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# The relation between model and real systems in heterogeneous catalysis research

Just for curiosity or more?

R. Schlögl, FHI, Berlin



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# Overview

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- Why catalysis?  
The relevance of catalysis in chemistry, justification of a large scale effort
- Why models in catalysis?  
The complexity issue, justification of the reductionistic approach
- What models in catalysis?  
Surface science is not the only model strategy required



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# Why catalysis?

The relevance of catalysis in chemistry, justification of a large scale effort



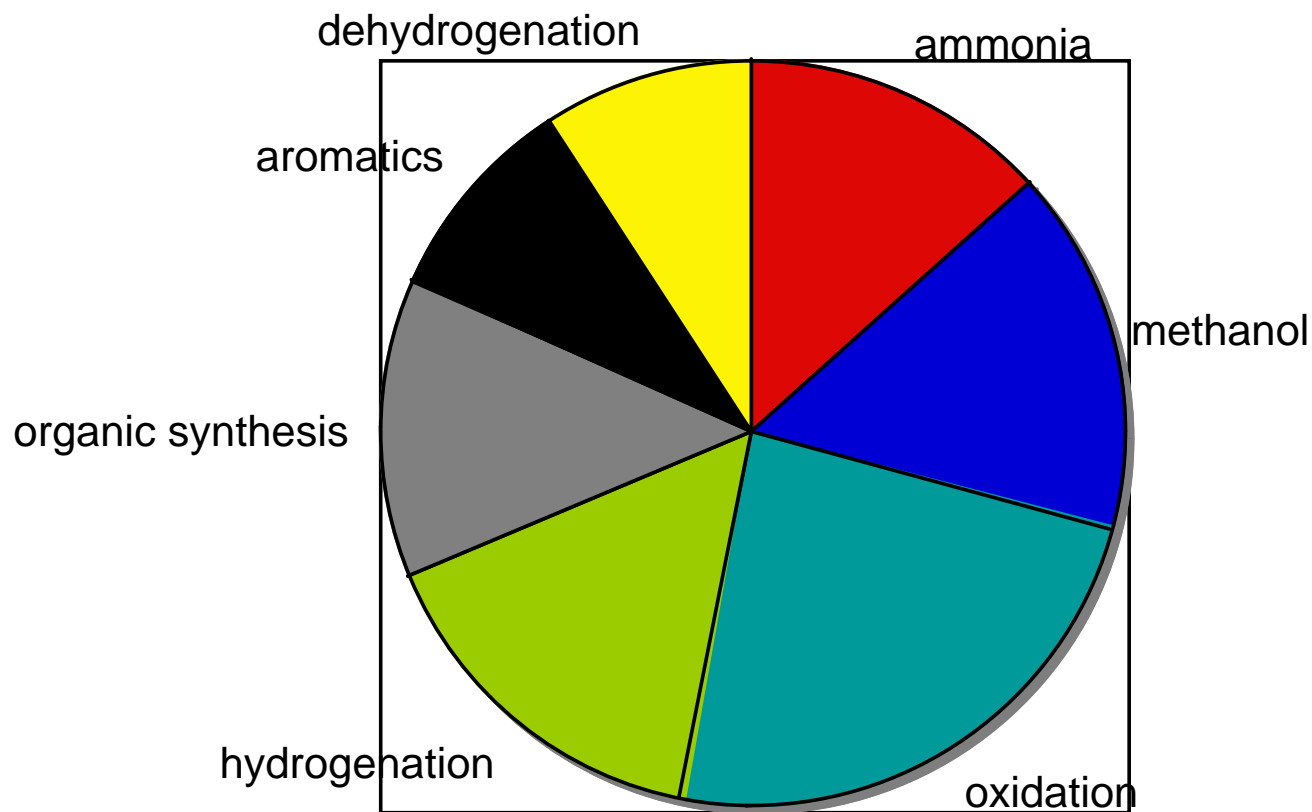
# Catalysis and economics (2004)

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- Catalysts were produced for 12 billion \$
- The value of products was 300 billion \$
- Distribution of catalyst applications
  - Refining 23%
  - Petrochemistry 26%
  - Polymerization (homogeneous) 16%
  - Environment 35%
  - All other applications (hydrogenation of complex substrates, fine chemicals) are within the estimate errors!



# Catalyst areas by value



F. Schmidt, in M. Baerns  
Basic principles in applied catalysis



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# Organic base products

Molecule	Demand mtons	Price per ton €
ethylene	105	510
propylene	62	437
butadiene	9	410
benzene	36	399

There is a huge incentive to replace  
steam-cracker feedstocks



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# The need to find an understanding of catalysis: sustainability of technology

Process	Size tons per a	Waste/product
refining	$10^8$	0.1
Bulk chemicals	$10^6$	5
Fine chemicals	$10^4$	50
Pharmaceuticals	$10^2$	50

