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# Temperature-programmed reaction spectroscopy

A variety of TD spectroscopy  
related to concepts about surface reactions

R. Schlögl, FHI, Berlin



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# Overview

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- Prologue: Model concepts
- The research target of TPRS
  - Method
  - Answers
  - Challenges and limitations
- The proptotype application: Ni (110)
  - Reactant modification, formic acid decomposition, pre-treatment
- A more challenging application Ag (110)
  - A complex adsorbate
  - The role of adsorbed and sub-surface oxygen
  - Methanol oxidation



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# Prologue

Properties and status of models in catalysis



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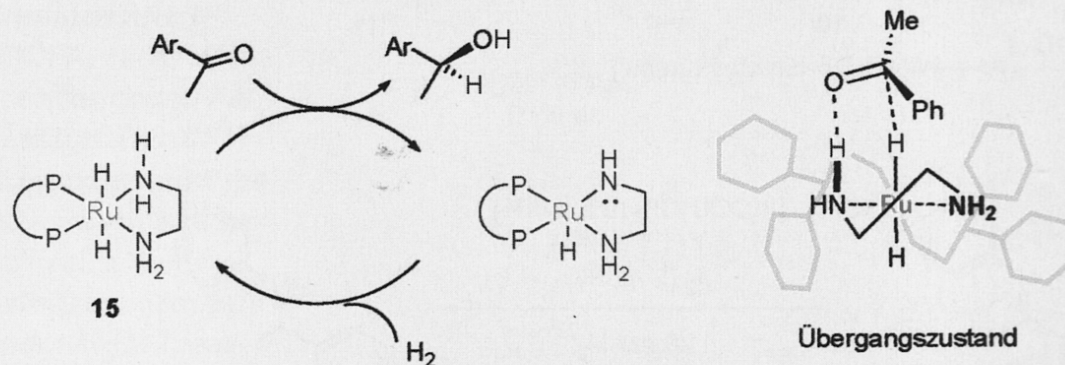
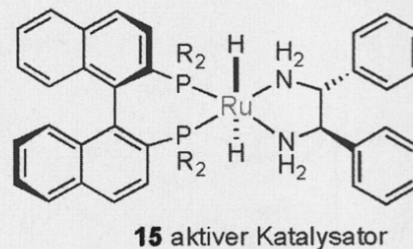
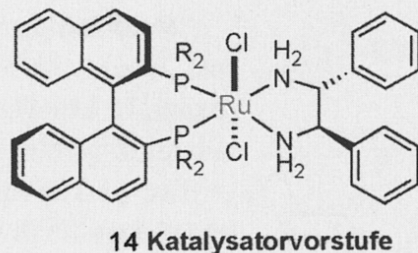
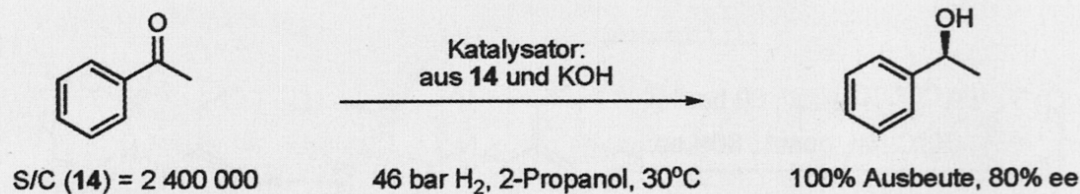
# Qualitative models “concepts”

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- In complex processes reaction mechanisms from chemical rules and predictions of “intermediates”:
- Synthesis or calculations of structural and thermodynamic properties of such intermediates:
- Problem of kinetic spectators or side reactions as no on-line verification possible
- Approximation of reaction experiments by TPRS and often with reactive models (alkyl-iodide instead of alkane)



# The molecular phenomenology



Ligand design to finetune electronic and geometric structure by distorting metal d-states and by shielding access to them

Reaction mechanism from structure-analysis of molecular intermediates: No TPRS required

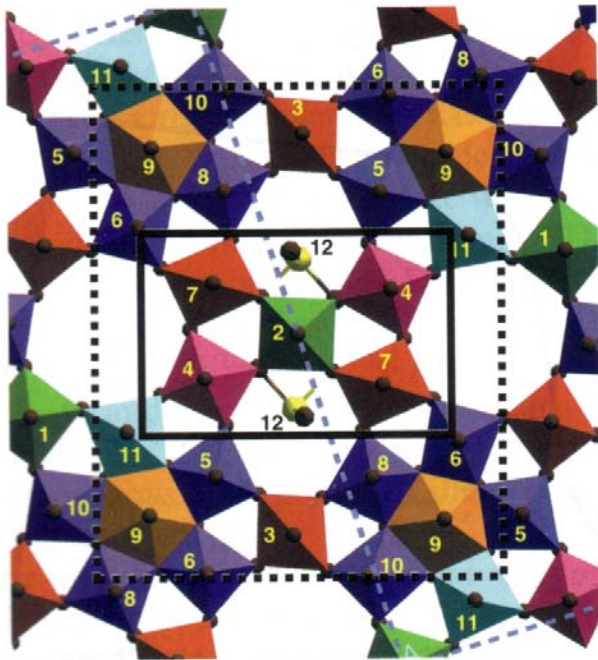
Enantioselective hydrogenation



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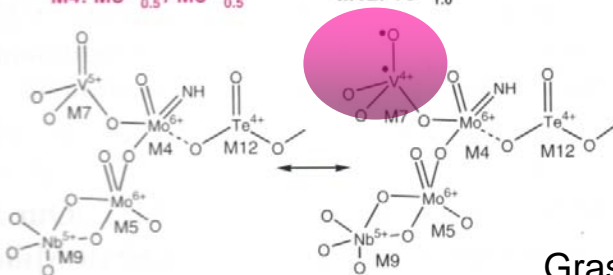
# The heterogeneous analogy



M1:  $V^{4+}_{0.2} / Mo^{5+}_{0.8}$   
 M2:  $V^{4+}_{0.8} / Mo^{5+}_{0.2}$   
 M3,7:  $V^{5+}_{0.5} / Mo^{6+}_{0.5}$   
 M4:  $Mo^{5+}_{0.5} / Mo^{5+}_{0.5}$   
 M5,6,8,10:  $Mo^{6+}_{1.0}$   
 M9:  $Nb^{5+}_{1.0}$   
 M11:  $Mo^{5+}_{1.0}$   
 M12:  $Te^{4+}_{1.0}$

Crystallography produced a structure susceptible to selected theoretical treatment

Microstructural analysis shows that this surface is almost non-existent yet can be found:  
Essential or curiosity?



Grasselli et al



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# Models: Necessity

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- Most catalytic reactions are too complex to be understood on “real systems”
- Multi-scale issues, structural dynamics and transport dynamics inhibit disentangling of reaction network
- In-situ analysis of real systems should define models; no a priori guess for demanding systems
- Models are required to verify qualitative conceptual suggestions; **they must be functional**
- Models for adsorption are usually not functional enough (except for CO oxidation)



# Model properties

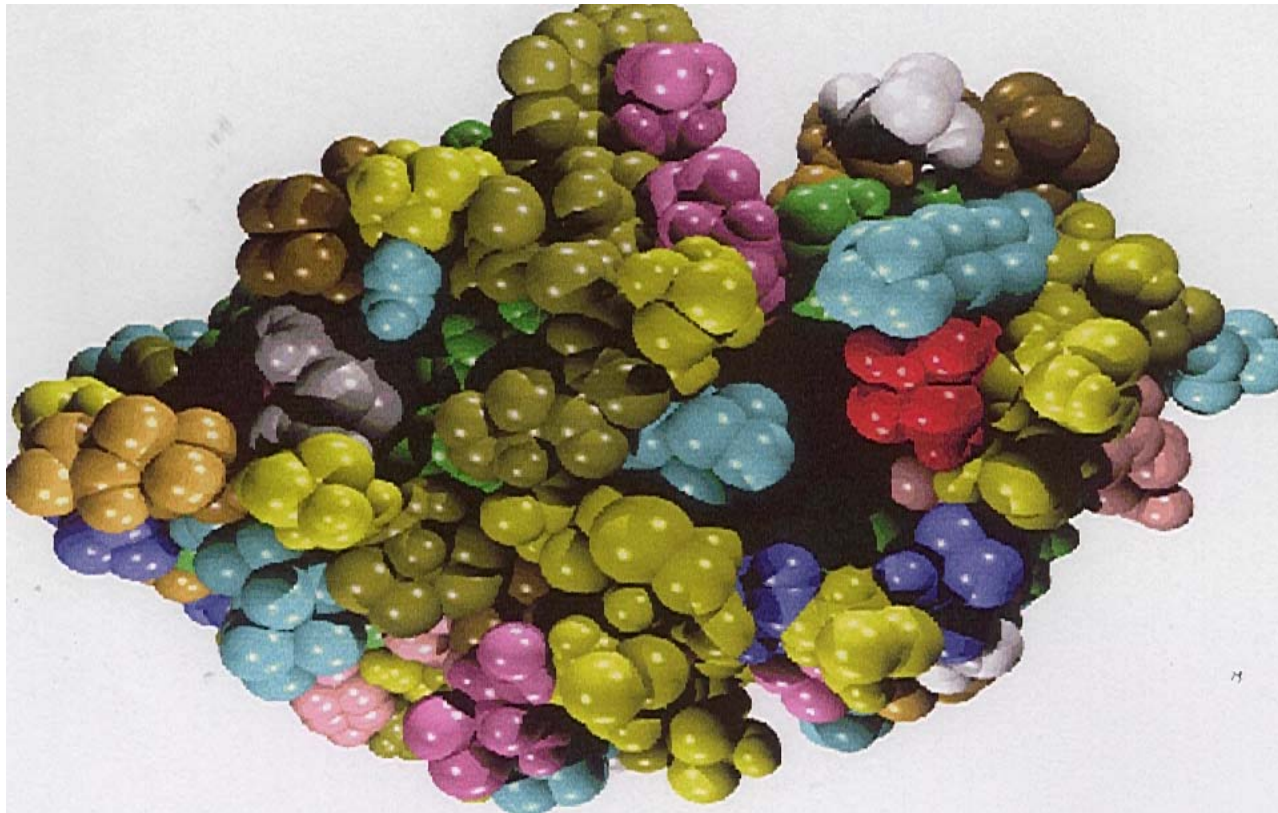
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- Models are structurally and chemically well-defined
- Models allow in-situ analytics (including TPRS)
- Models are slow in their function allowing to isolate individual reaction steps
- Models should not need structure-distorting activation steps (sputtering) such that their definition is lost
- Models perform the desired reaction, no proxys

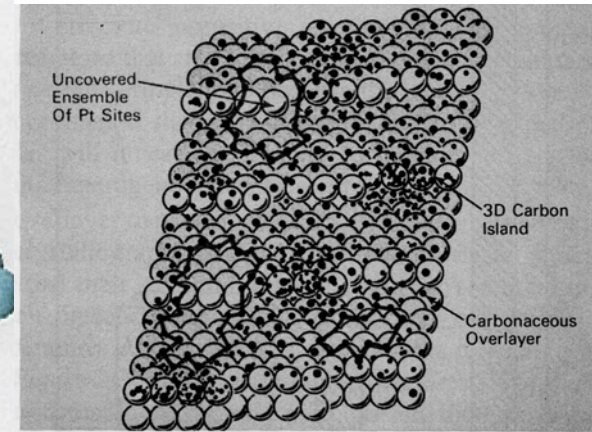




# Models of catalyst surfaces



Trypsin, an enzyme



Somorjai 1994



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# Model types

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- No model for any complete catalyst function (multi scale)
- Models on atomic scale; single crystal approach and multi-scale theory
- Only limited function as mesoscopic effects “surrounding”, molecular-molecular interaction are missing
- For these dimensions no models so far (beginning in enzymes and their genetic design)
- Nanostructured model approaches in heterogeneous catalysis under development
- In homogeneous catalysis models for (bio) reactions are available; no clear understanding of their function due to process complexity
- For macrokinetic domain textural models and computational models exist



# Research status

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- The single crystal model approach is conceptually correct and indispensable for quantitative kinetic understanding
- Its functionality is too low as no mesoscopic variability (steps); no generic approach
- Clusters on well-ordered oxides and oxide films offer potential; challenge of structural definition under operation
- So far not sufficient control over structure for non-metallic systems
- Bulk-surface interaction (sub-surface) and defect structuring (nano-engineering) still not under control and only poorly understood



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# Research concept of TPRS

What are the issues addressed?

What are the conditions and  
limitations?



# The dynamic catalyst

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- dynamical behavior arises from coupling of the catalyst material properties with those of the reaction environment
- the working catalyst is a unity between the material and its reaction environment; isolation of any part inhibits the correct function
- a catalyst takes part in its reaction but is regenerated in cyclic operation: no net change of the **metastable** catalytic material: in-situ observation mandatory



# The Concept of TPRS

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- Material science of catalysts contributes little to the identification of the mode of operation (mechanism) and thus to structure-function correlation
- Transient kinetic experiments are used to gain insight into the reaction processes
- High pressure experiments (flow experiments) although also counted to TPRS are fundamentally different from low-pressure experiments due to the re-adsorption issue and thus very hard to analyse quantitatively



# The Concept of TPRS

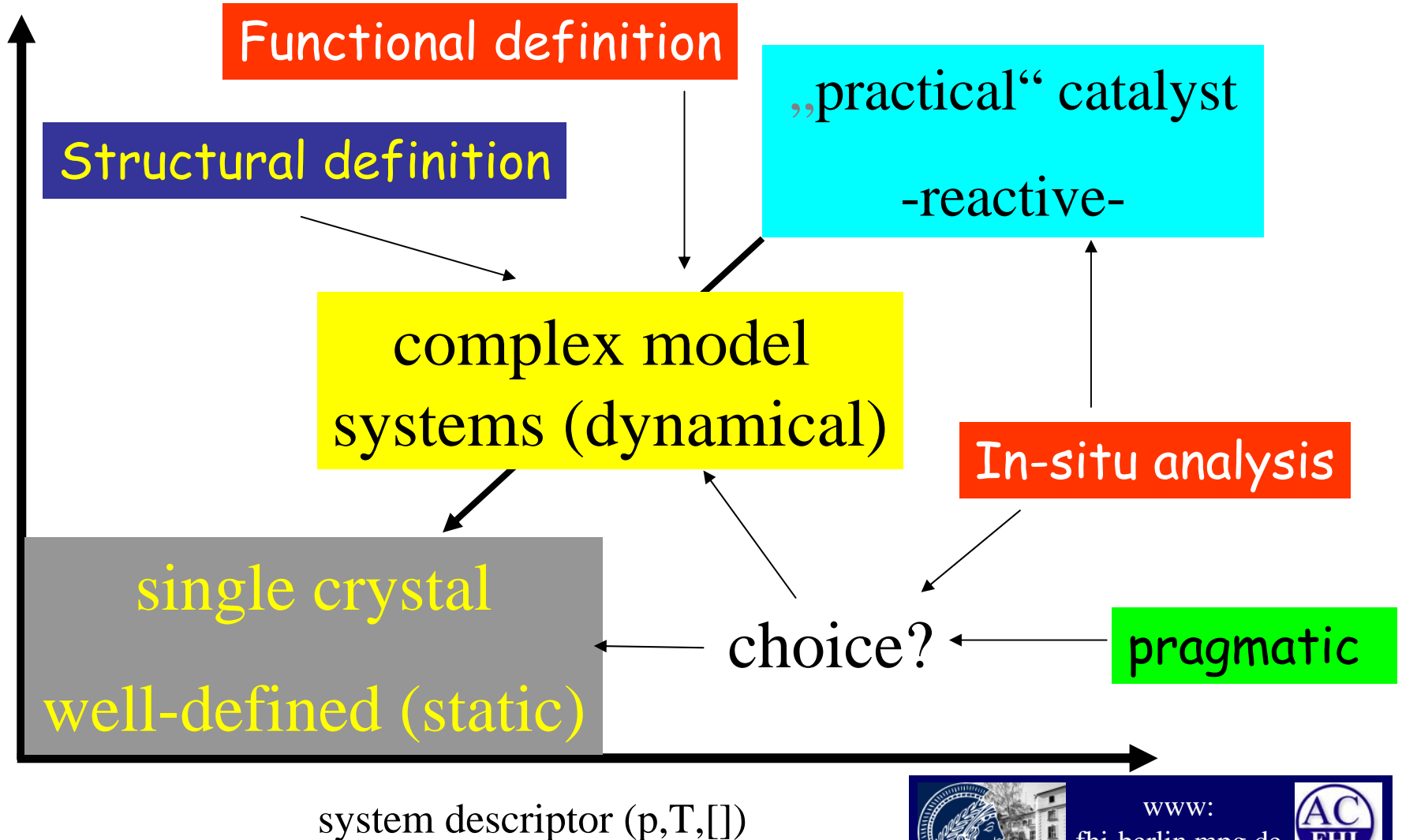
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- TPRS is the analogue to structural in-situ methods to gain insight into the function of a catalyst system
- Two main conditions must be provided:
  - The catalyst must be in its right material form despite very low conversion in the TPRS experiments (relevance of a pristine surface)
  - The process must be reversible or at least temperature-insensitive to the ramp employed for observation (never fully correct but sometimes a valid approximation)
- The reaction of study must be pressure-insensitive (very rarely the case!) if a prediction to real world is attempted (often not done in original literature)



