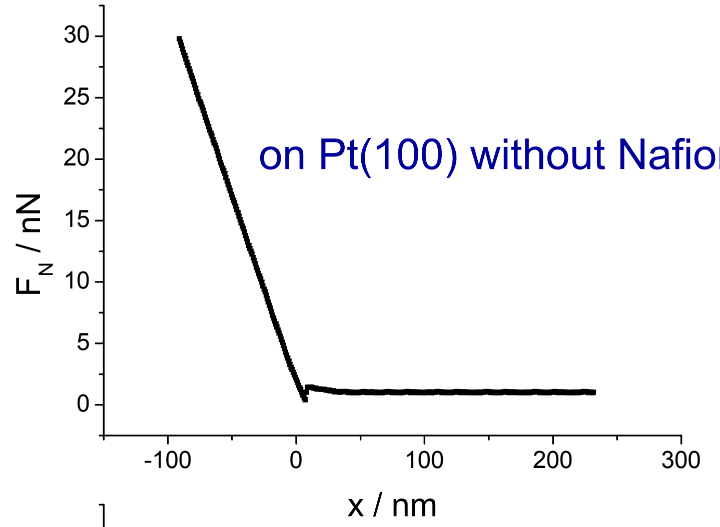
CV: No blocking of surface sites by nafion

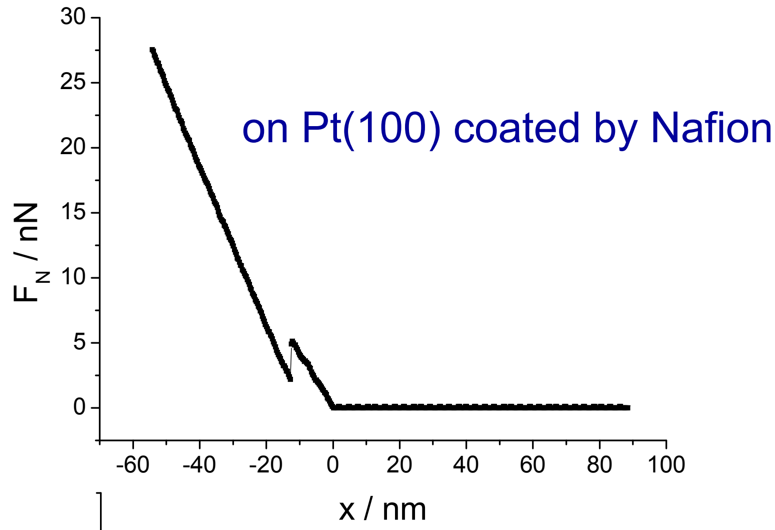


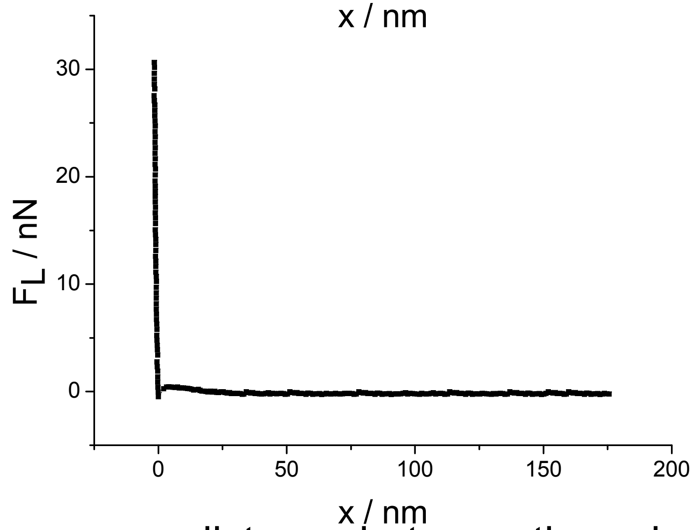


Friedrich et al.
Markovic et al.
Attard et al.

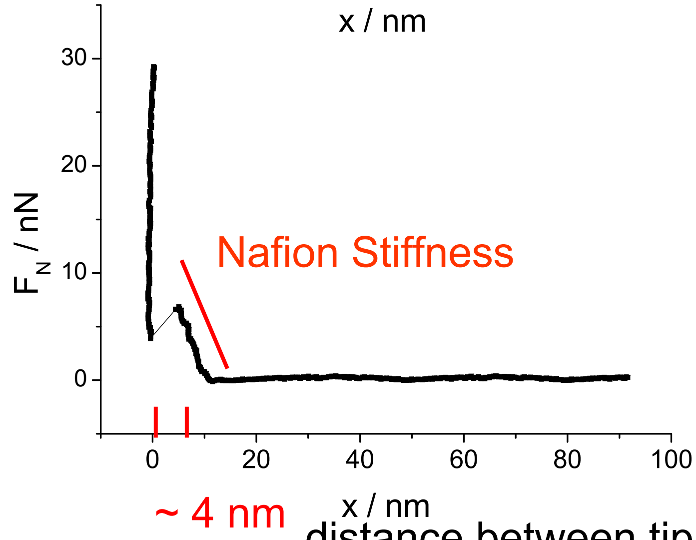
AFM: Force/Distance Curves







distance between tip and surface



distance between tip and surface

friction reduced by nafion

Effect observed in 50% of all cases.