R. A. Sheldon, 1997

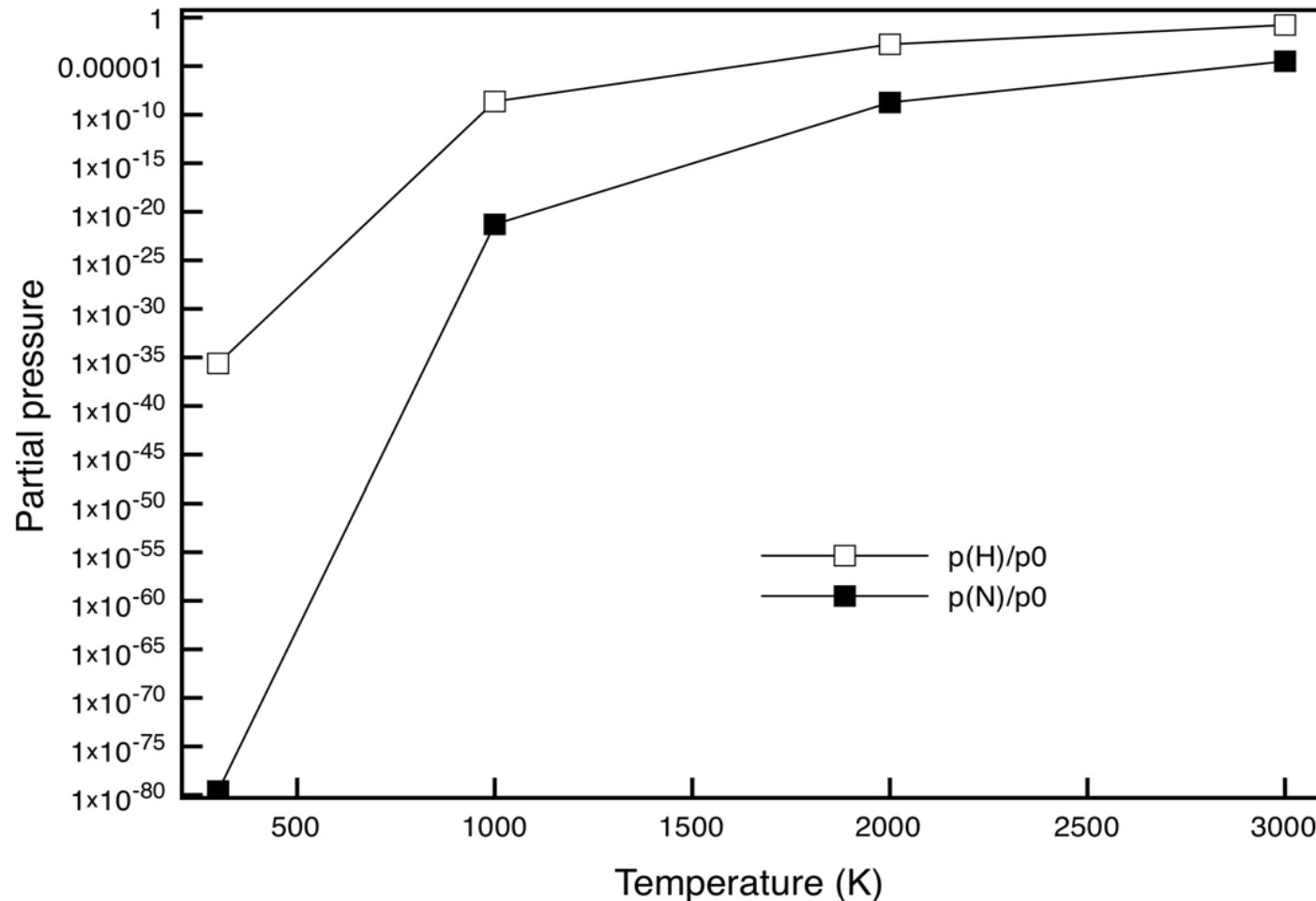
Excluding solvent waste



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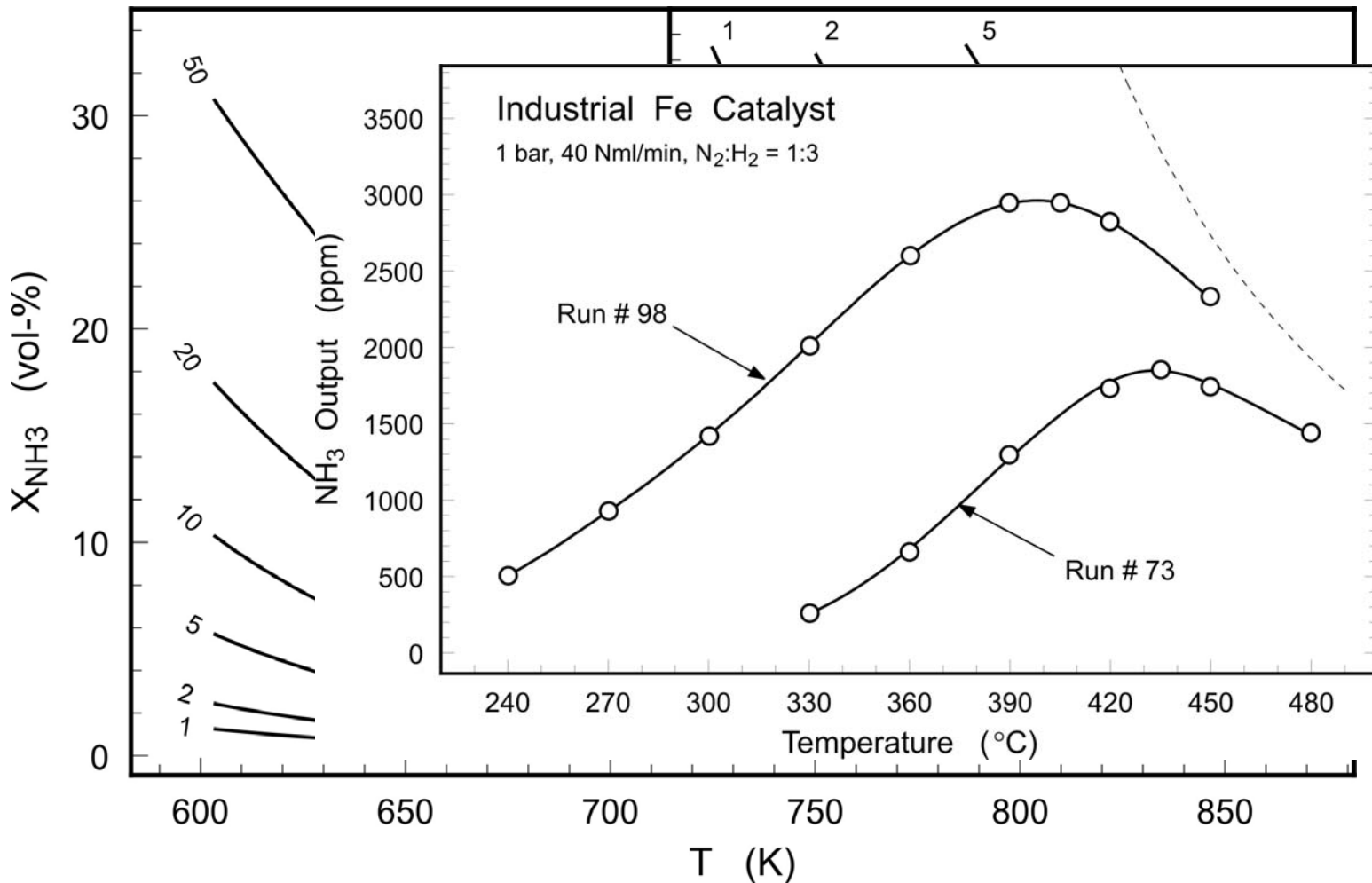


# Why we need catalysis: N/H uncatalyzed is unreactive

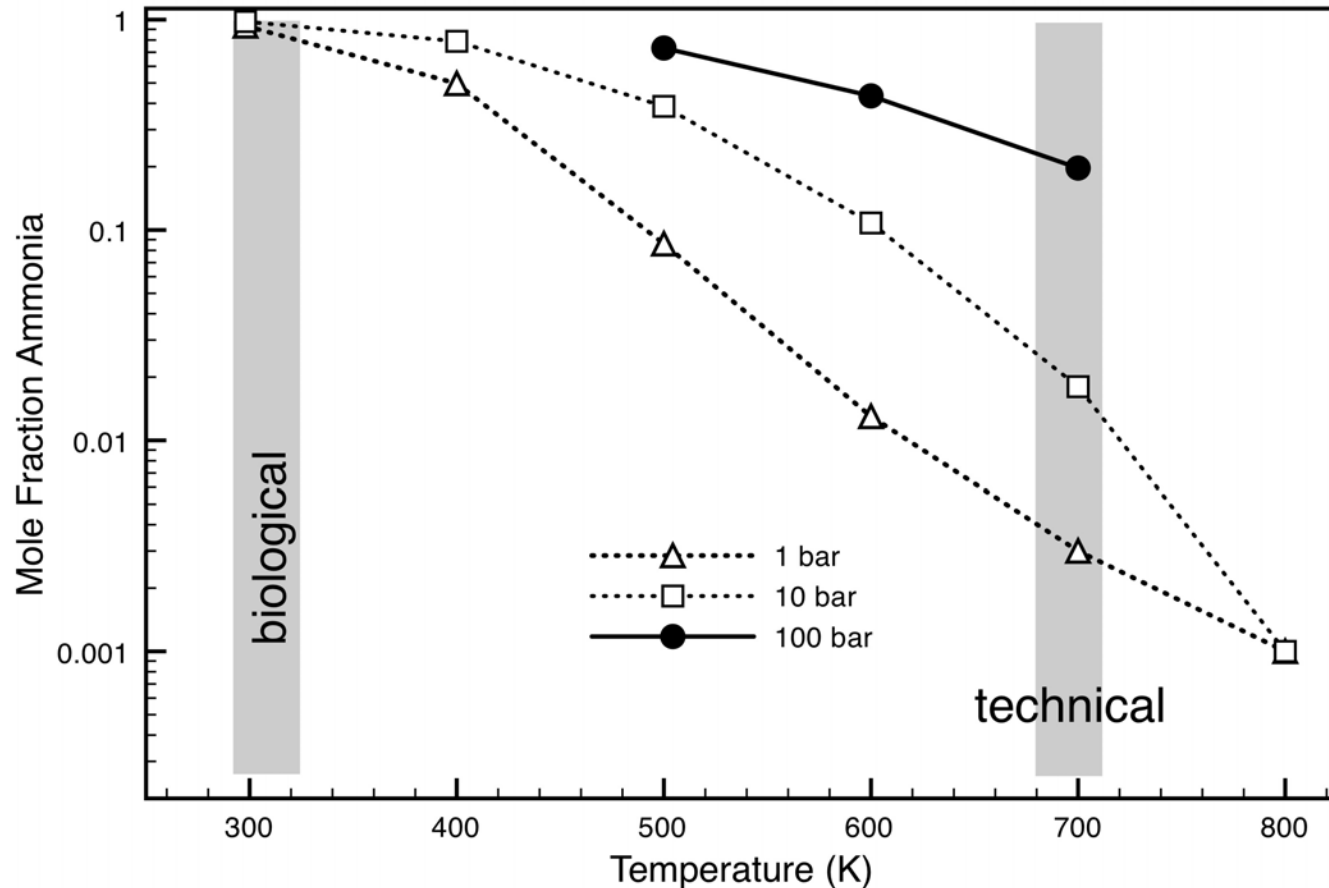




# Why we need a catalyst: A Haber Bosch system



# Process considerations

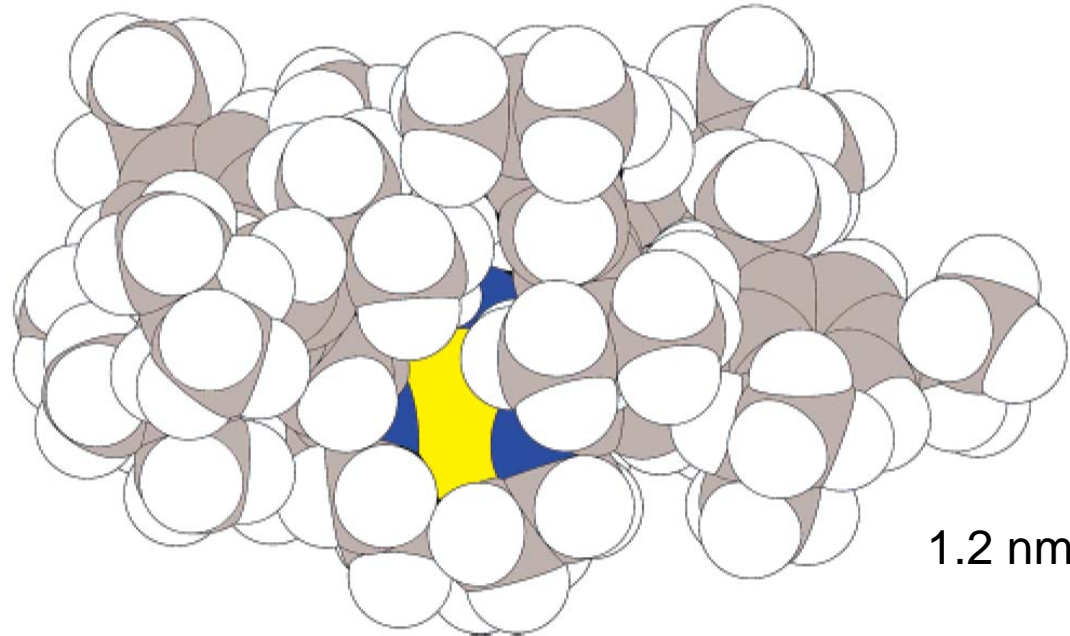


Consider the downstream use



# Molecular nanostructures

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R. Schrock, *Acc. Chem. Res.*, 2005, Mo tris-triamide for ammonia synthesis

**It is the surrounding "mesostructure" that makes the active site reactive**



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# Catalysis: a mature science ?