# Model strategy: TPRS is the bridging method

complexity



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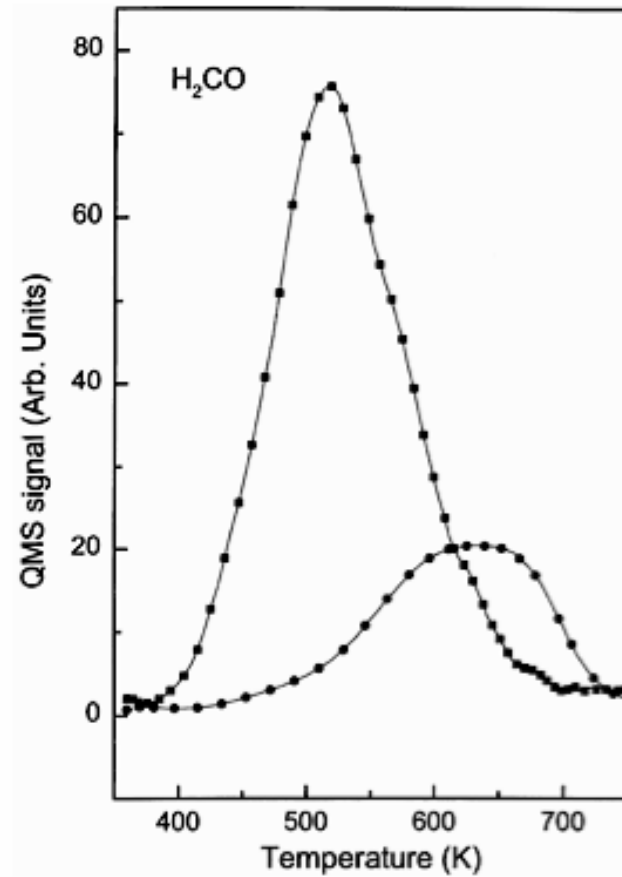




# TPRS: an invasive method

*Q. Wang, R.J. Madix / Surface Science 496 (2002) 51–63*

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MeOH oxidation over 1 ML  $\text{VxO}_y$  on  $\text{TiO}_2$  (110)

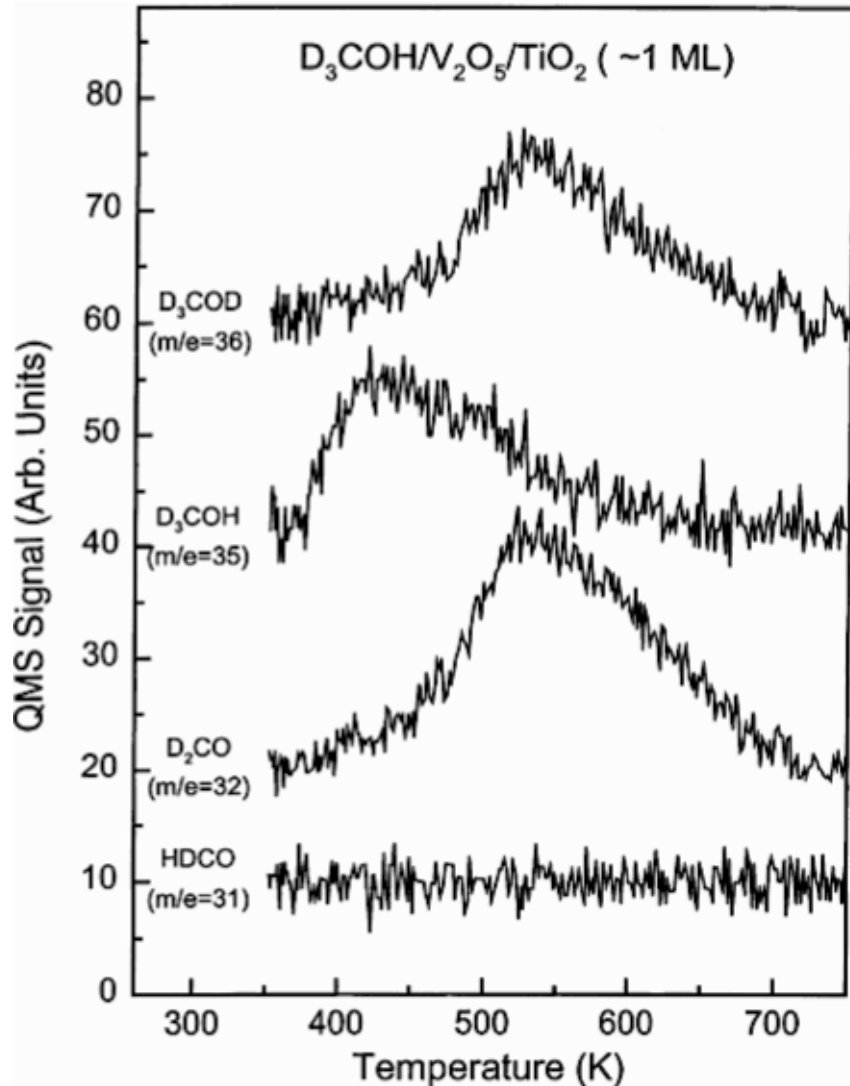


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# Isotopic exchange: additional info

## MeOH oxidation over $V_xO_y$ $TiO_2$ (110)



Acid-base active OD groups formed from abstraction of methyl deuterium: easy exchange with the acidic OH group of MeOH but the inverse reaction does not occur with the methyl hydrogens (much less reactive, not acid-base active)

Note the possible dependence on reaction conditions



# The Concept of TPRS

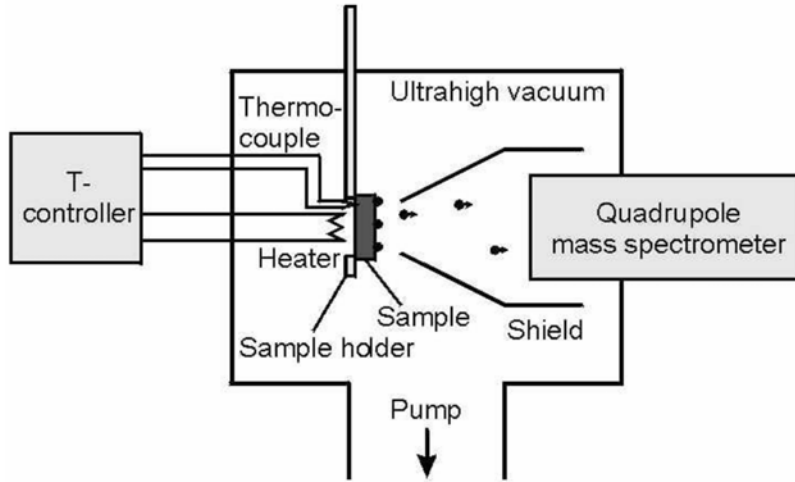
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- Low-pressure TPRS with reactive molecules
- Two modes:
  - multiple pulses: TAP
  - Co-adsorption and flash TDS: TPRS
  - Sub-mode: high-pressure reaction and TPRS with the educts (products) remaining at the surface after quench
- TPRS: observation of products and fragments of a surface reaction as function of temperature: main information: **co-incidence of products**
- Each peak in TPRS can be analyzed with all techniques known in TDS (many dimensions of quantitative information in principle accessible but rarely ever done).

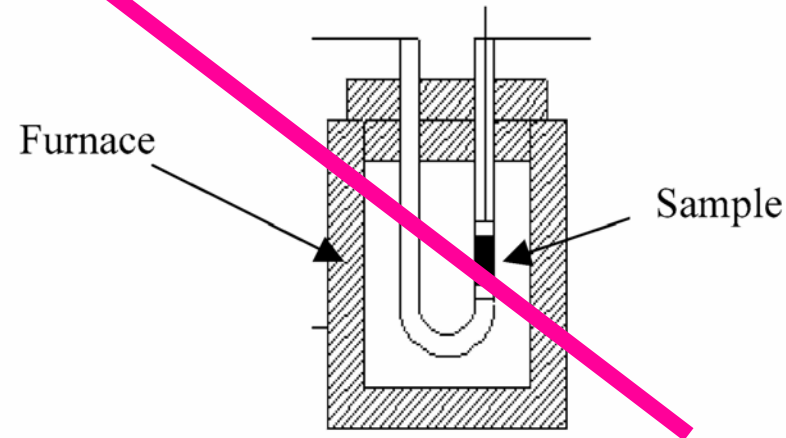


# Instrumentation and methodical limits

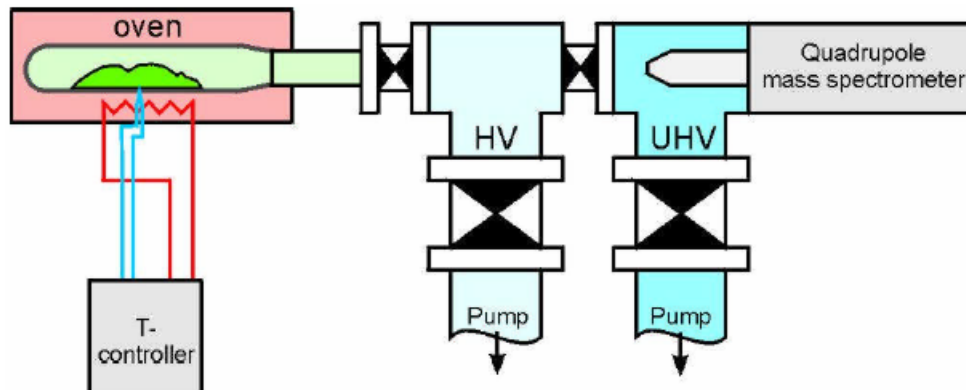
Typical TPD setup for single crystals or foils <sup>W. Ranke</sup>



continuous flow TPD reactor, operating under atmospheric pressure <sup>Kanervo et al</sup>



Typical TPD setup for powders <sup>W. Ranke</sup>



# Useful conditions for TPRS

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- Model systems are required to exclude problems of surface heterogeneity with respect to
  - Energetics (site types and distributions)
  - Transport (pores, diffusion)
- Real samples require careful parameter choice (thermal resistance, film diffusion) and transport modelling: maybe impossible with demanding reactions
- They cannot be used without concomitant model systems (at the appropriate pressures for material dynamics)



# Useful conditions for TPRS

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- The all-overriding issue is to avoid consecutive reactions by re-adsorption and thermal cracking: optimization of conditions is essential!!
- Use simple systems first and increase gradually the complexity of both reactant and surface



# Answers from TPRS

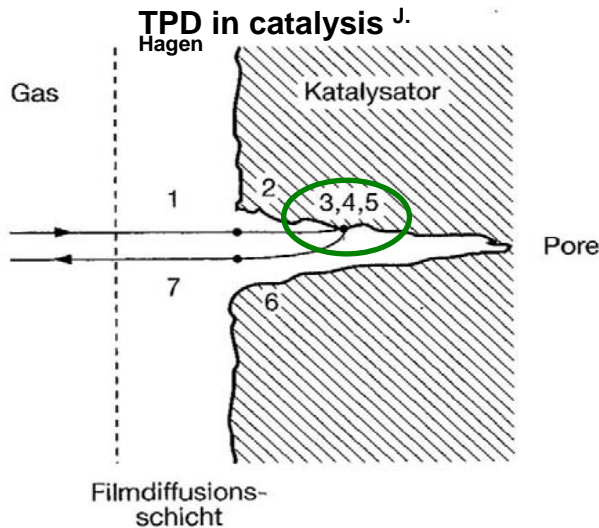
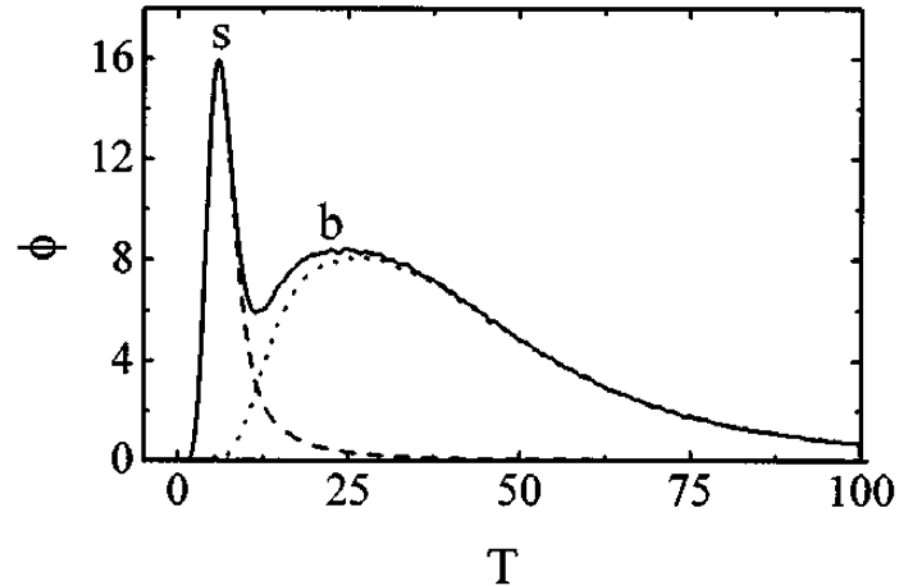
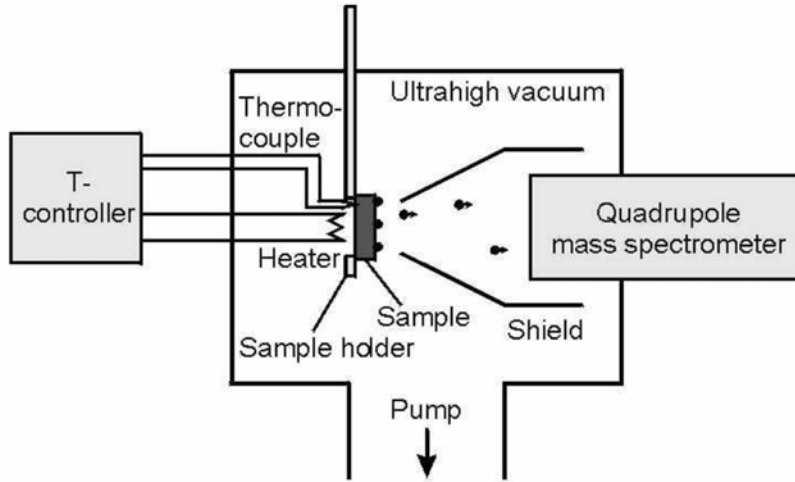
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- Possible reaction channels
- Kinetic parameters of all products (only for reversible processes)
- Structure-sensitivity
- Influence of pre-treatments (sub-surface species, compound formation) on reaction channels
- Mode of operation for consecutive processes



# Instrumentation and methodical limits

Typical TPD setup for single crystals or foils <sup>W. Ranke</sup>





# Main challenges

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- The method is very sensitive to the phenomenon of “kinetic gap”
  - Heating rate dependence of “desorption energy” (as in TDS)
  - Different surface diffusion processes for different products
  - Different strength of interaction of products from the same reaction with the surface
- The co-incidence is lost
- If this is folded with distribution of site properties (inhomogeneous surfaces) and superposition with transport: no more useful info
- Surface remnants! (TPRS with oxygen “TPO”)