Force necessary for penetration: 5 to 30 nN

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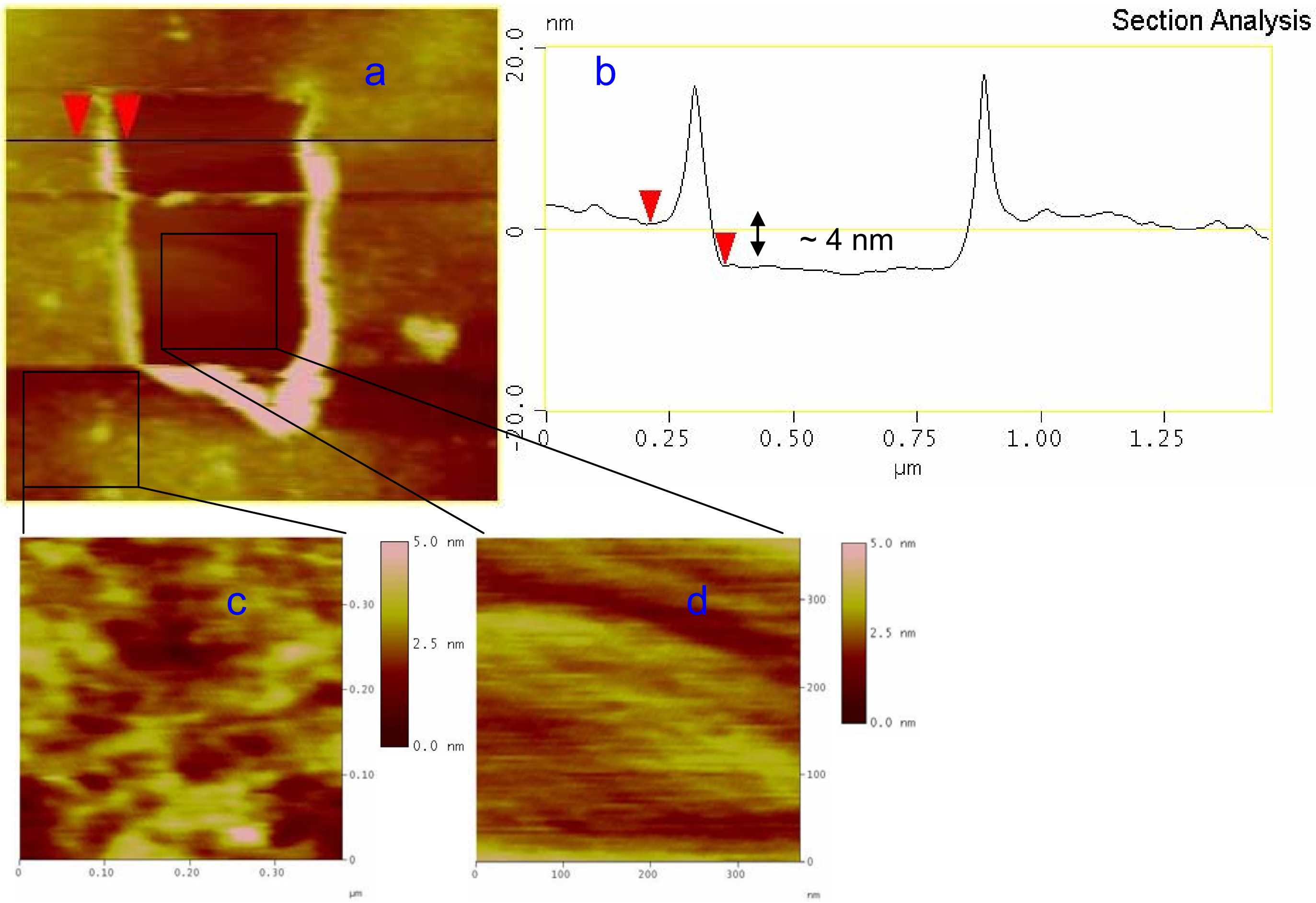
AFM- Image of Surface-Modification (Lithography)