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- The concept of catalysis as a kinetic phenomenon and some ways how it modifies the course of a chemical reaction are well-established
- Proof-of-concept systems have been studied to a great extent (ammonia synthesis, oxidation of CO and ammonia)
- Many chemically only slightly more complex reactions are still far away from a fundamental understanding (validated sequence of elementary reaction steps including the identification of the rds)



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# Why models in catalysis?

The complexity issue,  
justification of the reductionistic  
approach



# Model systems

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- are “real” (contrast to real systems) but are usually not functional
- serve as static counterpart for reacting systems
- are evaluated with simplified reactions
- are used under conditions (low T, low p) that minimize substrate adsorbate and adsorbate-adsorbate interactions
- are made to a maximum structural definition (equals minimal reactivity)
- Can be materials or theory or “concepts”



# The static catalyst (Langmuir, Taylor, Ertl)

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- A heterogeneous catalysts can be approximated by a single crystal surface
- This represents a checkerboard structure (termination)
- On it we find active sites (atoms)
- They can be defined precisely with atom coordinates
- They can be studied by surface science structural tools
- Single crystal approach



# Reductionism

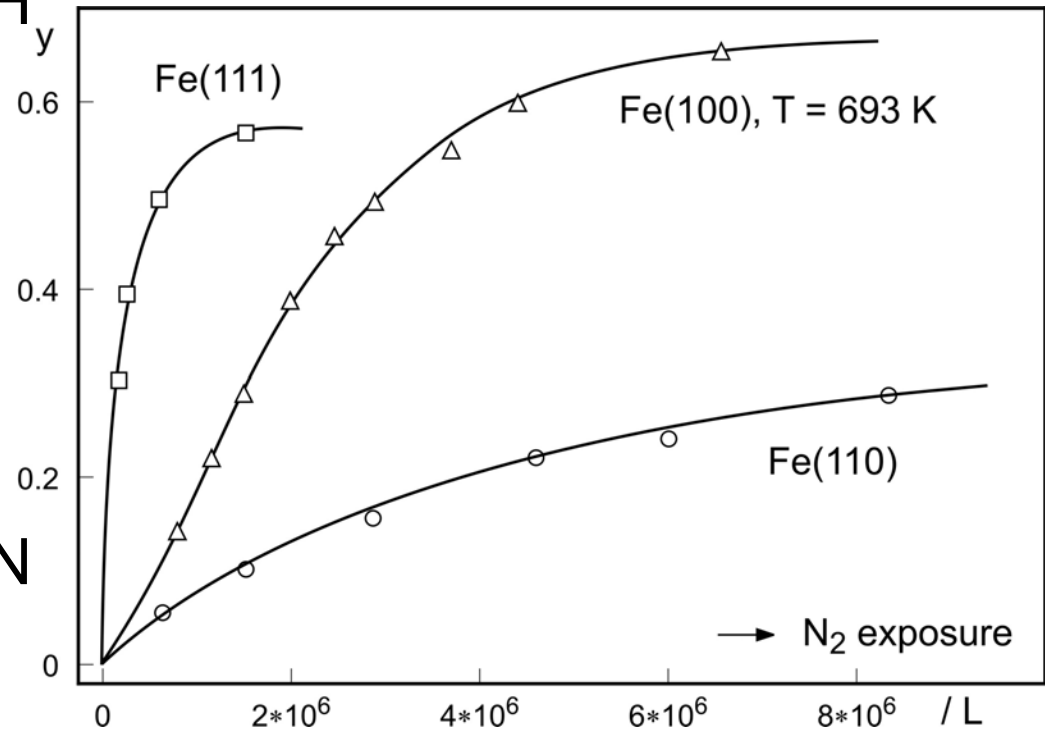
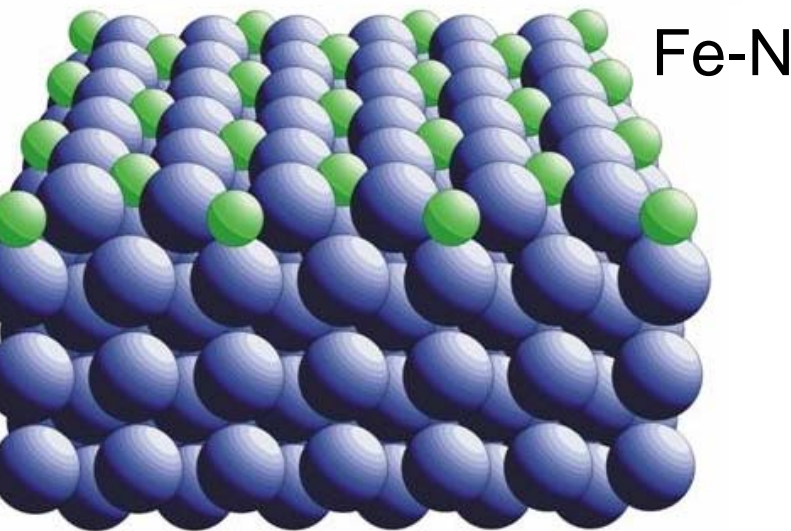
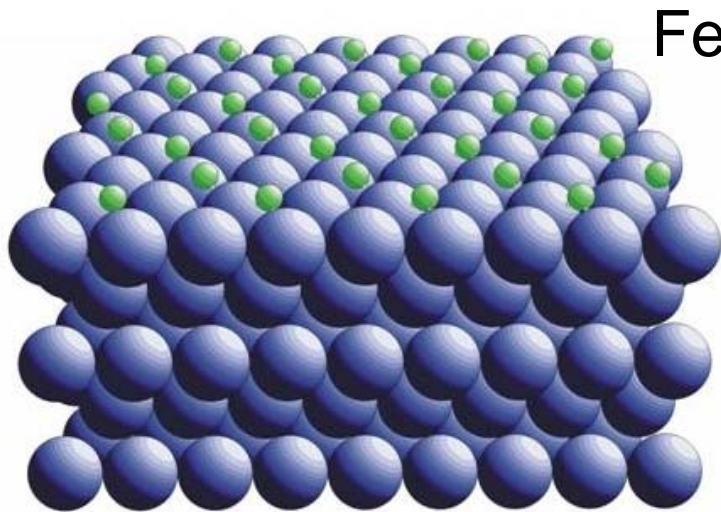
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- The single crystal approach
  - Removes chemical complexity (additives, contaminants)
  - Removes structural complexity (ordering)
  - Removes transport perturbations except surface transport
- This allows
  - To determine elementary step kinetic parameters
  - To find geometries and atomic coordinates of adsorbates
  - To couple experiment and high-level (ab-initio) theory