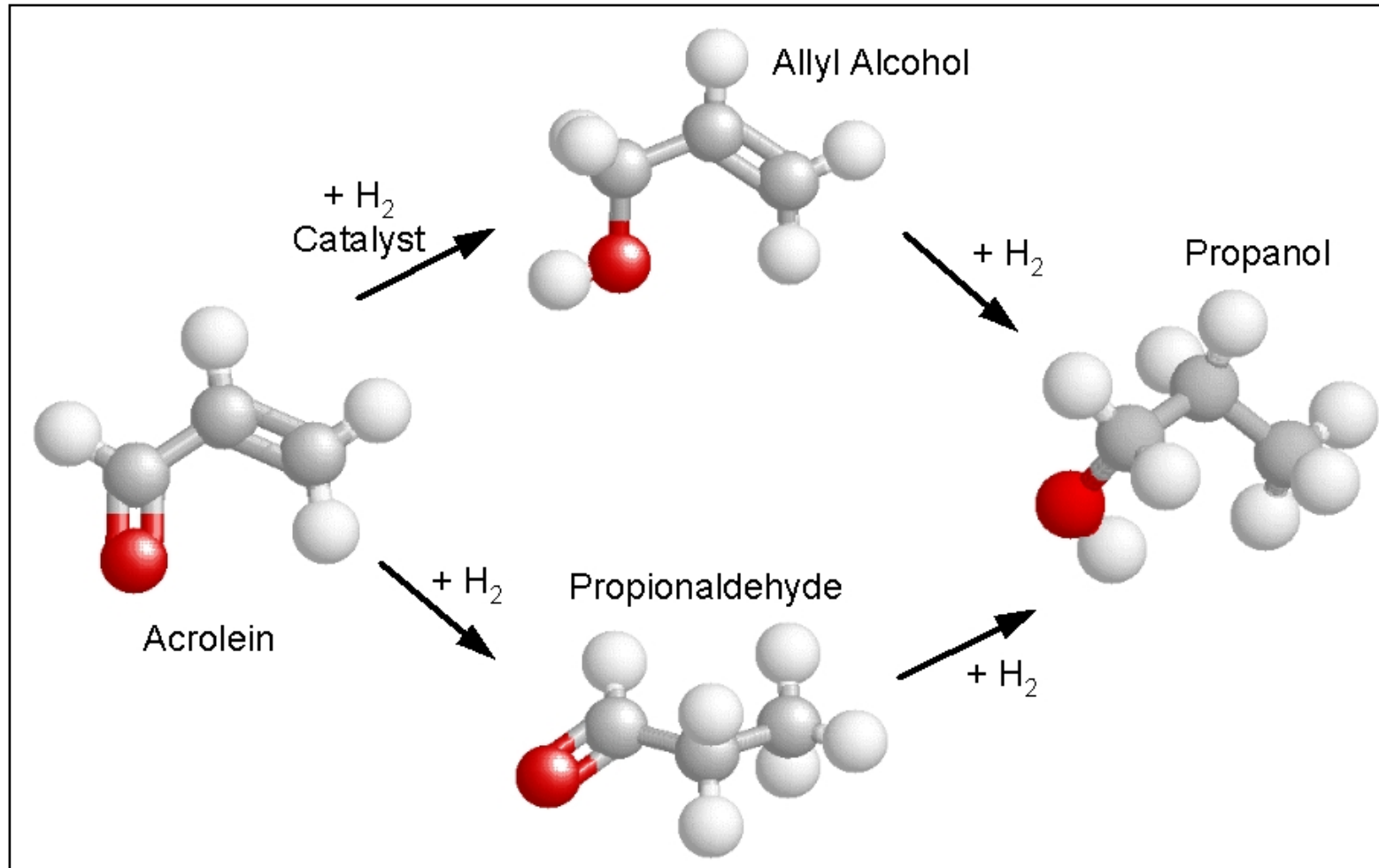
# Main challenges

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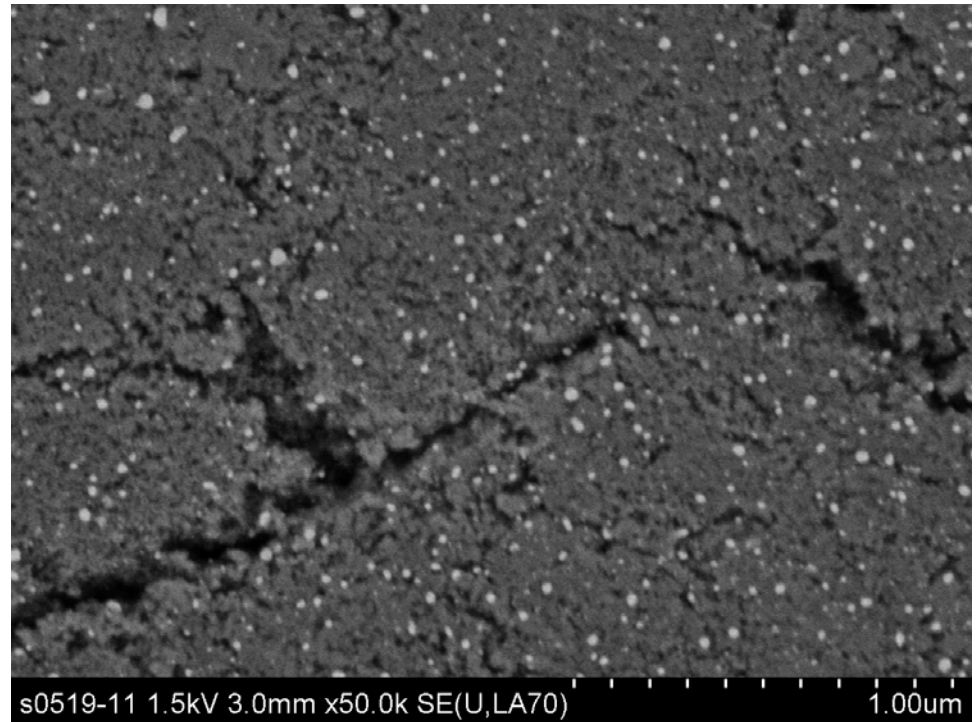
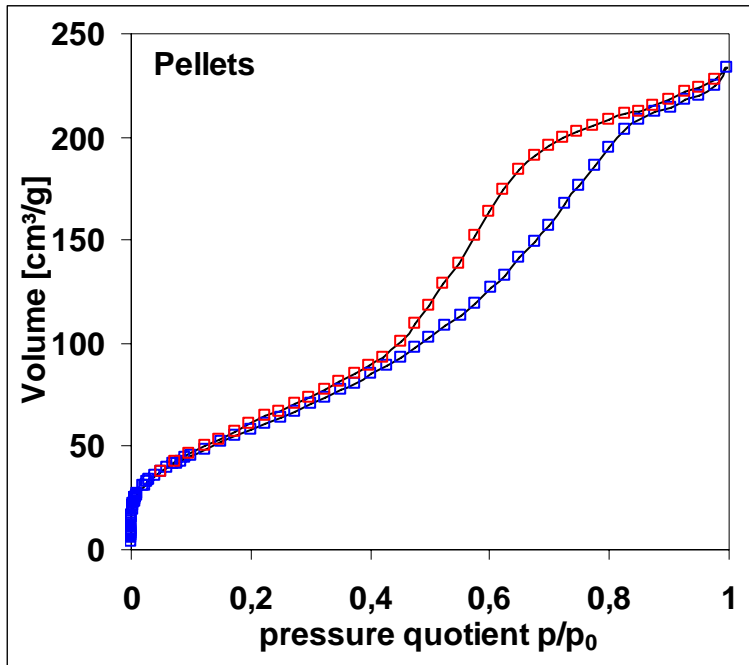
- Key problem: The temperature is varied during the observation and exceeds the reaction temperature for complete observation (desorption): irreversible modifications.
  - Cracking of products
  - Sub-surface compound formation
  - Opening of alternative reaction channels due to progressive desorption and change of spatial arrangements of adsorbates (example of acrolein on silver)
- Fast heating rates employed to be sensitive:
  - increase for complex molecules the kinetic gap
  - increase thermal burden on sensitive molecules (no real product as consequence of unintended post synthetic analytical follow-up reaction): no problem in CO oxidation and decomposition reactions



# A real-world problem (B. Steinhauer)



# A real-world problem (B. Steinhauer)



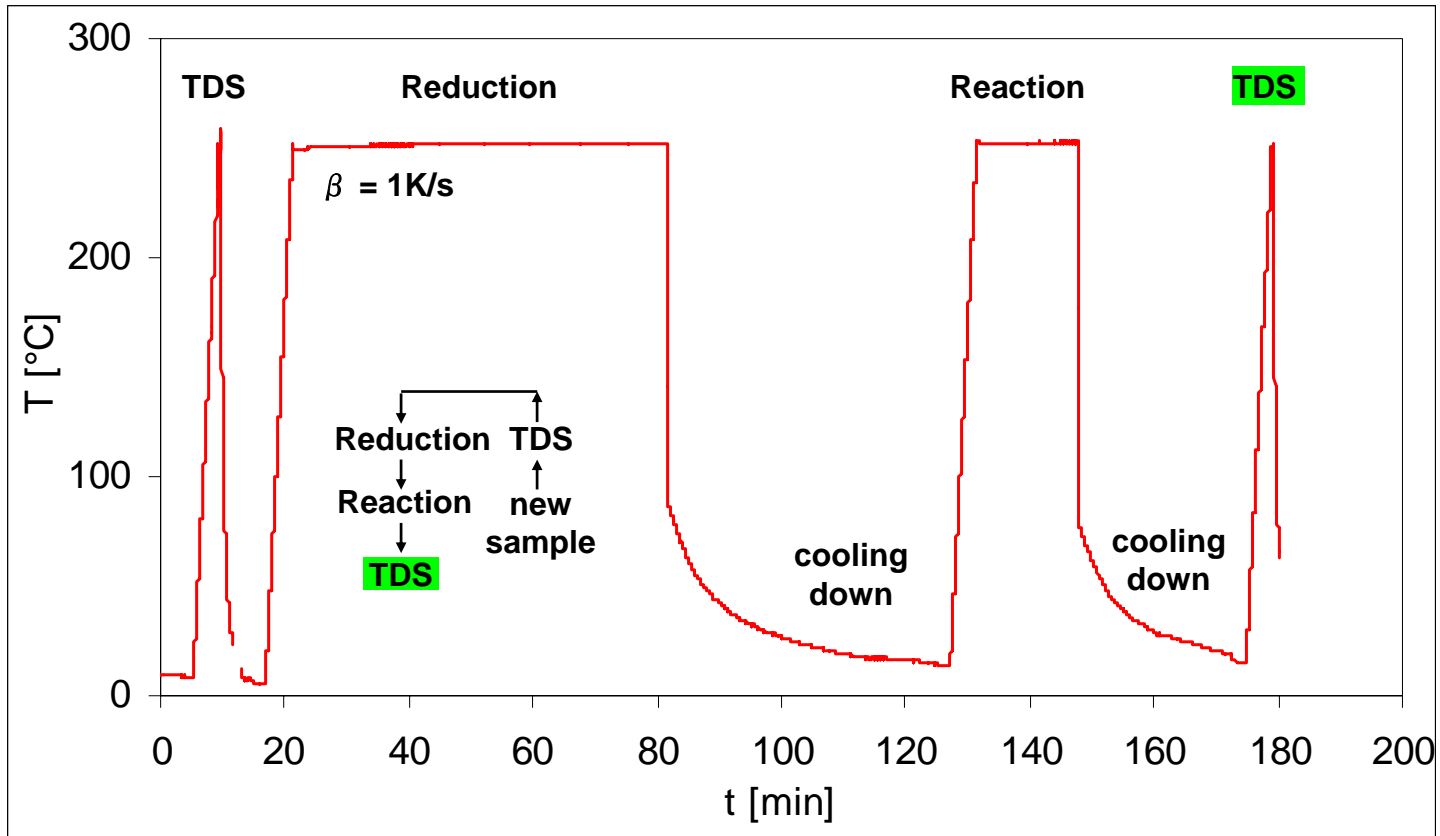
Bi-modal pore size distribution:  
Micropores as effective diffusion limiters



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# A real-world problem (B. Steinhauer)



Temperature profile of a total experiment

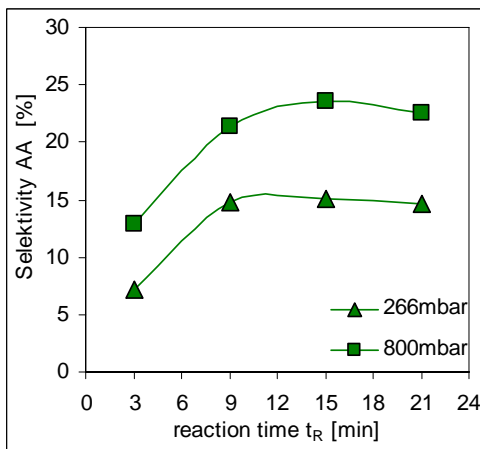
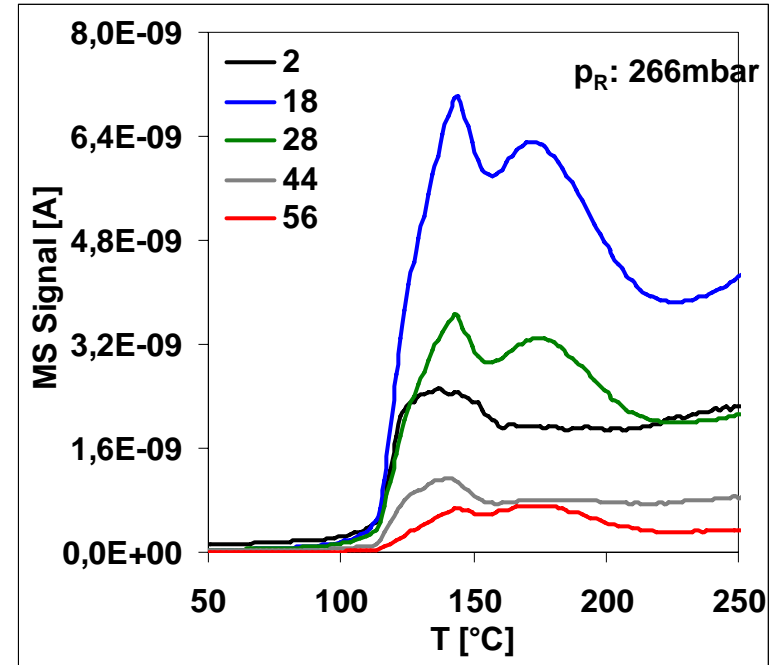
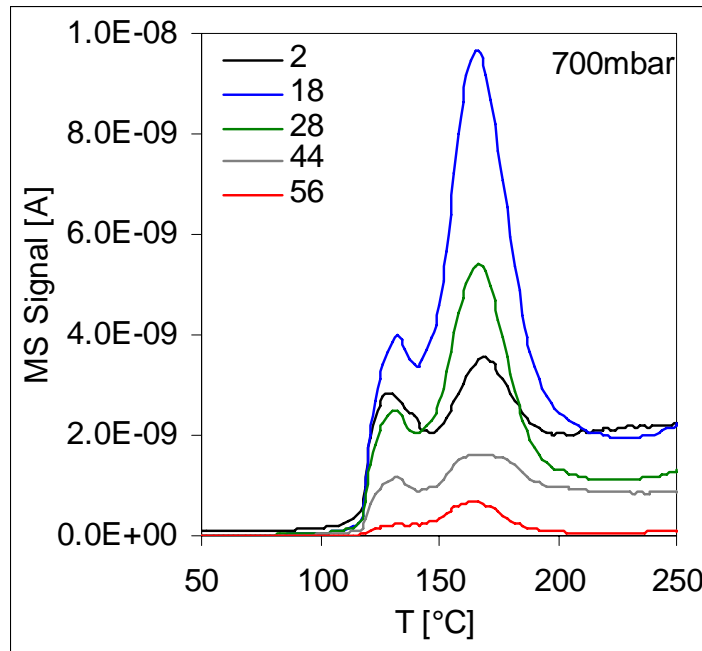
The real world adsorption cycle



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# A real-world problem (B. Steinhauer)



Is selectivity only a quantitative (kinetic) effect or are there differences in the reactivity of active sites? (site blocking by polymer products)