FN = 2 nN after continuously meassurement in central area with F_N = 30 nN

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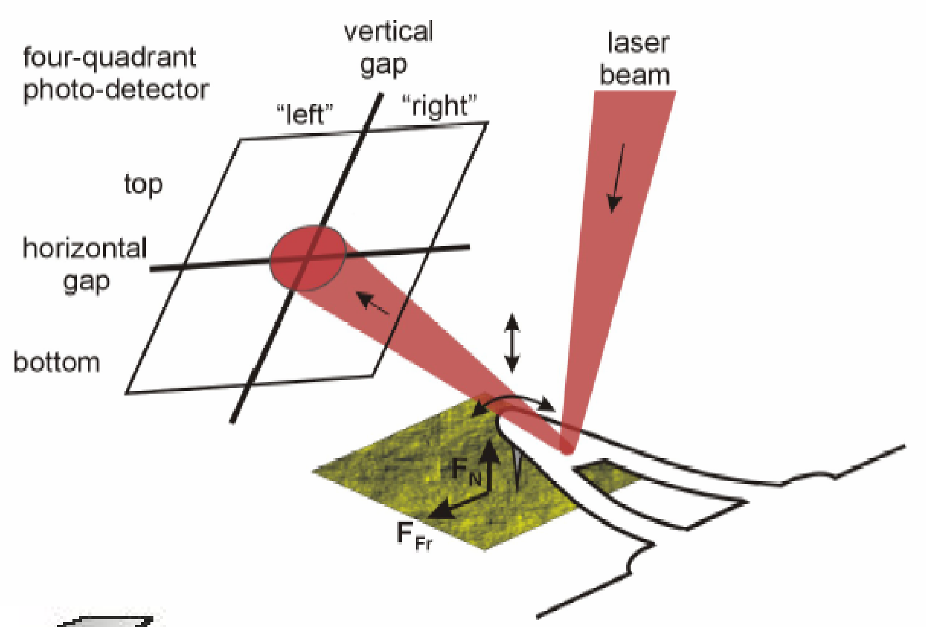
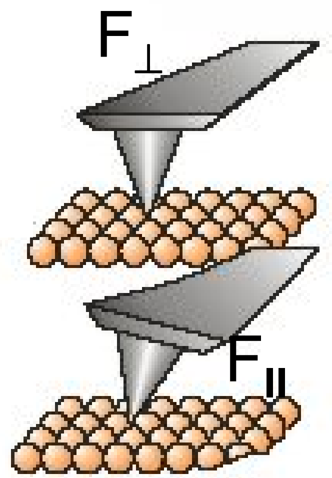
ad 4: friction

- Friction is of practical importance:
  - ➢ Utilizing friction as an operation mechanism → car brakes
  - ➢ Reducing energetic losses → efficiently working engines
  - ➢ Reducing materials losses due to wear
  - ➢ Optimising lubricants
- Developed countries could save up to 1.6% of their gross national product → ($100 billion per year in the US)

Atomic Force Microscope: Friction





Measuring of Topography:

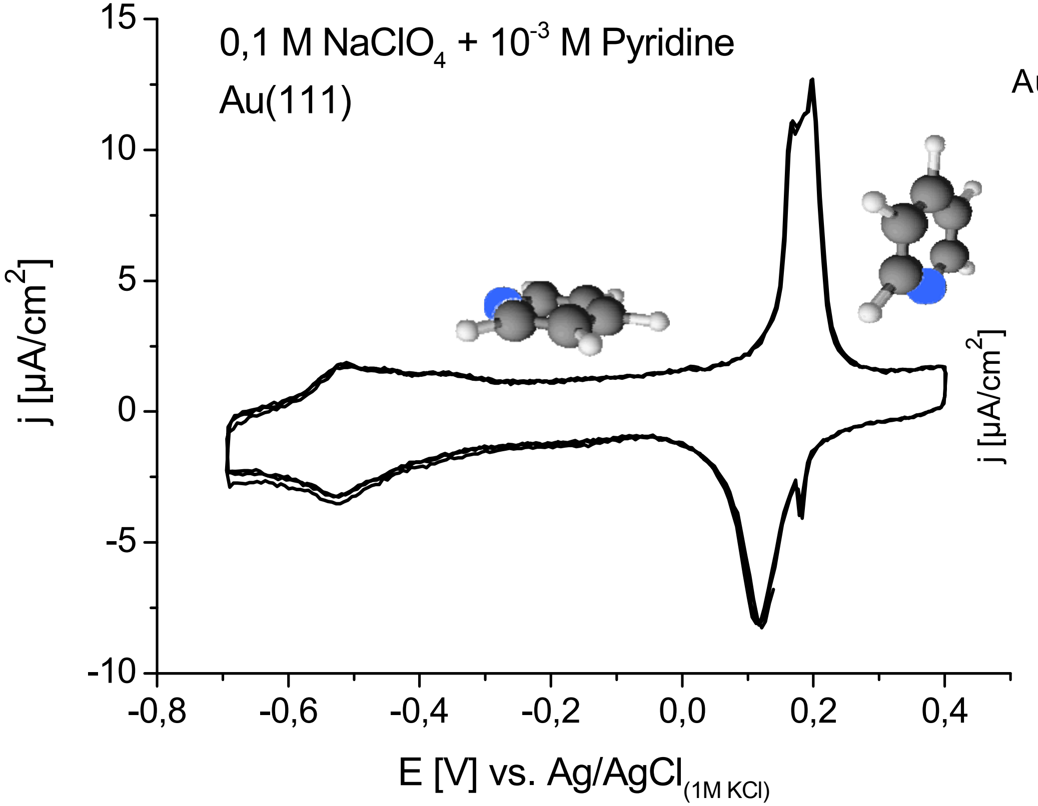
Up and down (deflection) of the cantilever is measured