# Surface science and ammonia synthesis



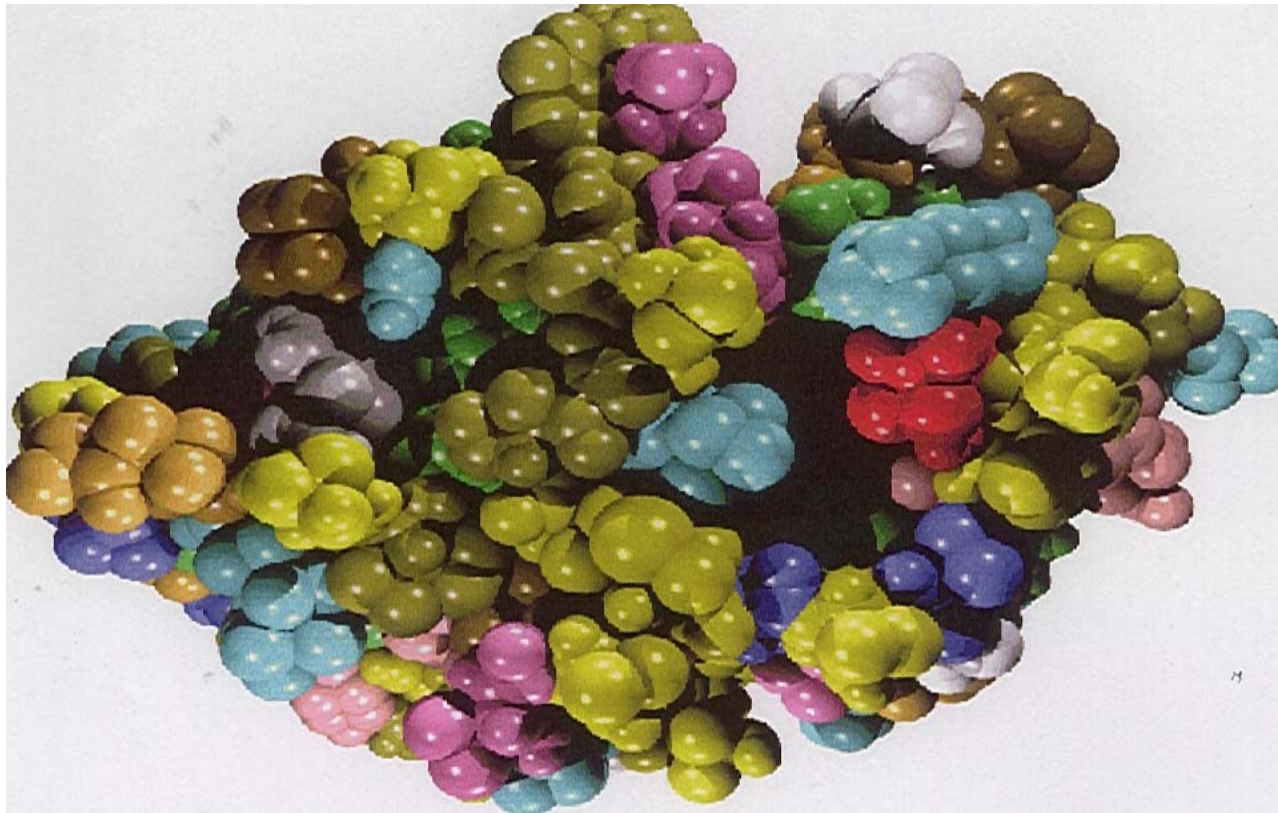
Low pressure static data



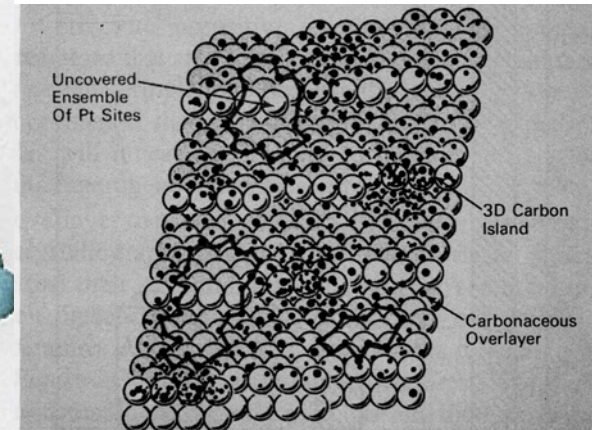
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# Models of catalyst surfaces



Trypsin, an enzyme



Somorjai 1994



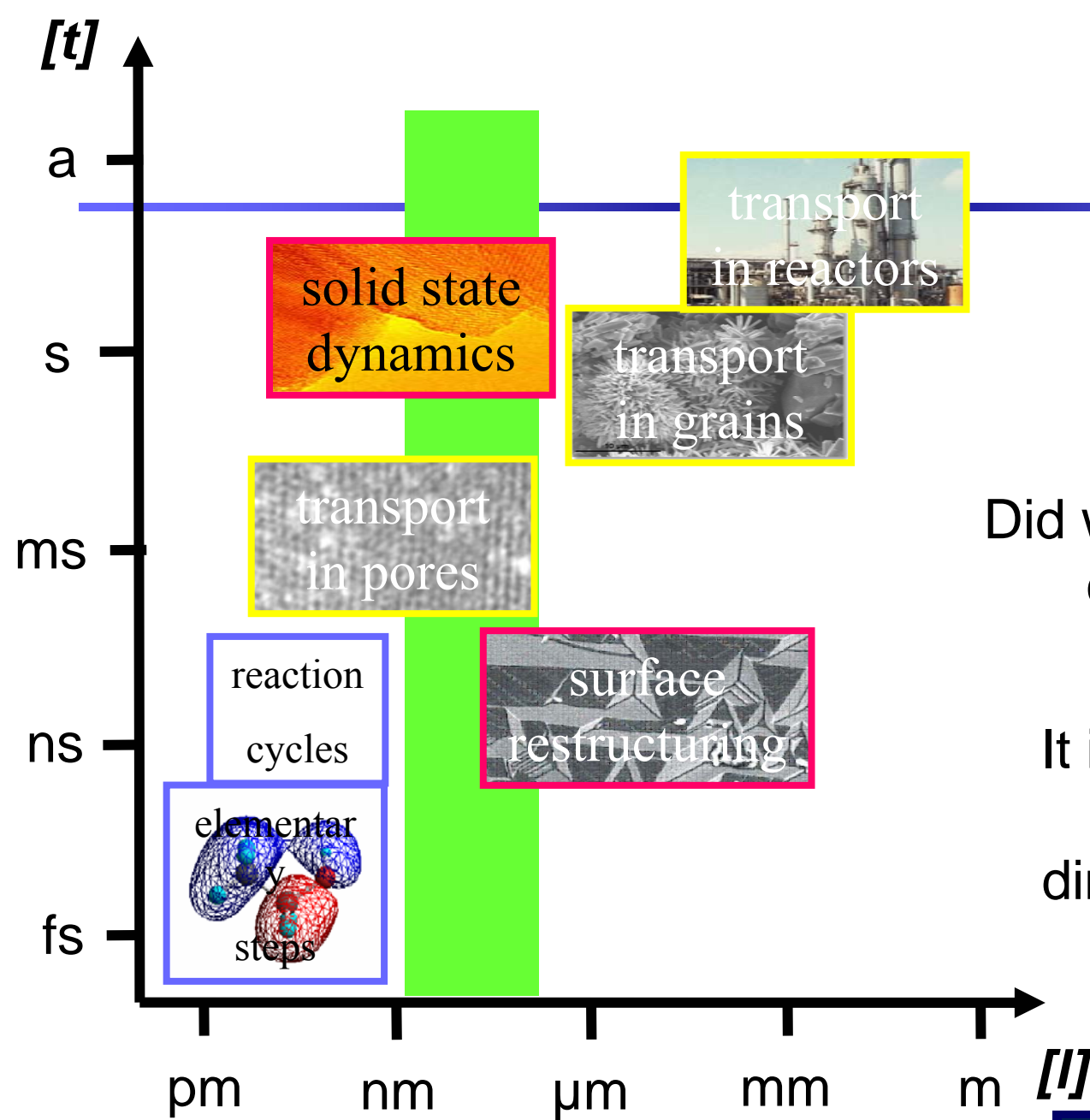
# The dynamic catalyst

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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







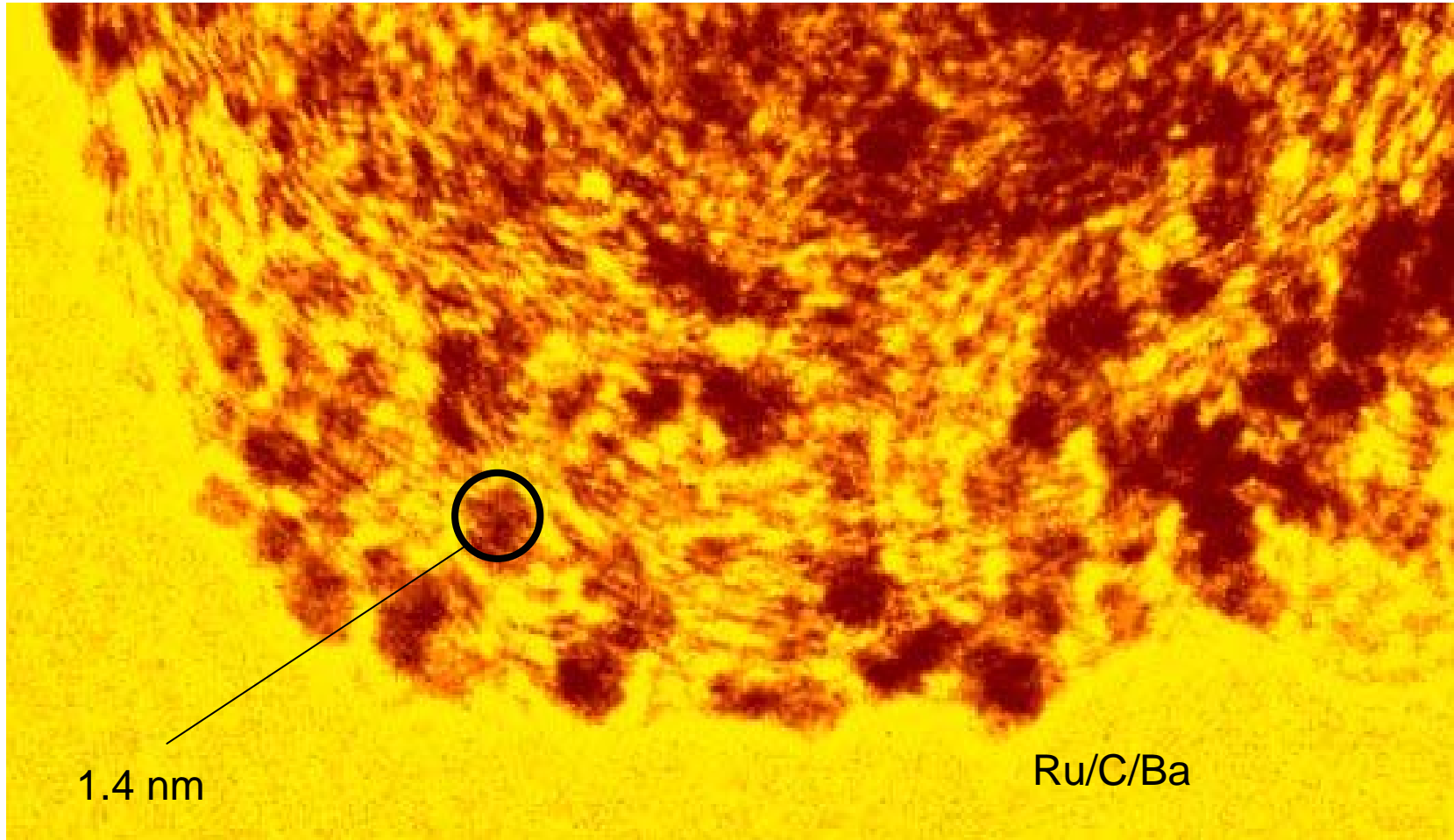
# Catalysis: a multi- dimensional function