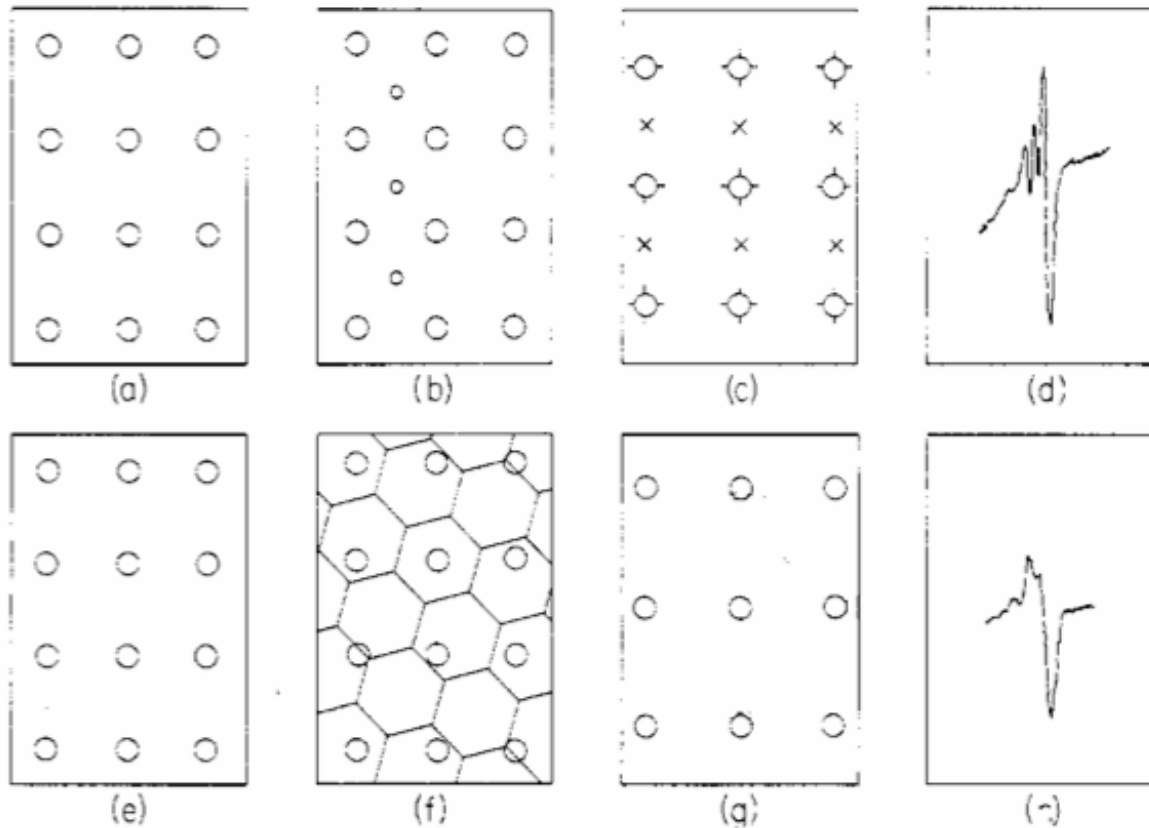
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The classic example:  
Ni (110) in formic acid decomposition

A consistent piece of surface  
science elucidating principles of  
heterogeneous reactions



# Ni (110) a model case (Madix 1979, Acc Chem. Res.)

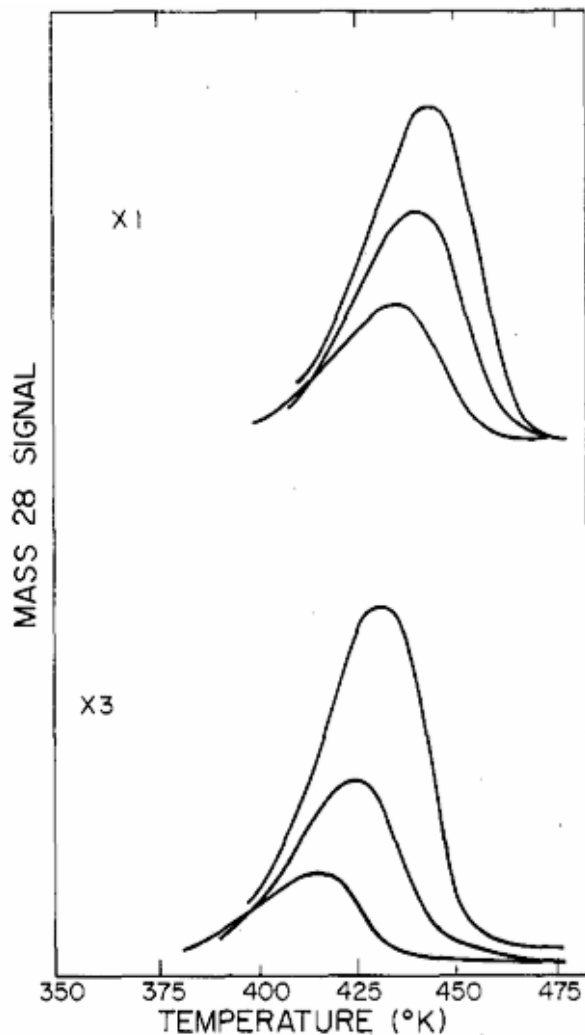


Structures of clean (a, e) and carbide (b-d) or graphite (f-h) precovered surfaces





# Ni (110) a model case (Madix 1979, Acc Chem. Res.)

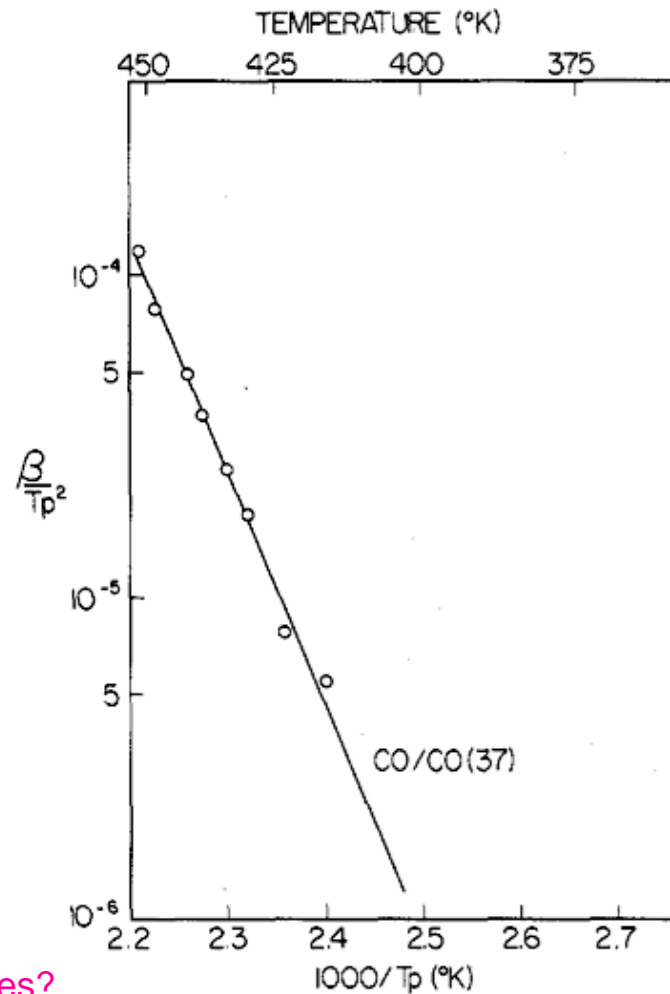


CO TDS with varying heating rates:

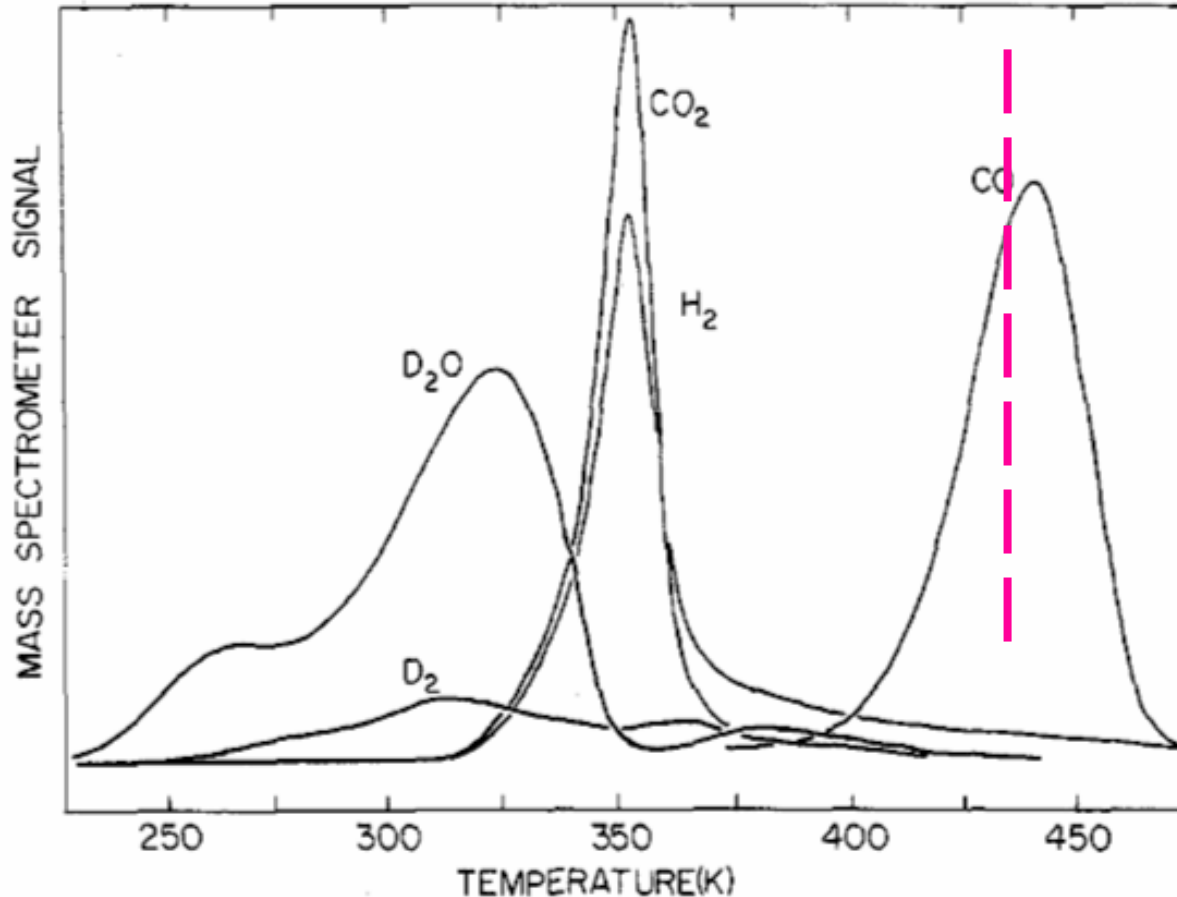
First order reaction, high  $E_a$  (37kcal/mol)

High preexp. factor of  $10^{15}$  said to be due to high mobility of the desorbing transition state

How well compare absolute T and heating rates?  
Think about heat transfer!



# Ni (110) a model case (Madix 1979, Acc Chem. Res.)



CO TDS

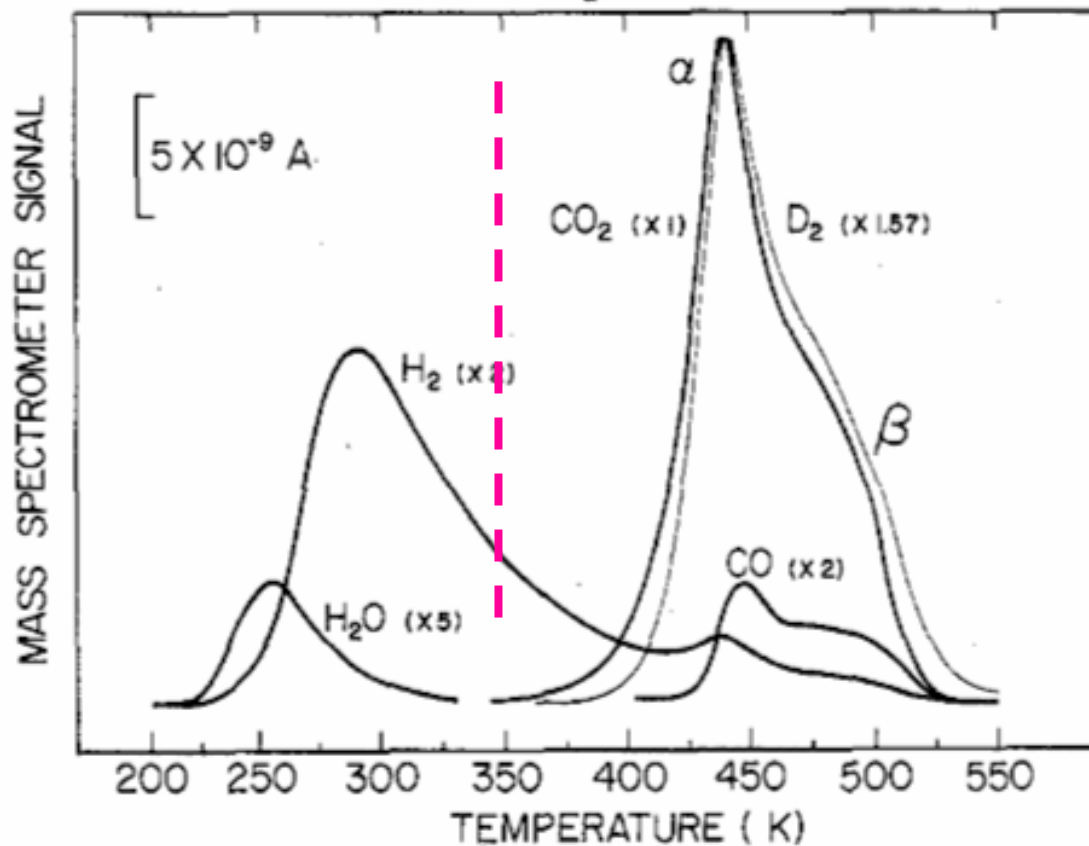
Formic acid decomposition over clean Ni: the desorption of CO is controlled by its adsorbate bonding and not by its appearance energy



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# Ni (110) a model case (Madix 1979, Acc Chem. Res.)



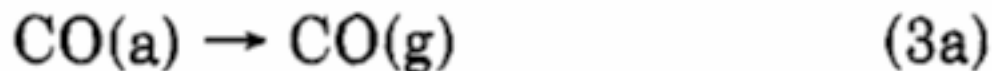
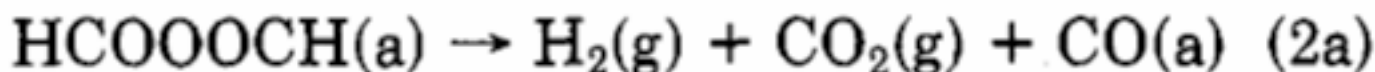
Formic acid decomposition over carbided Ni: the desorption of CO is controlled by its appearance energy: note the change of position of the hydrogen-deuterium peaks



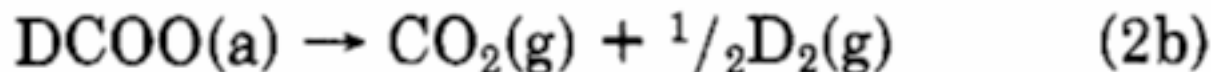
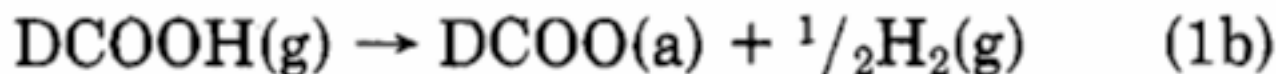
# Ni (110) a model case (Madix 1979, Acc Chem. Res.)

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## Mechanism A



## Mechanism B



(13) J. G. McCarty, J. Falconer, and R. J. Madix, *J. Catal.*, **30**, 235 (1973).