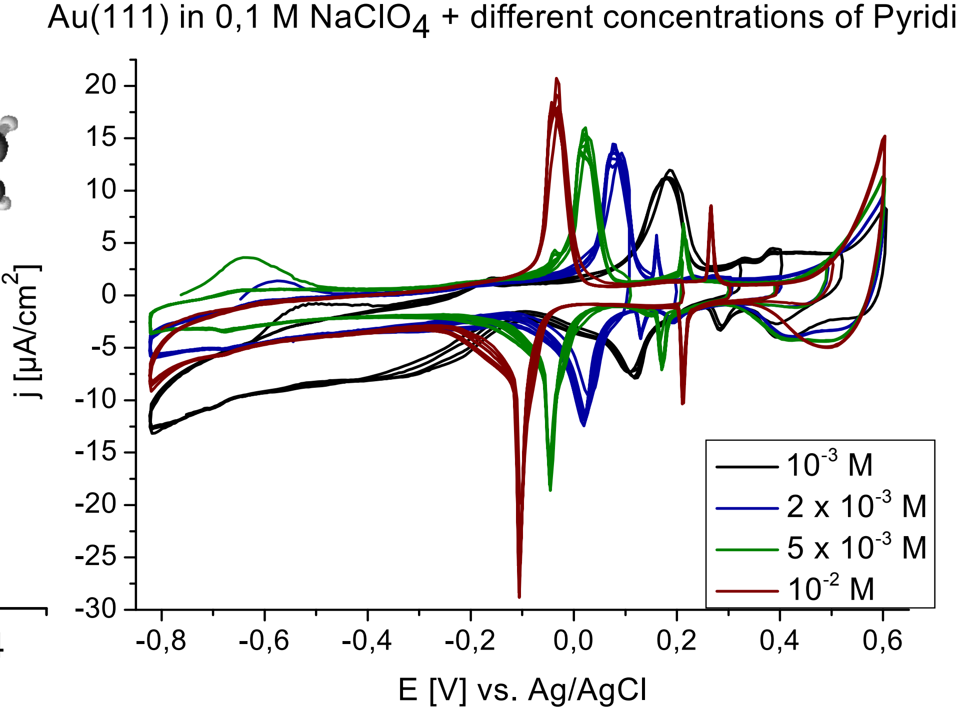
Measuring of Friction:

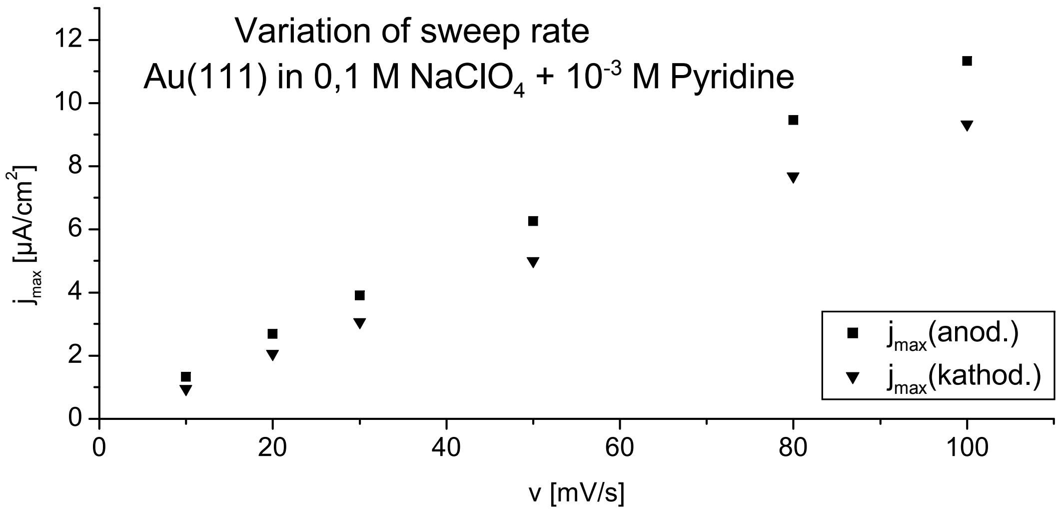
Friction force between the sample and the tip will produce a twisting of the cantilever.