Did we really capture all  
concepts in this  
scenario?

It is not sufficient to  
study only one  
dimension (e.g. the  
atomic one)

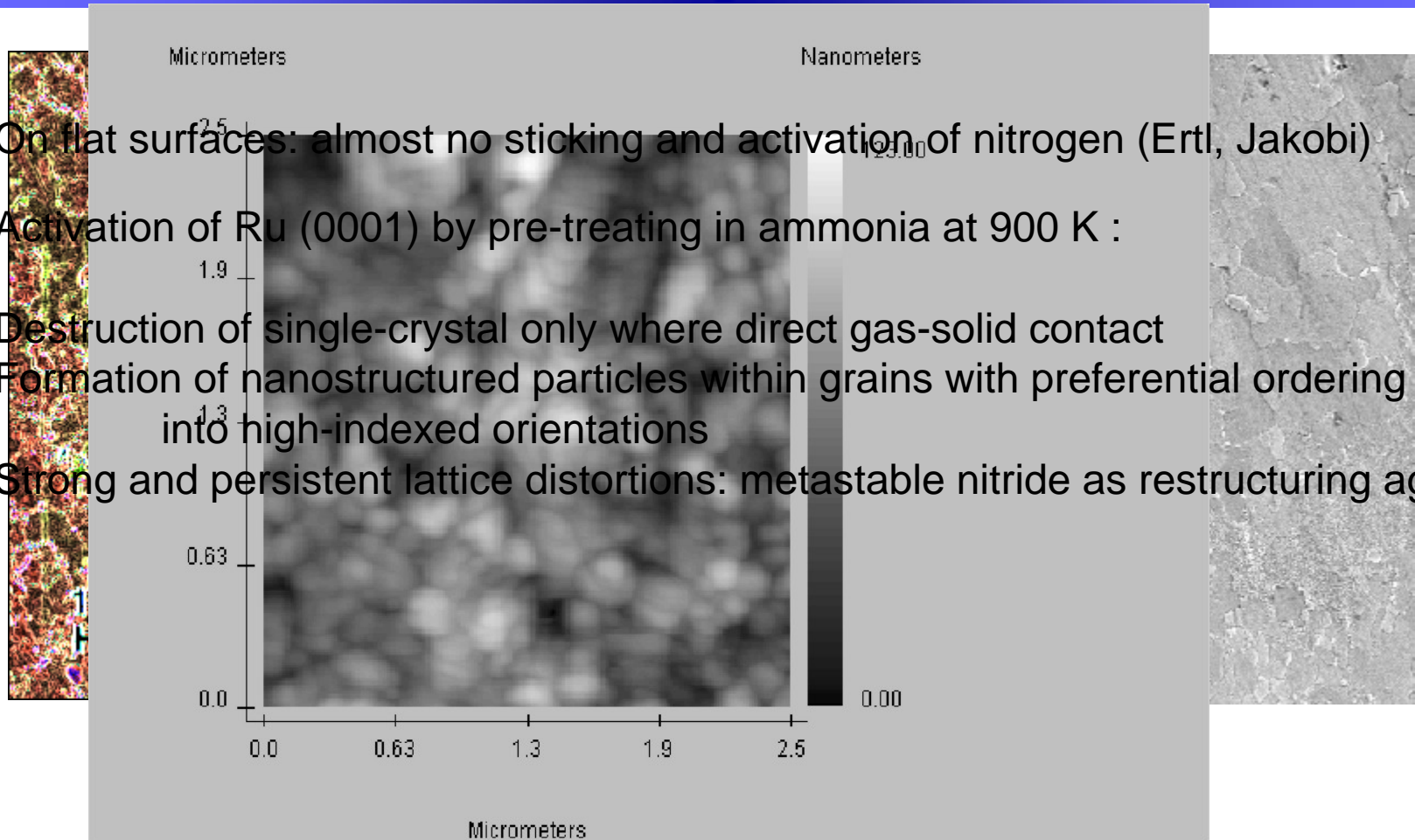


# Ru ammonia synthesis



# Ru ammonia

On flat surfaces: almost no sticking and activation of nitrogen (Ertl, Jakobi)  
Activation of Ru (0001) by pre-treating in ammonia at 900 K :  
Destruction of single-crystal only where direct gas-solid contact  
Formation of nanostructured particles within grains with preferential ordering  
into high-indexed orientations  
Strong and persistent lattice distortions: metastable nitride as restructuring agent?



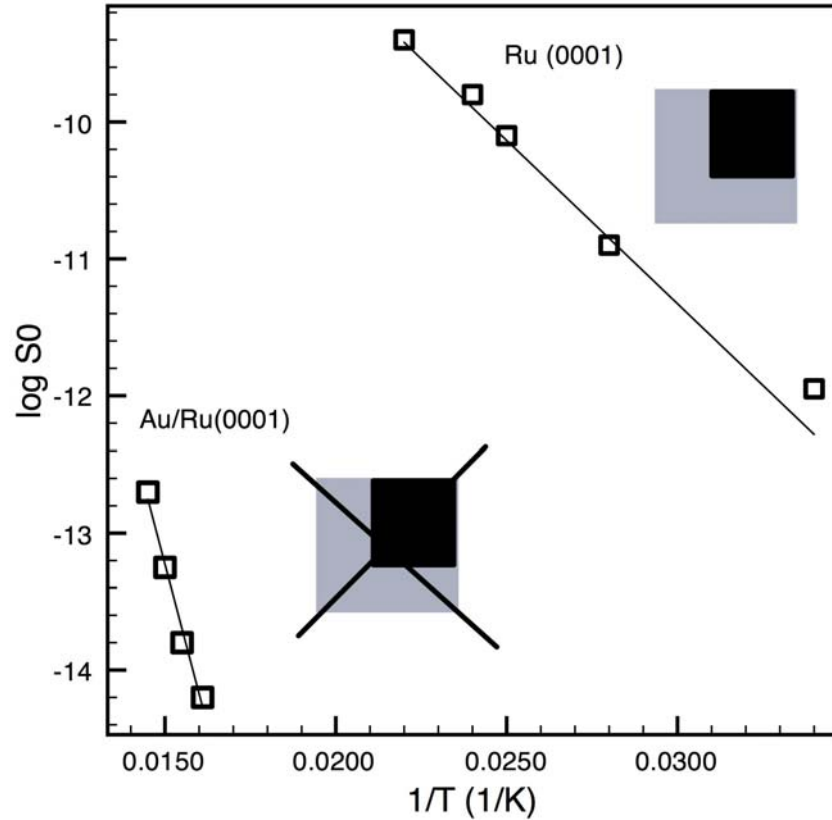
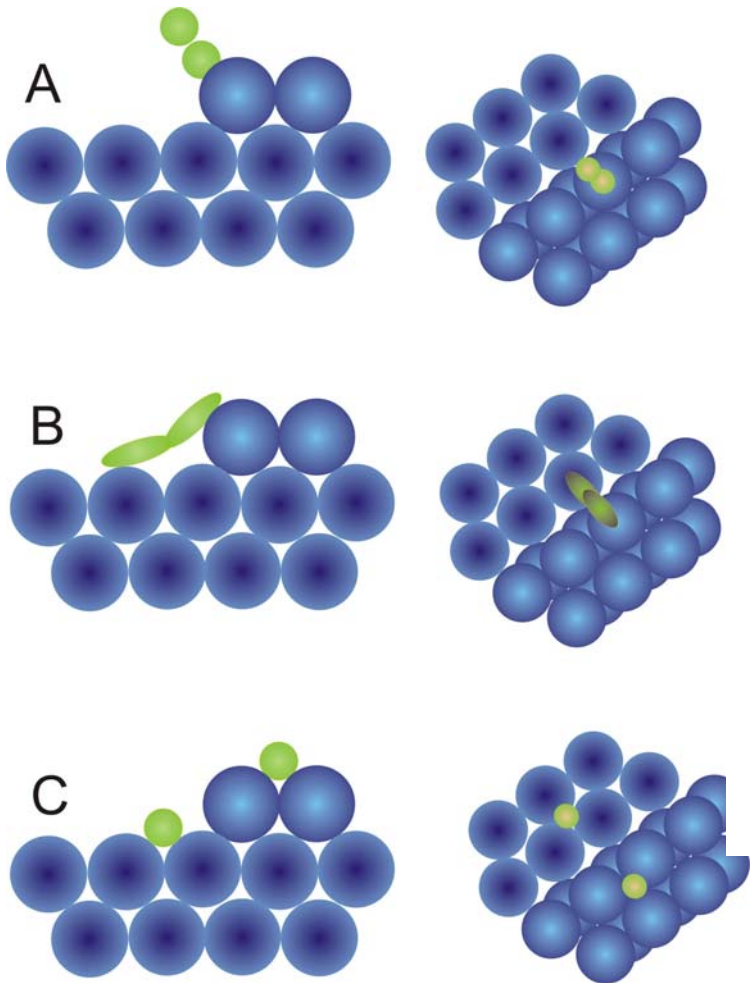
# Holistic approach