# Ni (110) a model case (Madix 1979, Acc Chem. Res.)

surface	$E_{app}$ , kcal/ mol	$A_{app}$ , $s^{-1}$	$T_p$ , K	intermediate
Ni(110) (clean)	26.6	$2 \times 10^{15}$	$\sim 370$	anhydride
Ni(110) ( $2 \times 1$ )C	25.5	$5 \times 10^{12}$	$\sim 430$	HCOO
Ni(110)O	N.D.	N.D.	$\sim 440$	HCOO
Cu/Ni(110)- (65/35)	27.6	N.D.	$\sim 400$	HCOO
Cu(110)	31.9	$1 \times 10^{14}$	$\sim 475$	HCOO

Anhydride

Formate



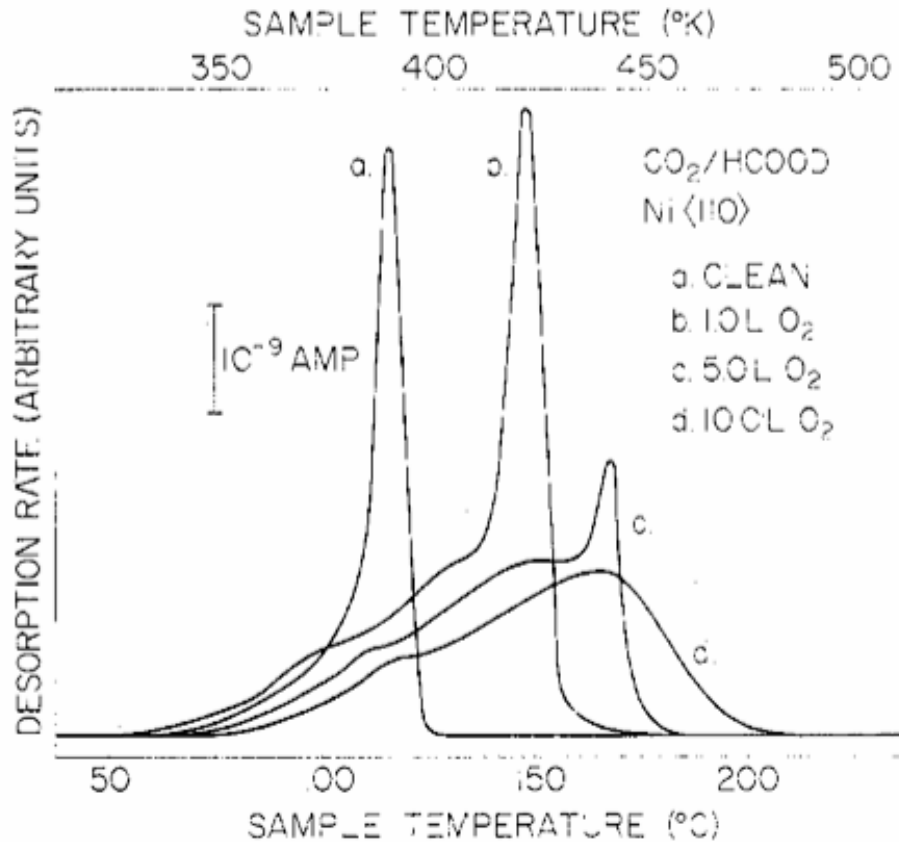
# Ni (110) a model case (Madix 1979, Acc Chem. Res.)

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- TPRS has shown the structure-sensitivity of the formic acid decomposition in probing the surface state of Ni: structural dynamics found already in 1979
- An acid anhydride as complex surface species was postulated and identified by its decomposition products
- Perfect use of isotope labelling for mechanism discrimination



# Ni (110) a model case (Madix 1979, Acc Chem. Res.)



need for additional characterizations; sub-surface identification problem

Oxygen pre-coverage creates adsorbates and oxide phases



# Ni (110) a model case (Madix 1979, Acc Chem. Res.)

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- The co-adsorption of oxygen causes two effects:
  - Change of energetics of the process of clean metal (modification of the Ni surface)
  - Opening of a novel reaction channel (combustion without cleavage of C-H, low energy, oxygen diffusion-controlled)
- TPRS as a very sensitive yet indirect tool probing surface states (oxidation state)





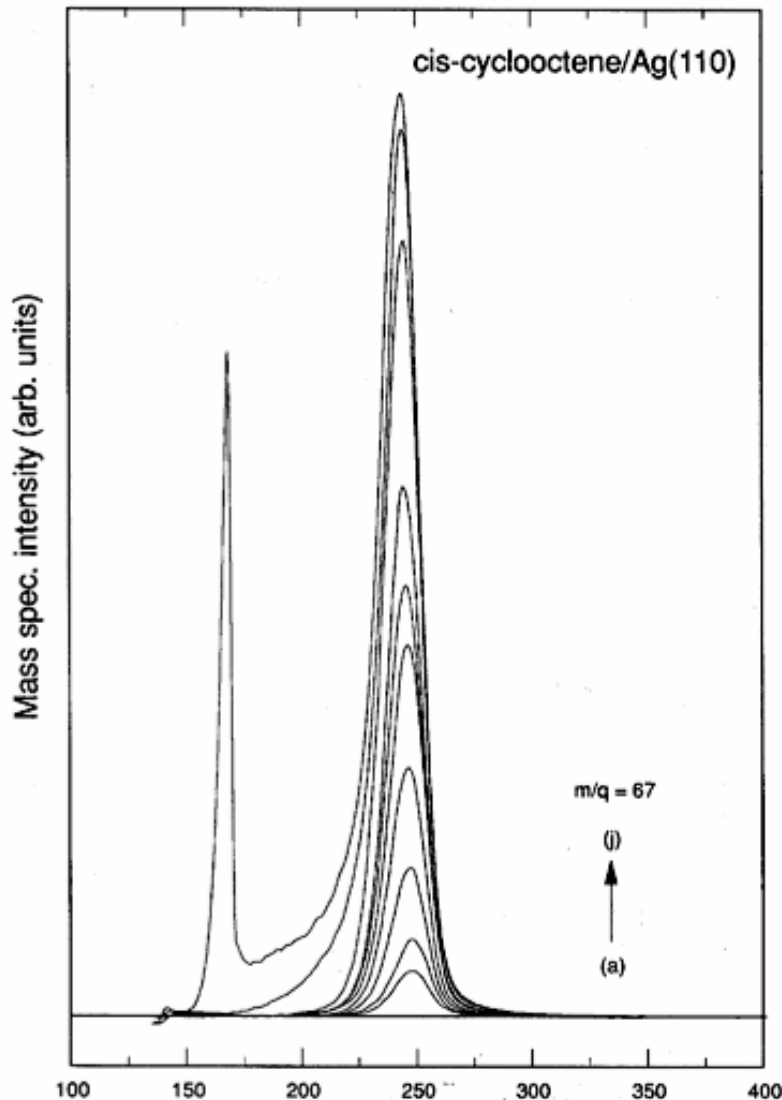
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# Ag (110) in oxidative dehydrogenation of cycloalkenes

A case with a complex substrate



# Ag (110) and cyclo-octenes (R.J. Madix et al Surf. Sci., 1996)



Clean unimolecular substrate interaction, no intermolecular interaction, no residues

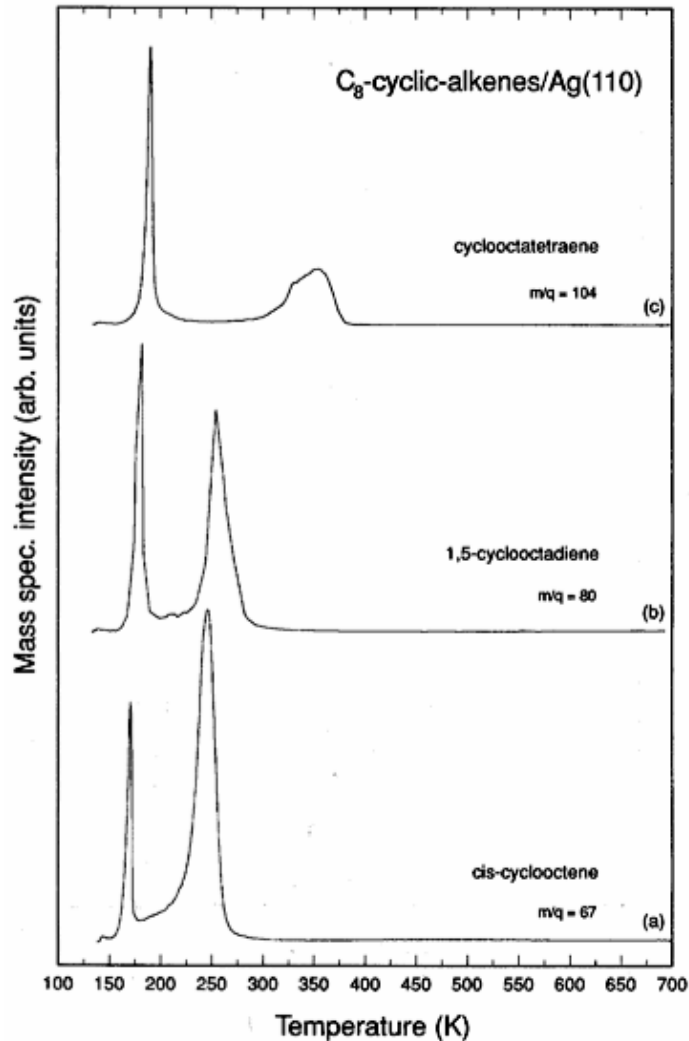
$E_a$  ca. 17 kcal/mole (method dependent), formal reaction order about 1.2 from leading edge analysis



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# Ag (110) and cyclo-octenes (R.J. Madix et al Surf. Sci., 1996)



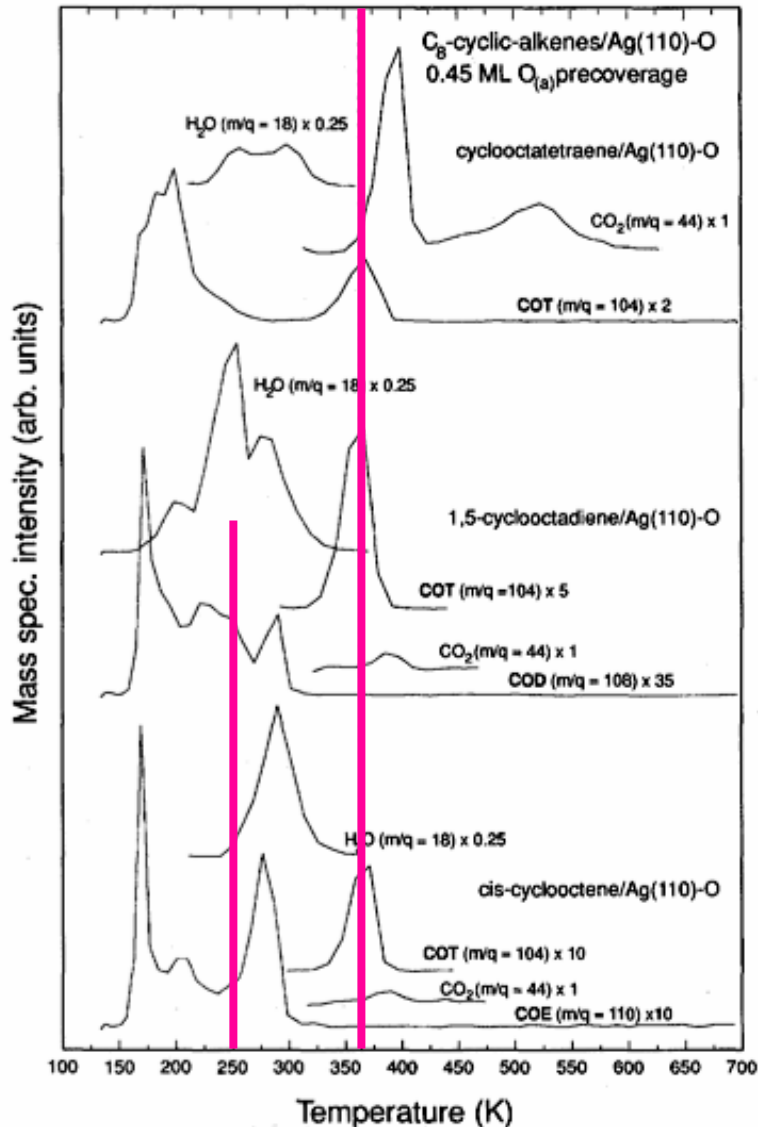
No differences for the mono- and di-olefin

A major difference for the tetra-olefin:

Reaction order 1.6,  $E_a$  23 kcal/mol, strongly coverage dependent, residues (TPO), multiple interactions with substrate (mono- and di-bridged)



# Ag (110) and cyclo-octenes (R.J. Madix et al Surf. Sci., 1996)



Strong modification of desorption and reaction due to oxygen pre-coverage

Oxidative dehydrogenation (water as by-product) and total combustion occur.

From integration it becomes clear that strong polymerisation with carbon residues is also occurring (not visible in data, would become evident when TPO were performed)



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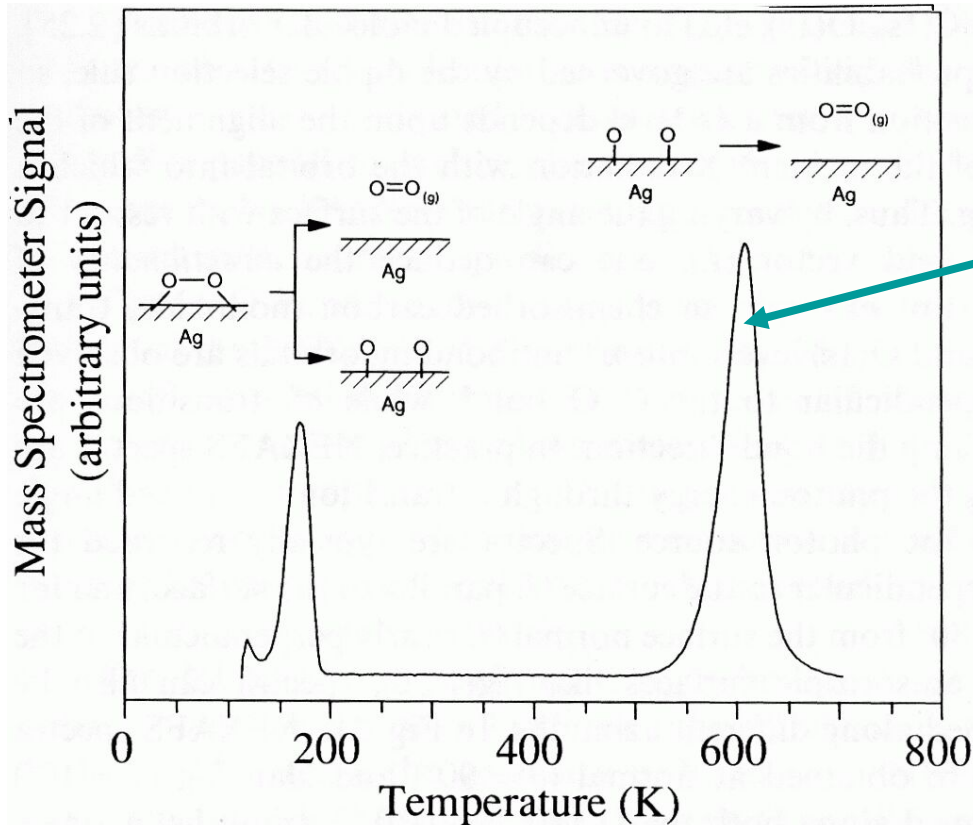
# Ag and “pre-adsorbed” oxygen: a complex ongoing story

Methanol oxidation as pertinent test reaction  
(runs almost to completion) with technical  
relevance (BASF process for formaldehyde):