S. Sundararajan, B. Bhushan, *J. Appl. Phys.*, **2000**, 88, 4825

Pyridine on Au(111): Cyclic Voltammetry







L. Stolberg et al., *J. Electroanal. Chem.*, 307 **(1991)**, 241.

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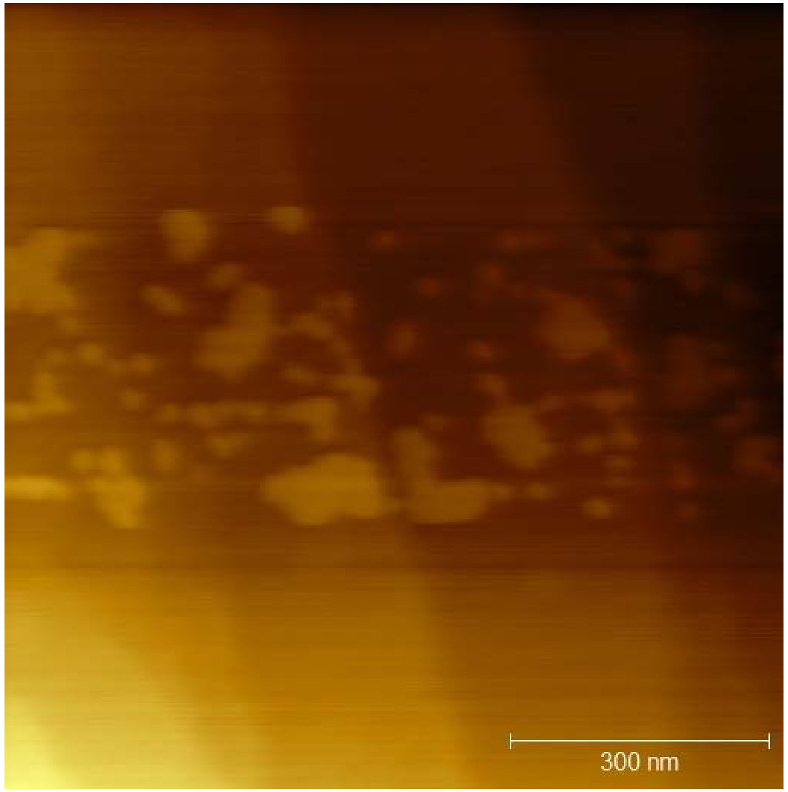
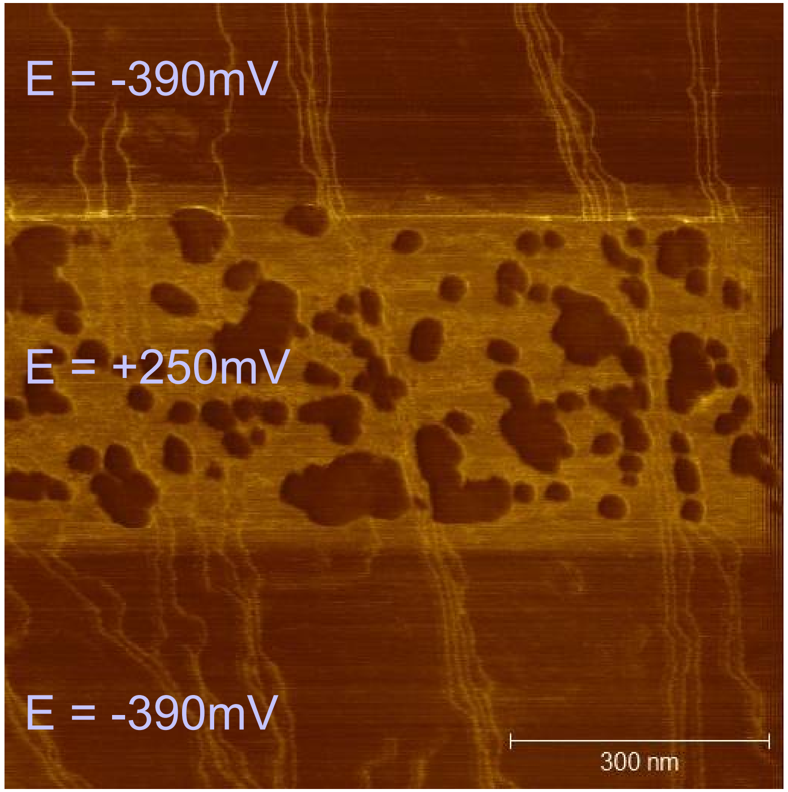
Pyridine on Au(111)