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- Even in simple cases the dynamic nature of working catalysts transforms geometric and electronic structure apart from the chemically and structurally well-defined situations
- Catalysis is probably a local phenomenon, for which extended structures are only in kinetically non-demanding situations working substitutes (powerful only in adsorption processes, as little specificity)
- Models of working catalysts are in most cases still too complex: a model is a system in which the geometry of the active site can be controlled
- We will have to live for a long time with a bracketing concept: models are either compromises in function or in structural definition: approach from two sides



# Non-translational models: ammonia synthesis



Chorkendorff and Norskov 2000

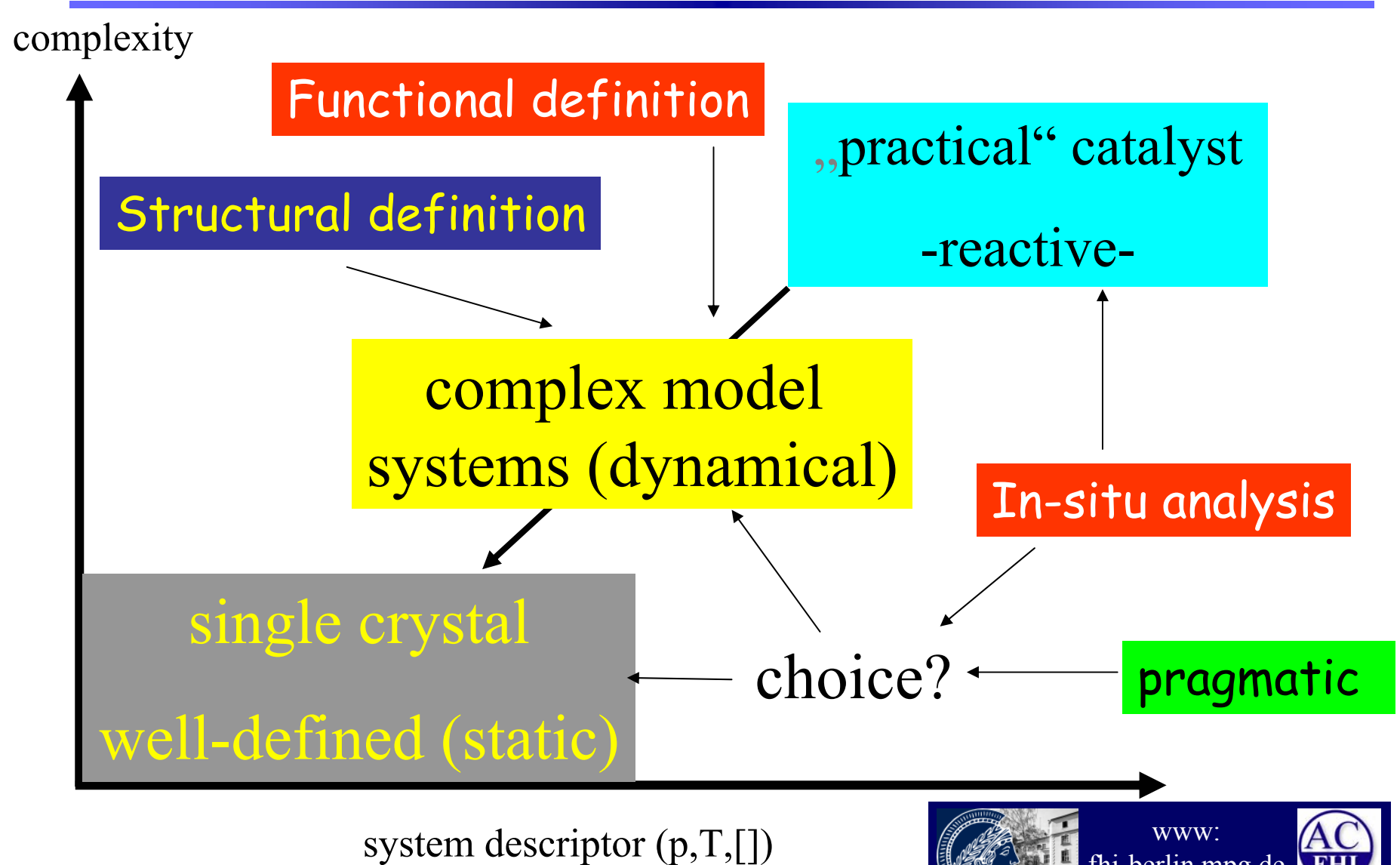


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# Model strategy



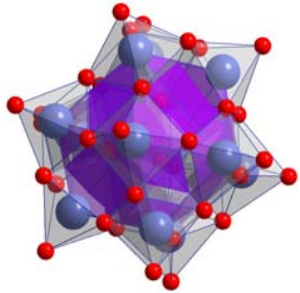
# Structure of working catalysts

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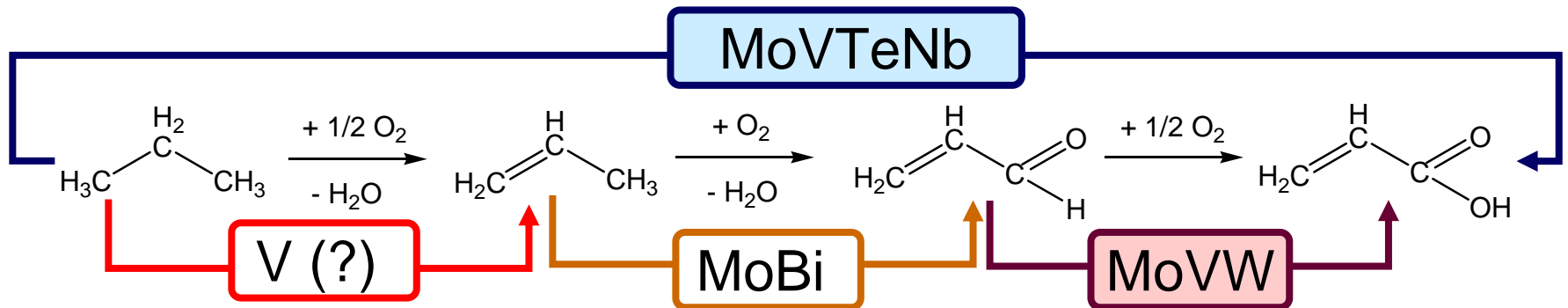
- Normal is site isolation, i.e. active sites are complexes embedded or self-supported on a matrix made from the bulk of thought-to be active material
- The autogeneous transformation of the surface-near part of a catalyst from a pre-catalyst into the active form is controlled by solid state kinetics and the chemical potential of the gas phase
- Synthesis needs to provide suitable flexibility for the transformation without destabilizing the matrix system



# A kinetically demanding reaction



Can we hope to ever get a functional model?  
No success until now with single crystal systems



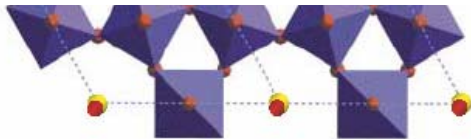
# Literature: The active structure



✓ There is no evidence of amorphous  
Through combinatorial and high throughput testing a complex multi-element multi phase oxide “MoVTe” was identified as good catalyst  
(more than 10 patents and about 40 publications).

It was speculated that two phases M1 and M2 act together to achieve high performance.

The reproducibility of structures and performance is poor and not (yet) suitable for technical use.



available to them under reaction (redox) conditions.

R.K. Grasselli et al.