Ethylene oxidation (also technical) as  
reaction complement



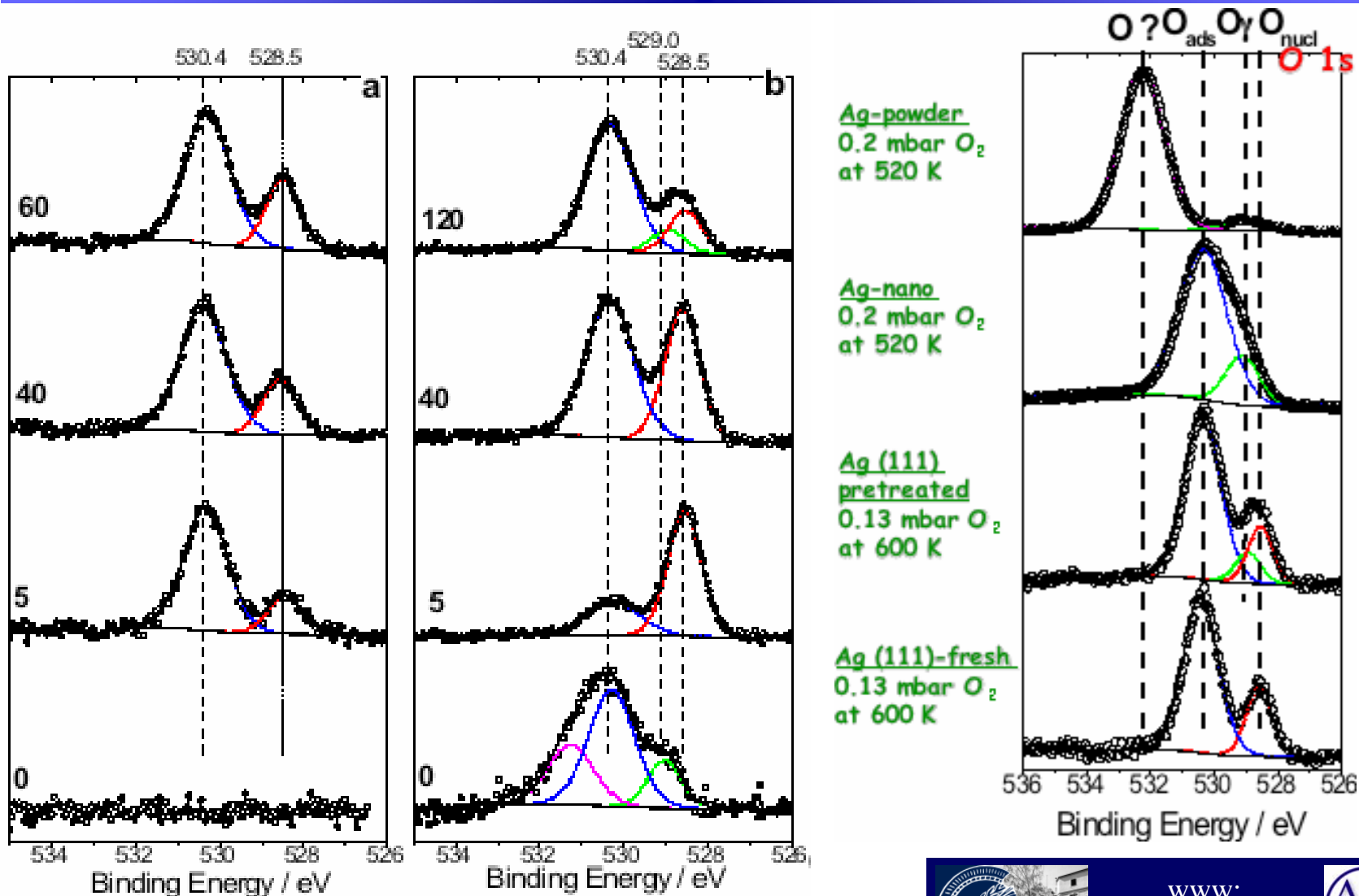
# Oxidative Dehydrogenation of Methanol over Ag



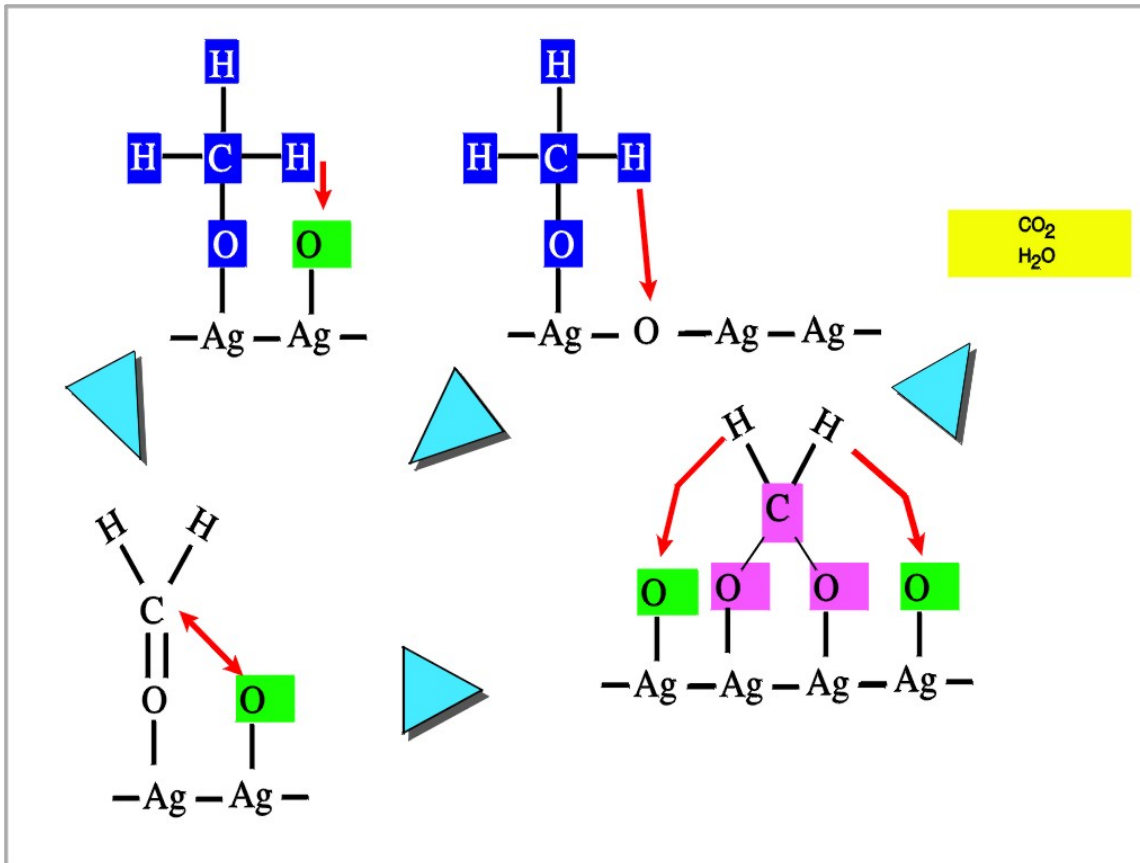
Surface science model experiments identify one chemically active atomic oxygen species

Assigning, however several chemical functions to the same species (acid-base vs. oxidative)

# Dynamics: AgO (gaps)



# Ag-O: mode of action: MeOH



Surface abundance of alpha oxygen (green) is detrimental for selectivity

Alpha oxygen is required to form other atomic oxygen species:

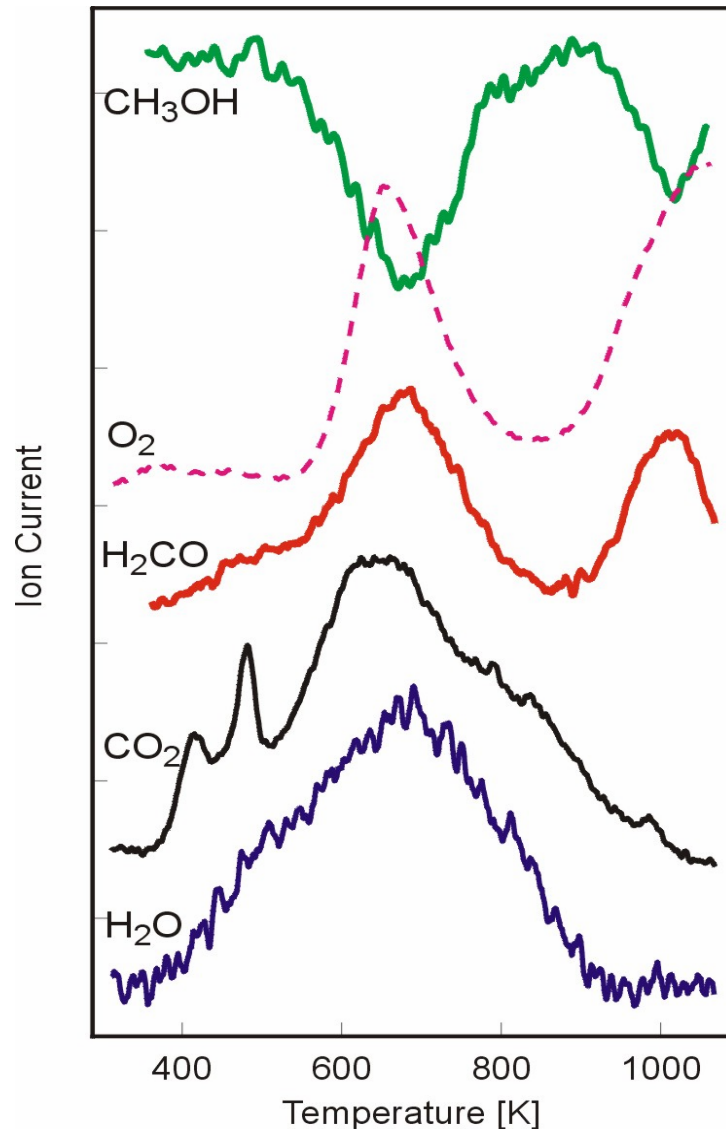
Site separation?





# TPRS of methanol oxidation

Tegtmeier et al., Catal Lett., 1991



There are clearly two reaction pathways for MeOH oxidation with differing selectivities

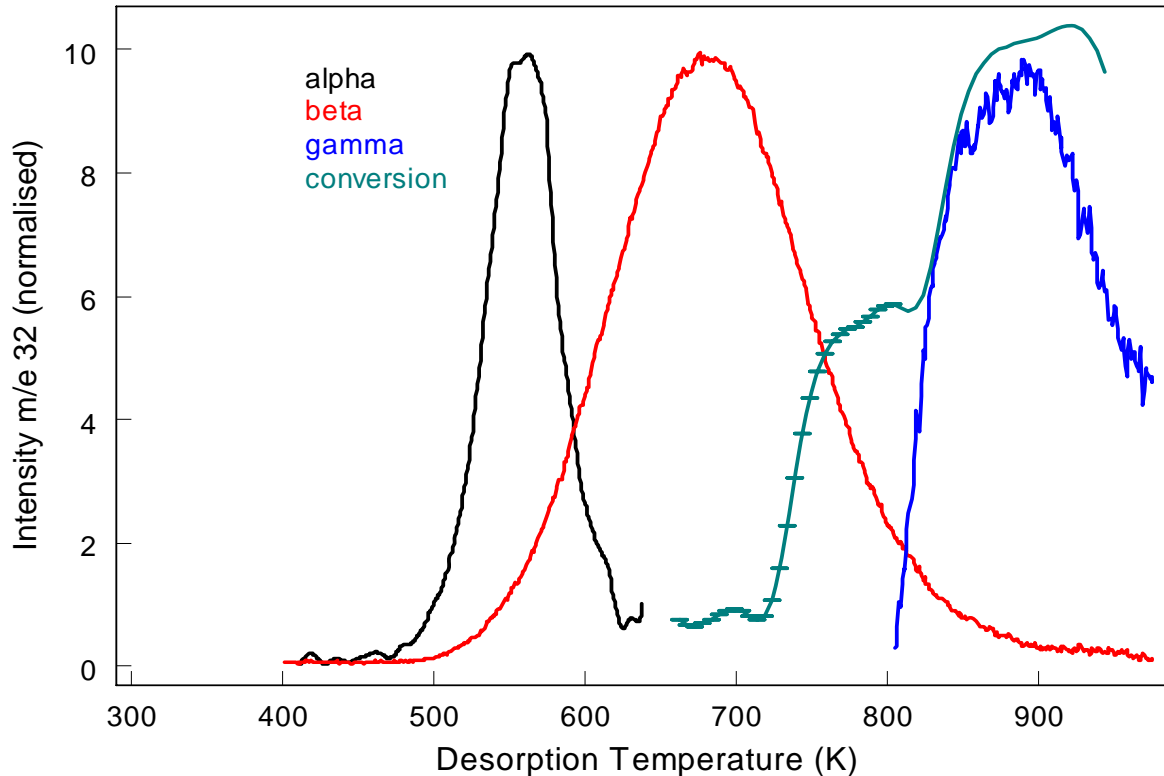
Electrolytic silver pre-dosing with 100 mbar oxygen at 873 K for 5 min in MeOH at  $10^{-5}$  mbar



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# Ag-O: speciation for methanol oxidation by TDS

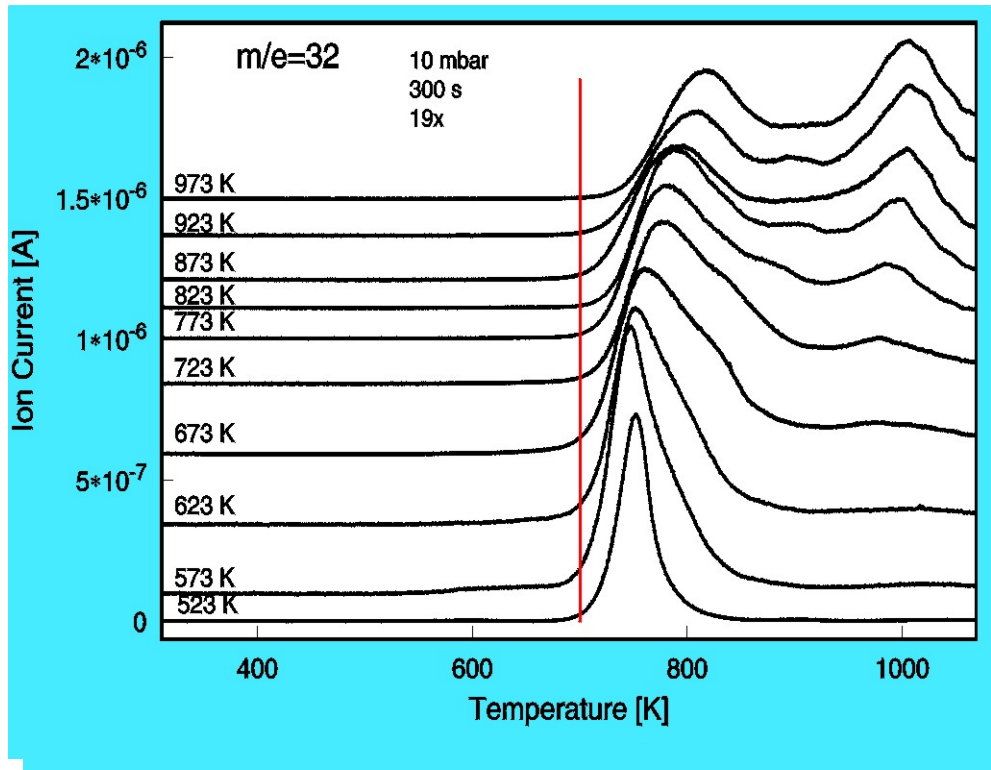


TDS allows isolating 3 different atomic oxygen species

Catalyst conversion coincides not with the „surface atomic“ oxygen species



# Ag-O: solid state transformation in TDS



Note the changes in ordinate scale!