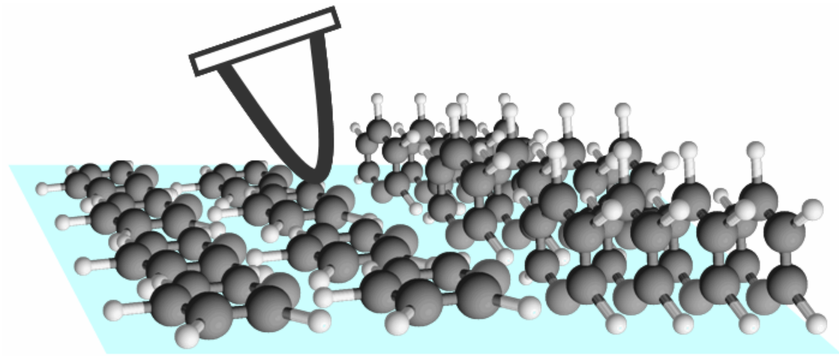
Topography



Friction

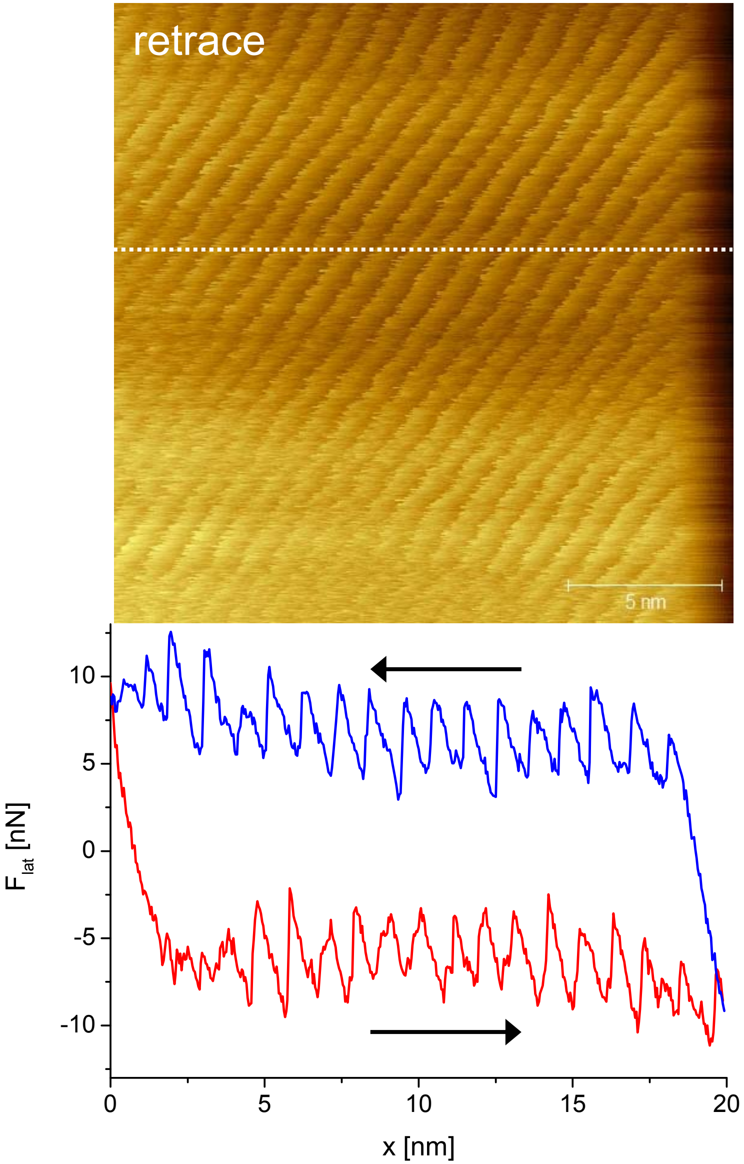


py flat	py vert.
electrostatic attraction	electrostatic repulsion
low apparent height	elevated app. height
high friction	low friction
	hydrophobic? (zero slip approx. for electrolyte not valid?)