# Preparation of $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.125}\text{O}_x$ : „Slurry method“

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  (0.126 mol Mo) / 100 ml  $\text{H}_2\text{O}$   
 $T = 80^\circ \text{C}$  /  $\text{pH} = 5.0$

$\text{NH}_4\text{VO}_3$  (0.038 mol V)  
(powder)

$\text{MoV}_{0.30}$   
 $T = 80^\circ \text{C}$  /  $\text{pH} = 5.5$

$\text{Te}(\text{OH})_6$  (0.029 mol Te)  
(powder)

$\text{MoV}_{0.30}\text{Te}_{0.23}$   
 $T = 80^\circ \text{C}$  /  $\text{pH} = 5.0$

$(\text{NH}_4)[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$   
(0.016 mol Nb) / 30 ml  $\text{H}_2\text{O}$   
 $T = 23^\circ \text{C}$  /  $\text{pH} = 0.8$

cool down to  $40^\circ \text{C}$

$\text{MoV}_{0.30}\text{Te}_{0.23}\text{Nb}_{0.13}$   
(slurry)  
 $T = 25^\circ \text{C}$  /  $\text{pH} = 3.2$

$\text{MoV}_{0.30}\text{Te}_{0.23}\text{Nb}_{0.13}$   
(activated)

spray-drying

$\text{MoV}_{0.30}\text{Te}_{0.23}\text{Nb}_{0.13}$   
(precursor)

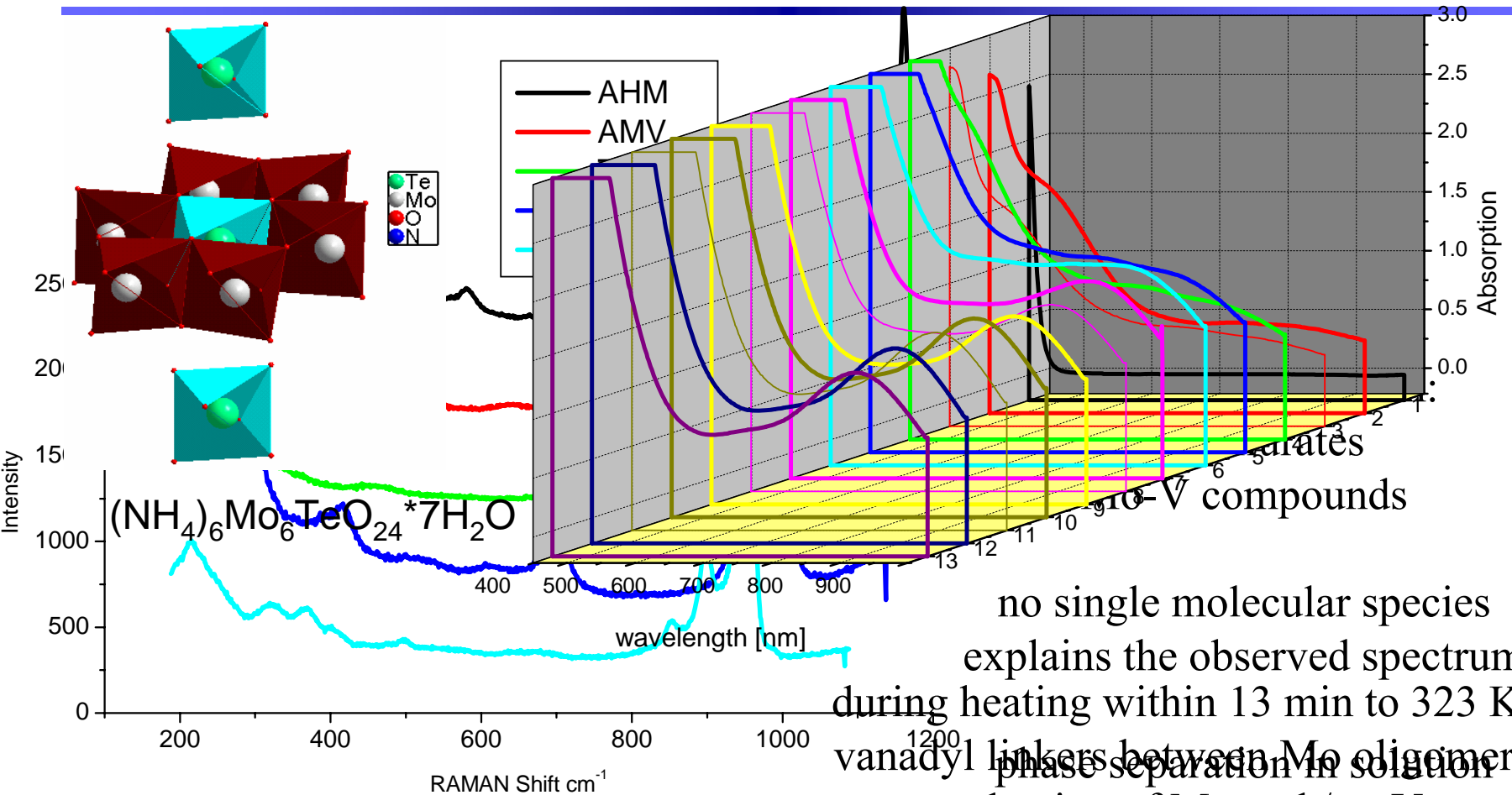
$275^\circ \text{C}$   
( $10^\circ \text{C}/\text{min}$ ) / 1h  
static air

$\text{MoV}_{0.30}\text{Te}_{0.23}\text{Nb}_{0.13}$   
(calcined)

$600^\circ \text{C}$  (2  
 $^\circ \text{C}/\text{min}$ ) / 2 h  
He flow



# The liquid phase in synthesis



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# Ag: in EO synthesis

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- The technical catalyst is metallic silver nanoparticles (plus additives and promoters on alumina)
- Ag (111) is used since 40 years as model system
- Theory (van Santen, Scheffler et al) has found several atomic oxygen species, a surface oxide and metastable (disputed) sub-surface species
- Recently the structure of the surface oxide has been solved in a model situation



# Reactant-induced nanostructuring of Ag (111)

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Zur Anzeige wird der QuickTime™  
Dekompressor „TIFF (LZW)“  
benötigt.

Oxygen reconstructs  
the Ag surface into  
“nanoclusters” of  
metal atoms with  
oxygen atoms as  
insulators: site  
formation

J. Schnadt,<sup>1</sup> A. Michaelides,<sup>2</sup> J. Knudsen,<sup>1</sup> R. T. Vang,<sup>1</sup> K. Reuter,<sup>2</sup> E. Lægsgaard,<sup>1</sup>  
M. Scheffler,<sup>2</sup> and F. Besenbacher<sup>1</sup> PRL 2006

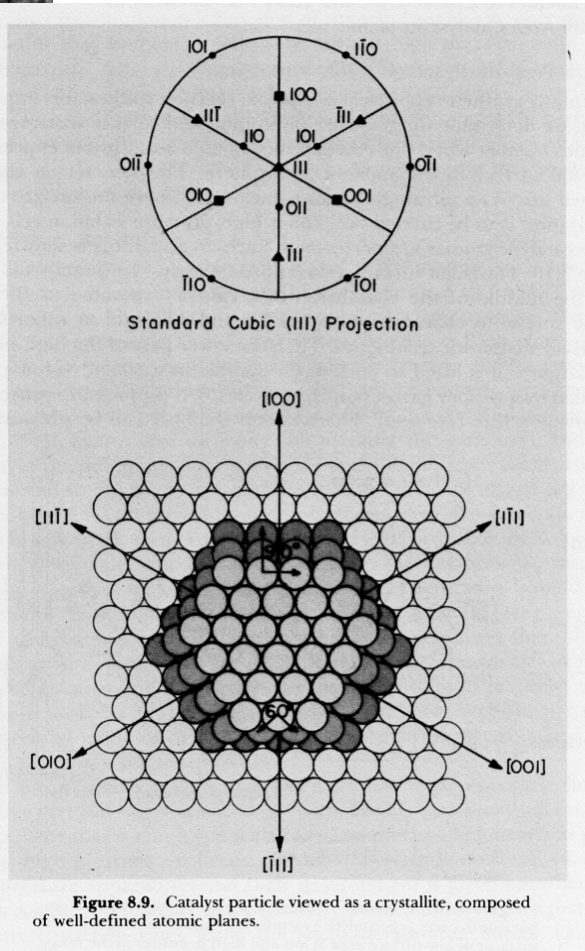


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# Ag nanoparticles: why size can matter