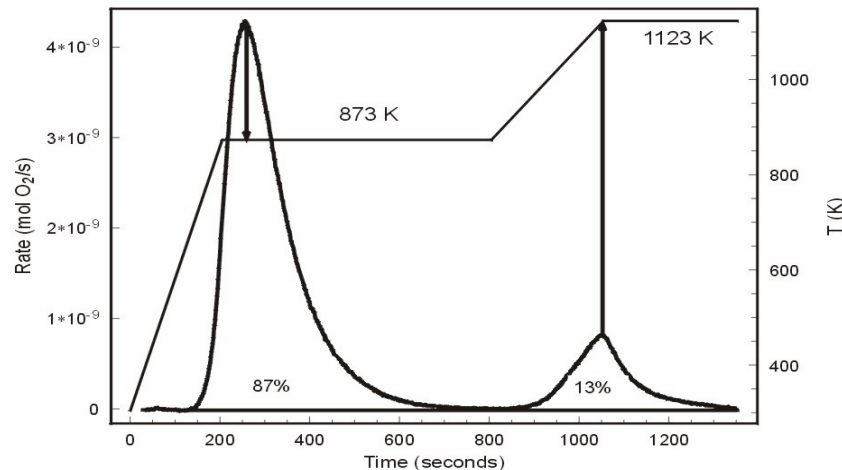
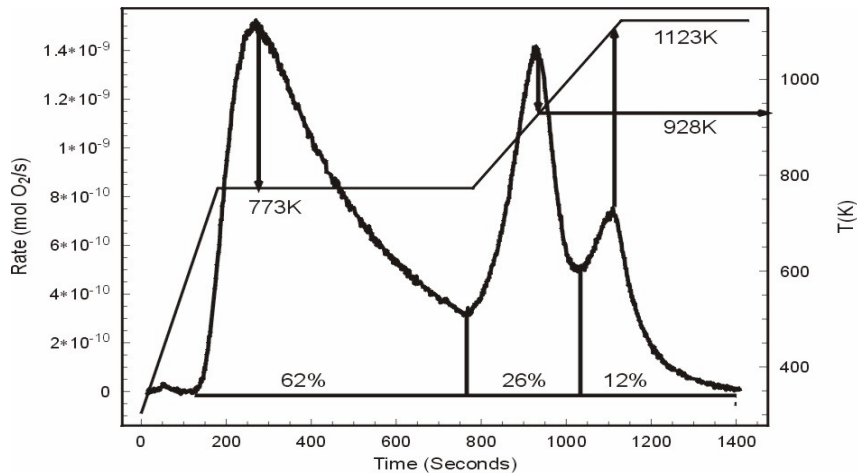
multiple experimental series are required to obtain characteristic desorption traces

high-pressure dosing and cyclisation essential,

little effect in static experiments



# The non-equilibrium nature Nagy et al 1996



The identification of bulk dissolved and surface-embedded oxygen depends critically on the conditions of TDS (2.5 K/s)

Electrolytic silver

pre-dosing with 100 mbar oxygen at 873 K for 5 min

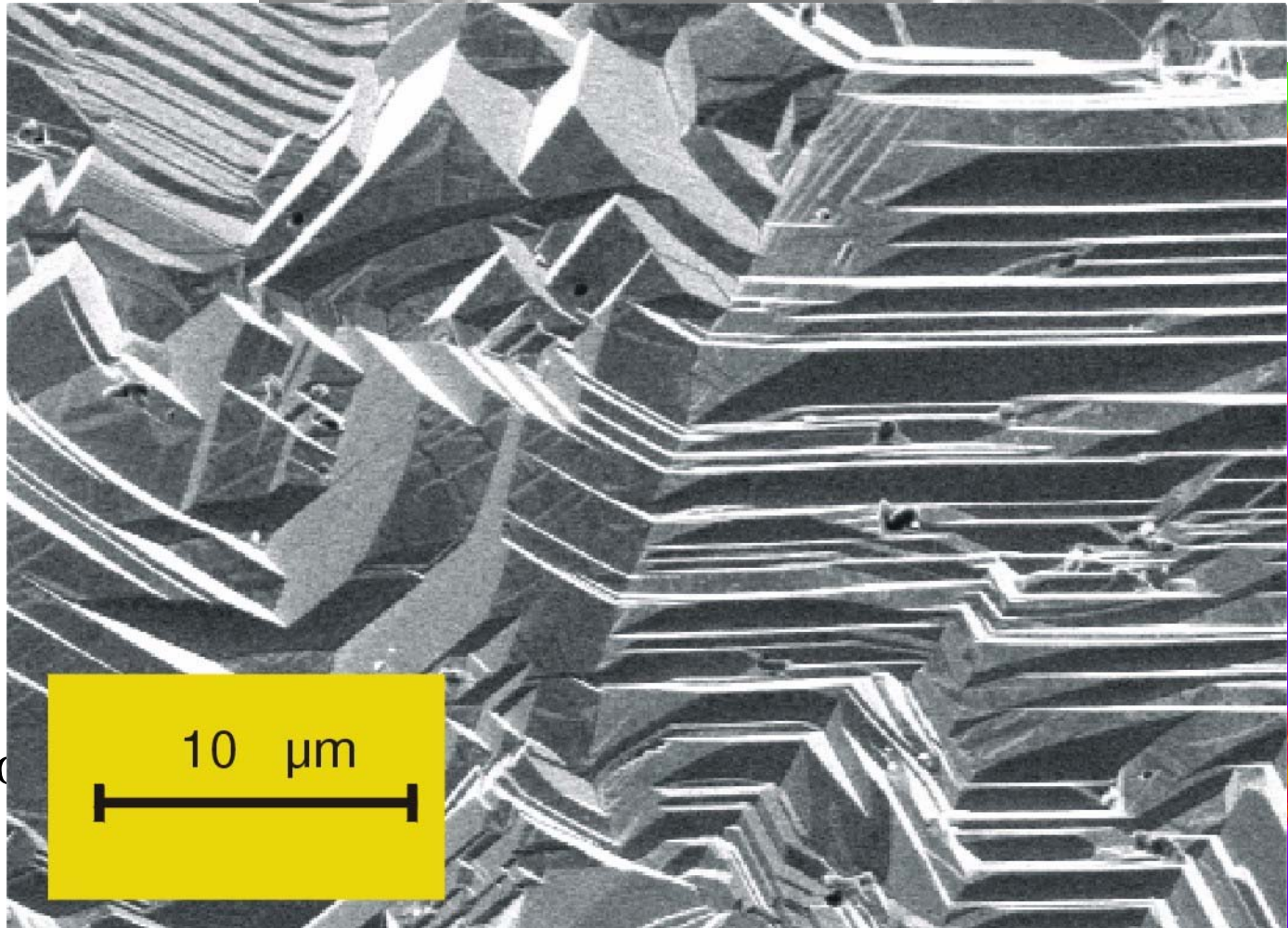


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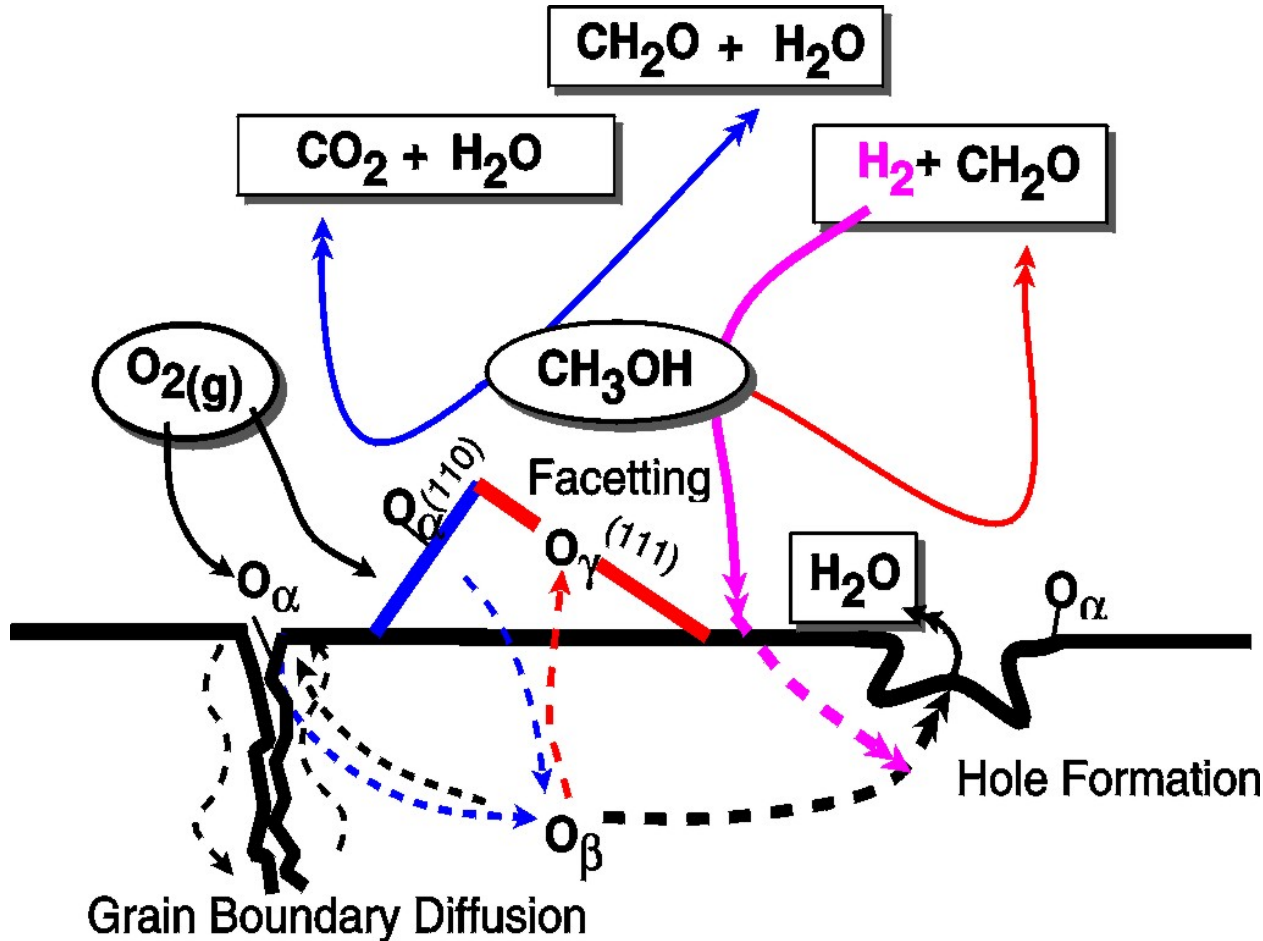


# The non-equilibrium nature



Facetting  
in oxygen  
under reactive  
conditions

# Ag-O: a dynamic system

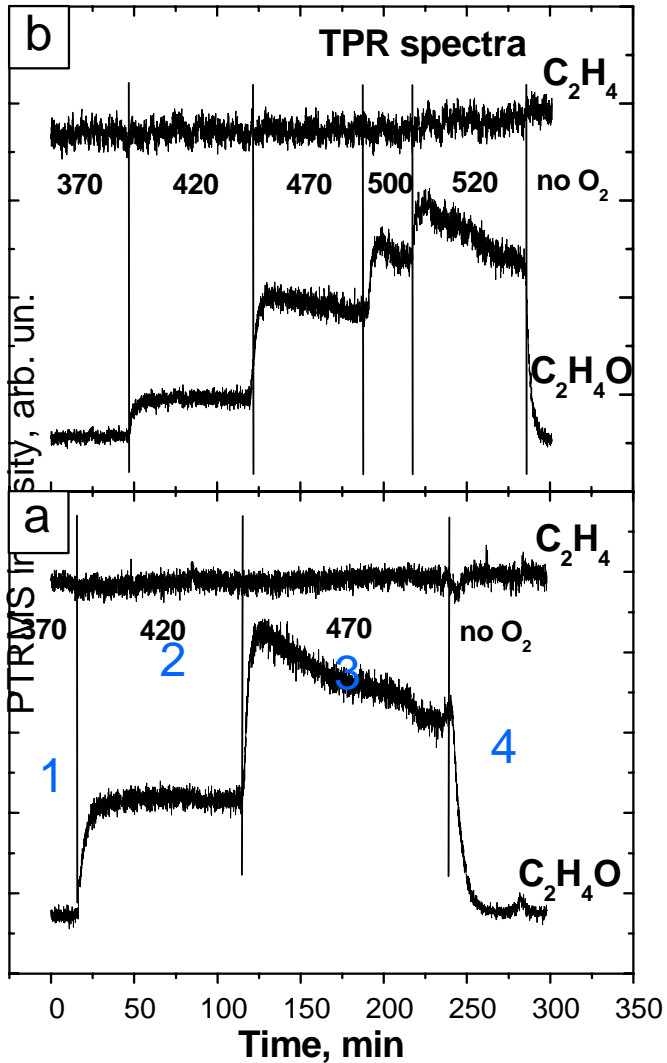


situation at above  
573 K and 1 mbar  
oxygen pressure

steady state  
depends  
critically on  
defect density

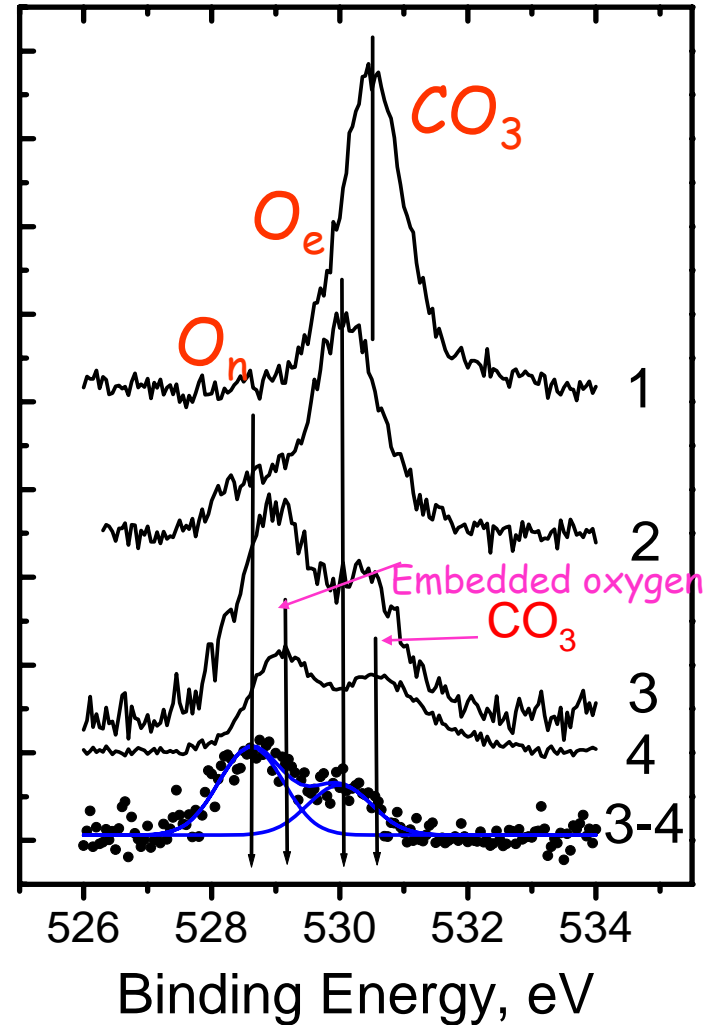


# Ethylene Epoxidation over Ag



a)  $p(C_2H_4) = 0.1$  mbar,  $p(O_2) = 0.25$  mbar  
 b)  $p(C_2H_4) = 0.24$  mbar,  $p(O_2) = 0.25$  mbar

$O_{1s}$  signal, arb.un.