Baltruschat, 2012

Stick-slip friction

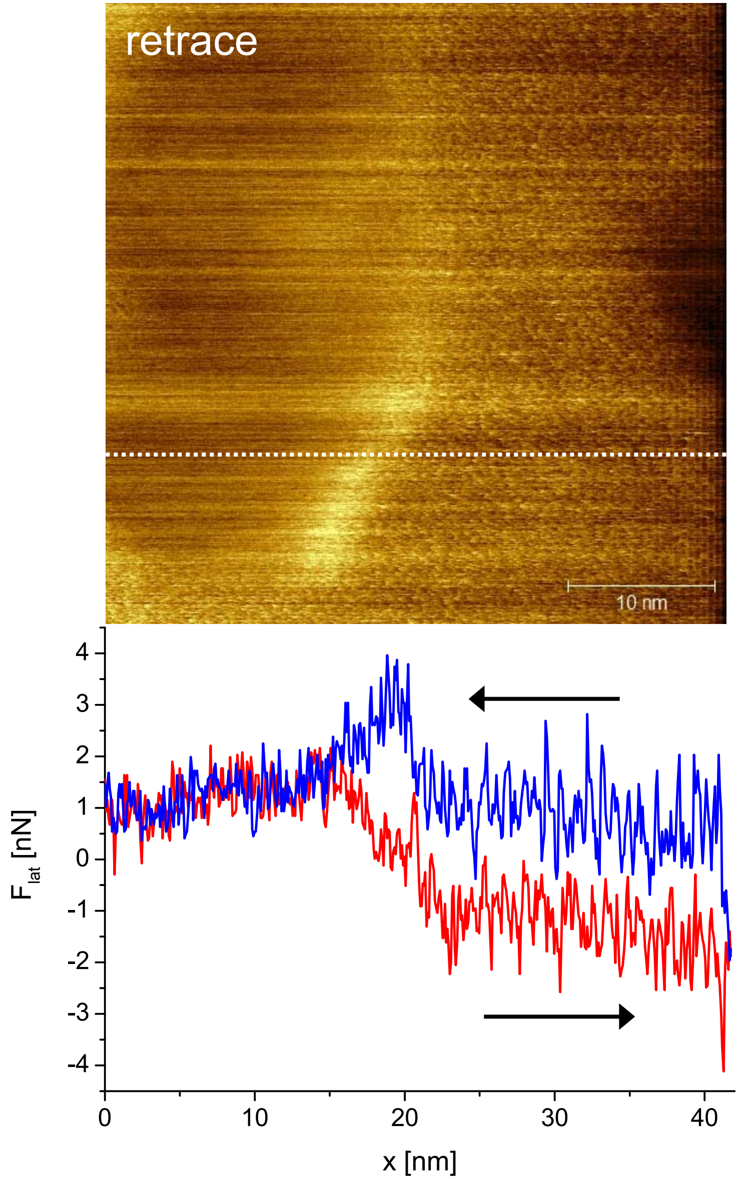


Electrolyte: 0,1 M $NaClO_4$ + 10^{-3} M Pyridine

E = -580 mV vs. Ag/AgCl

F_n = 42 nN; scan rate = 4 Hz

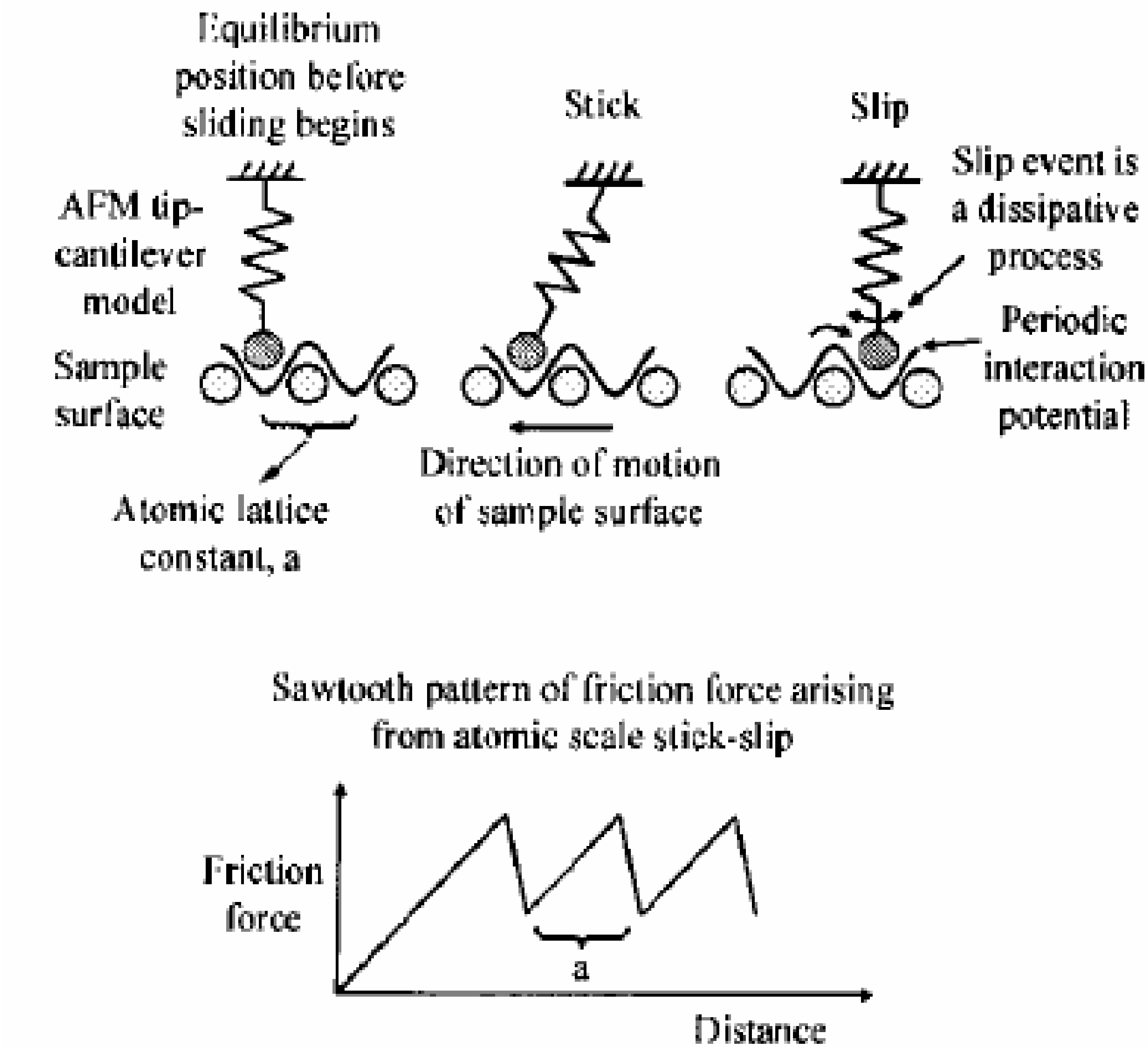
Baltruschat, 2012



Electrolyte: 0,1 M $NaClO_4$ + 10^{-3} M Pyridine

E = +330 mV vs. Ag/AgCl

F_n = 15 nN; scan rate = 10 Hz



N. S. Tambe; B. Bhushan *Nanotechnology* **16** *(2005)* 2309-2324.

Bhushan, 2012

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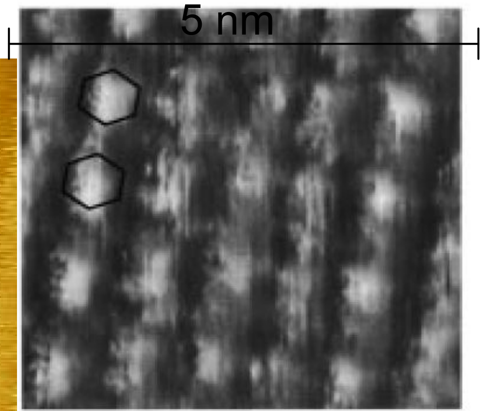
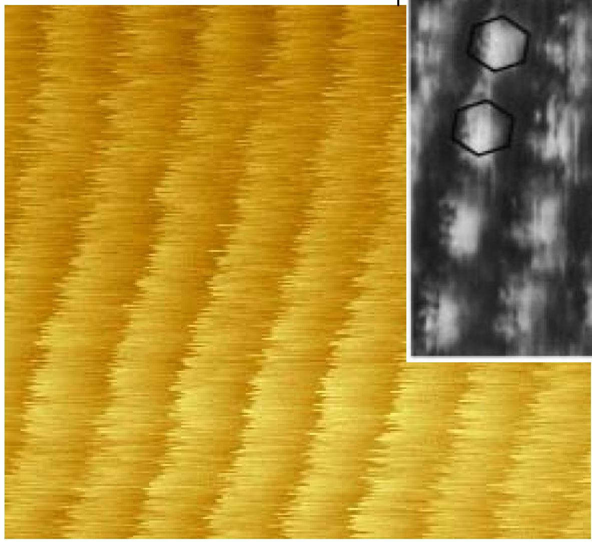
Stick-Slip resolution - II





STM

(W.-B. Cai et al., *Langmuir* 14 (**1998**), 6992.)

AFM

Motivation:

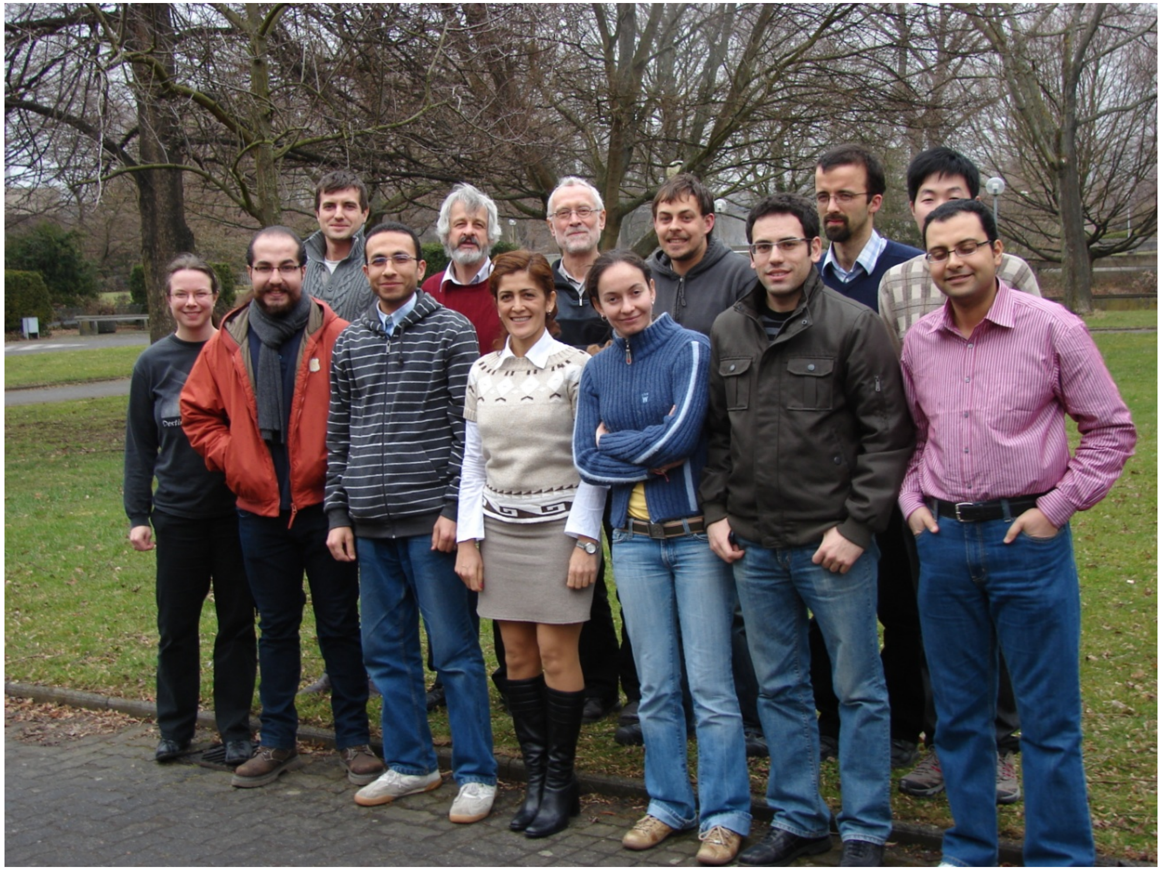
1. Vergleich zur fest/Gas Grenzfläche („akademisch“)
2. (Bedeutung in Galvanik und Korrosion (Damaszen-Prozess))
3. Intermediate in Brennstoffzelle (Energie) etc.
4. Reibung

- hohe Reaktivität von Pt ==> viele Raktionskanäle, viele Ads.-Produkte
  (dies schließt Selektivität für Endprodukt nicht aus)
- Vergiftung des Katalysators durch eines der Adsorbate
- starke Abhängigkeit der Reaktion vom Reaktionsplatz („site“)
- komplexe Beeinflussung der Reaktivität durch Kokatalysatoren
- Beeinflussung mechanischer Eigenschaften durch Adsorbate

Dank:

- G.A.Attard
- R.Bennewitz

DFG, SFB 624
DAAD



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