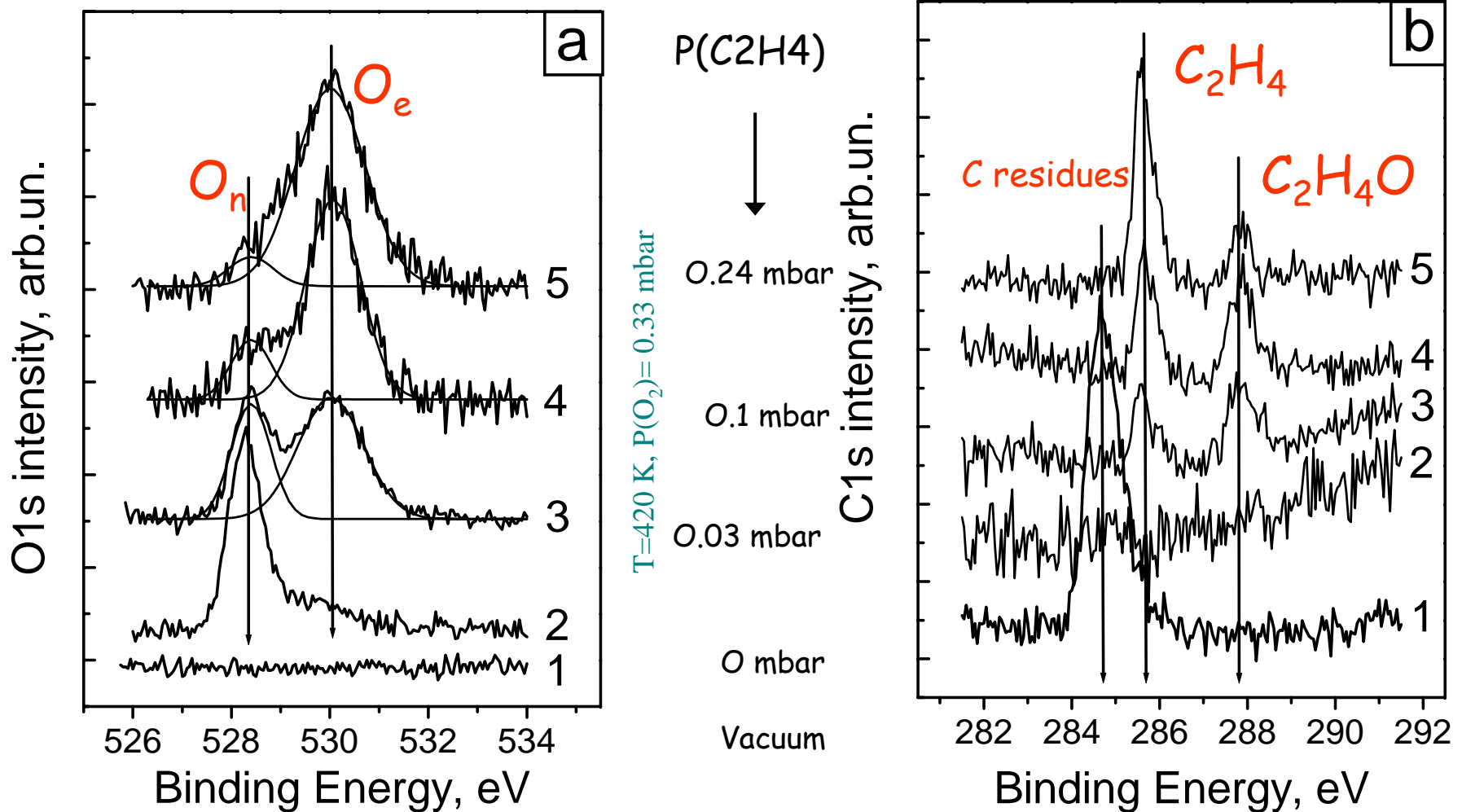


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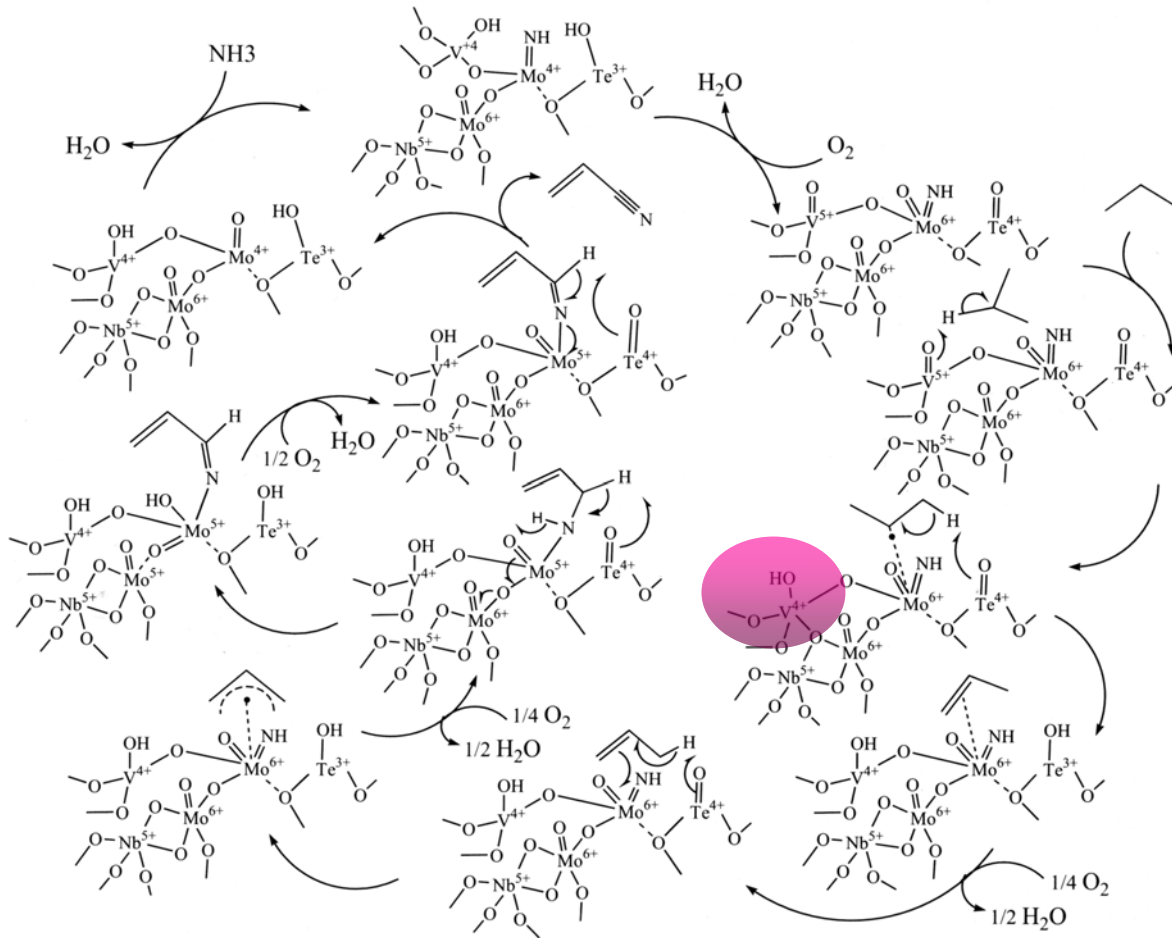




# Formation of Active Species



# The heterogeneous analogy



Some critical intermediates and the configuration of the active sites were found **to be not impossible** from isolated but high level quantum chemical calculation: By far too complex for any rigorous treatment, active sites not identified

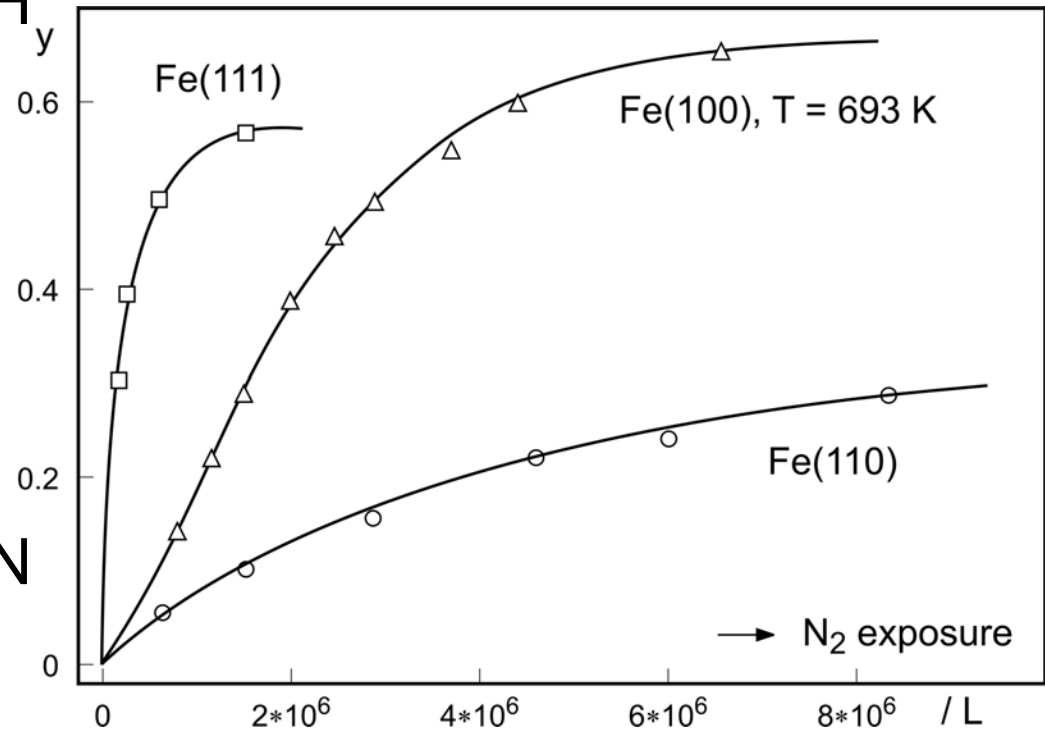
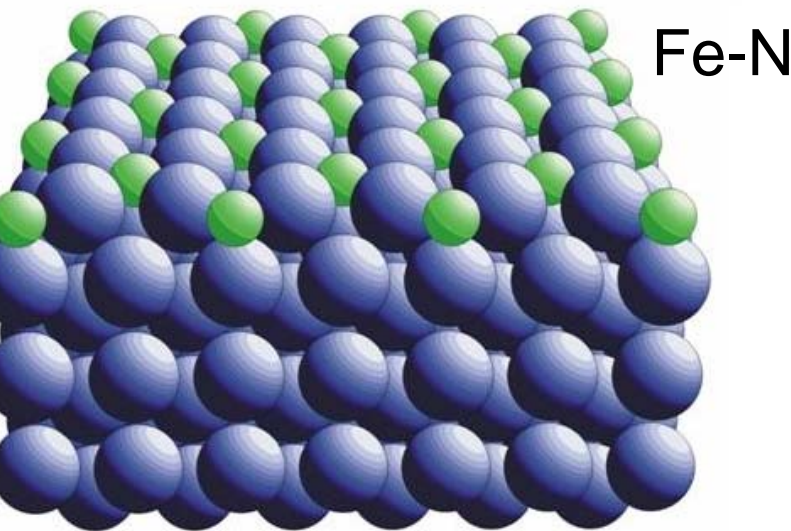
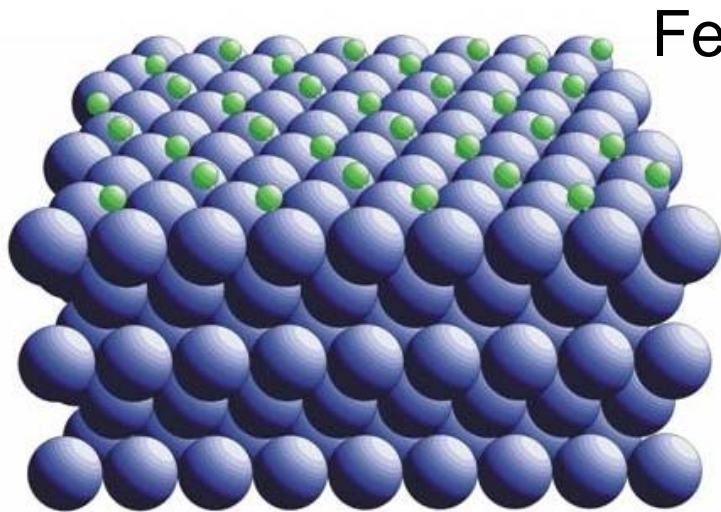
Grasselli, Goddard et al



www:  
fhi-berlin.mpg.de



# Surface science and ammonia synthesis



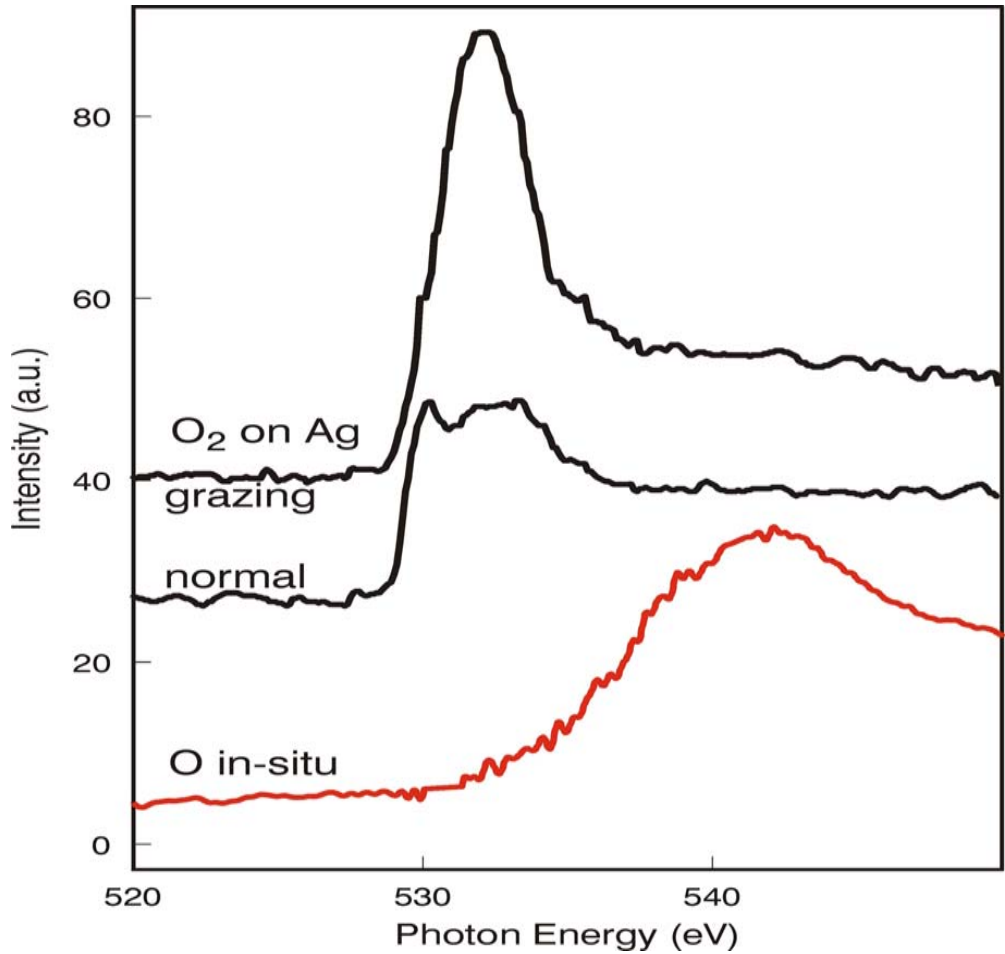
Low pressure static data



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# Electrophilic Oxygen is no peroxide



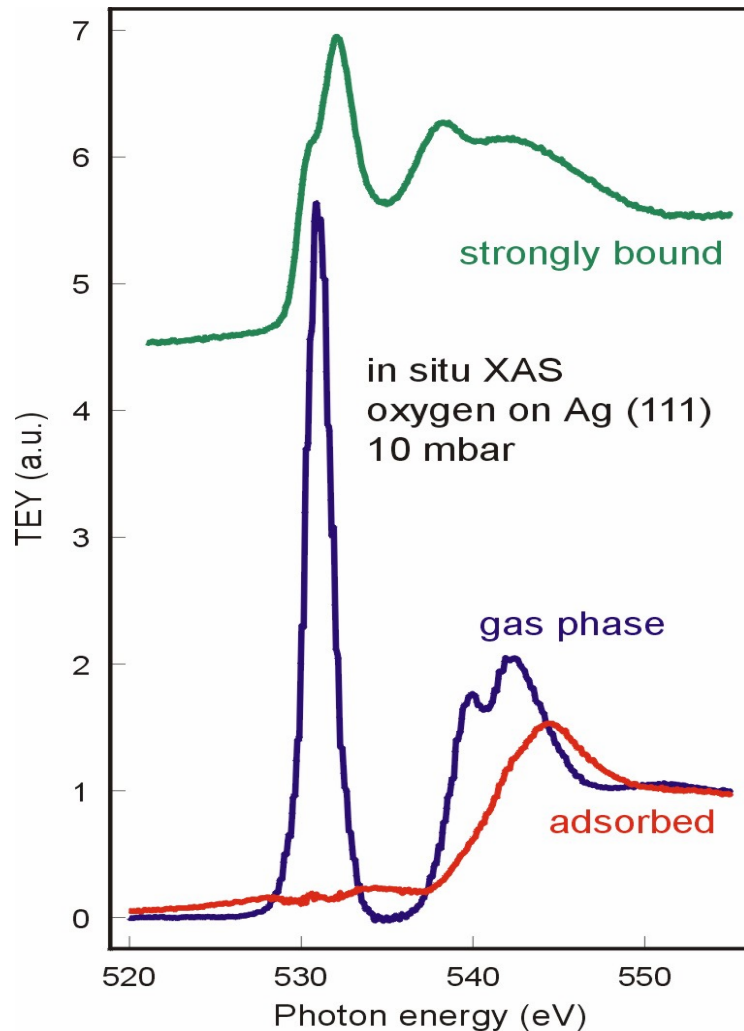
In-situ NEXAFS at 0.2 mbar ethylene/oxygen mixture

Comparison to low-T adsorbed molecular oxygen on Ag (111)

Electrophilic oxygen is atomic in nature as no O-O sigma\* resonance

Reference: J. Pawela-Crew, R.J. Madix, J. Stöhr, Surf. Sci., 339, (1995), 23

# Speciation of weakly bound oxygen



Only in the presence of a gas phase of ethylene and oxygen an additional atomic species without any Ag -d band interaction is found.

Pumping off to  $10^{-1}$  mbar removes this species which produces ethylene oxide