Somorjai 1981

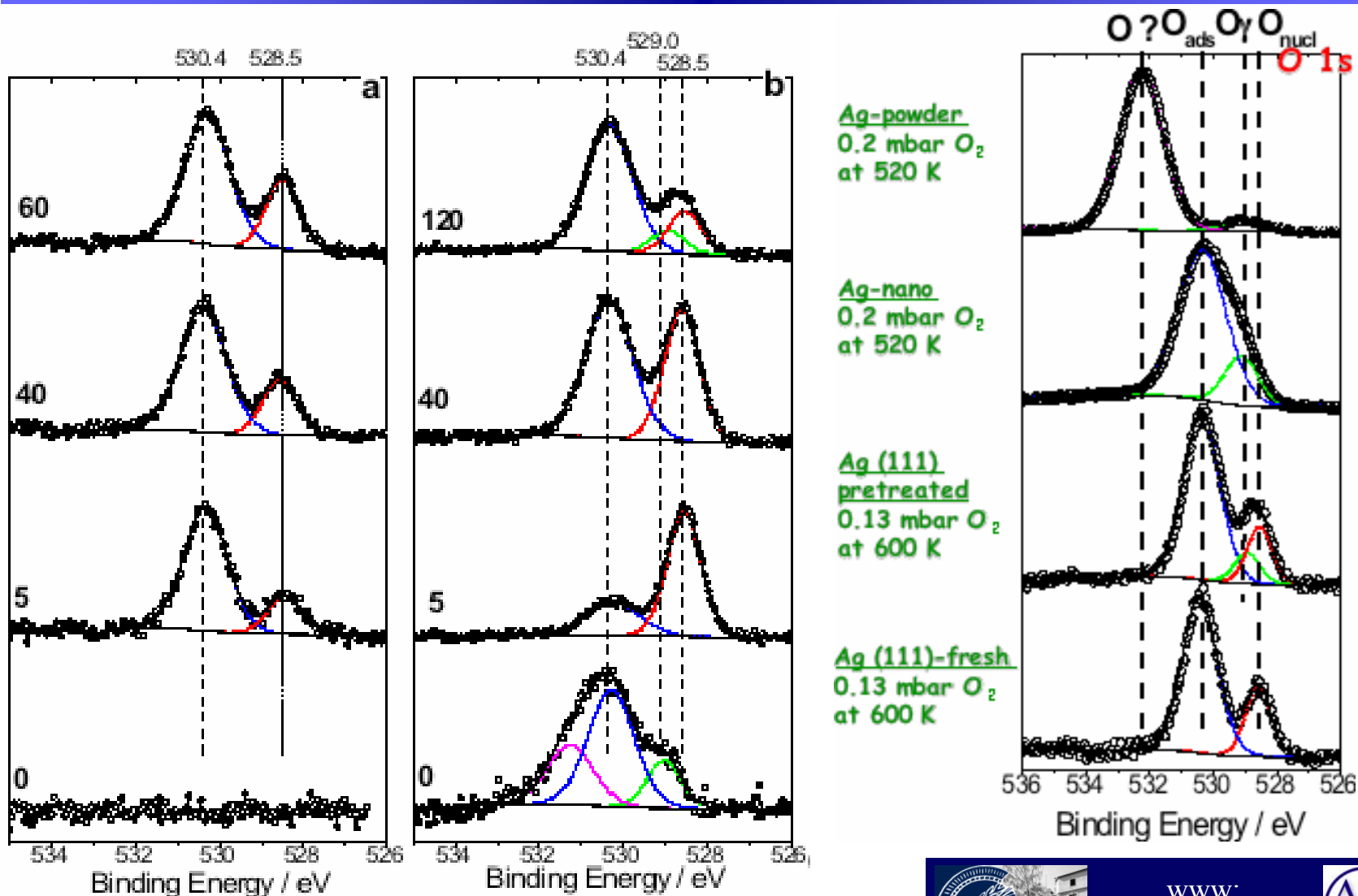
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# Dynamics: AgO (gaps)



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# What models in catalysis?

Surface science is not the only  
model strategy required



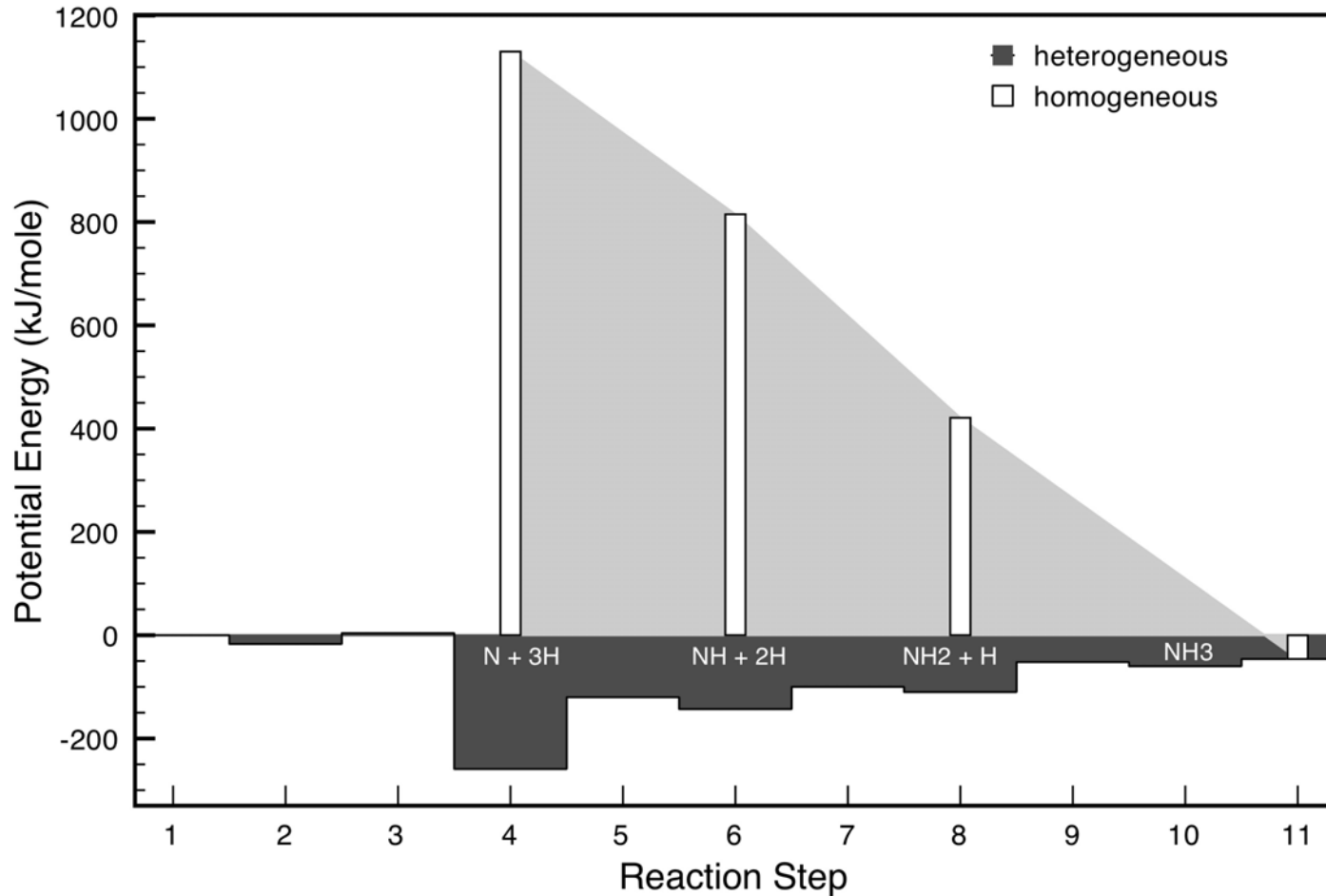
# Numerical models

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- Microkinetics with a set of elementary steps derived from surface science experiments
- Identification of the rds from energetics
- Ab-initio calculation of critical steps and their transition states
- Incorporation of experimental values from key steps (adsorption, activation)
- Prediction of rates from statistical methods
- Comparison with experiments (see textbook Chorkendorff and Niemantsverdriet)
- In fortunate cases hierarchical theoretical models without any experimental values

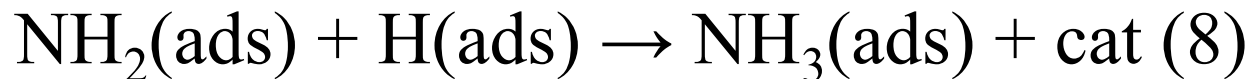
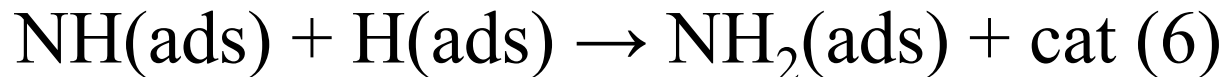
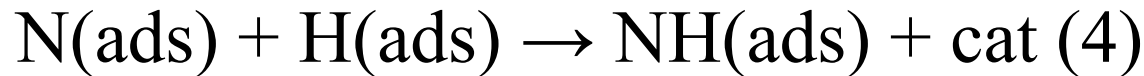
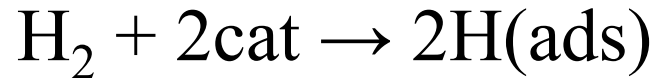
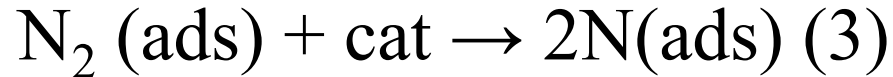
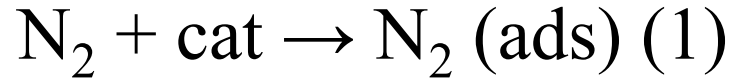


# Why we need a catalyst: Haber Bosch

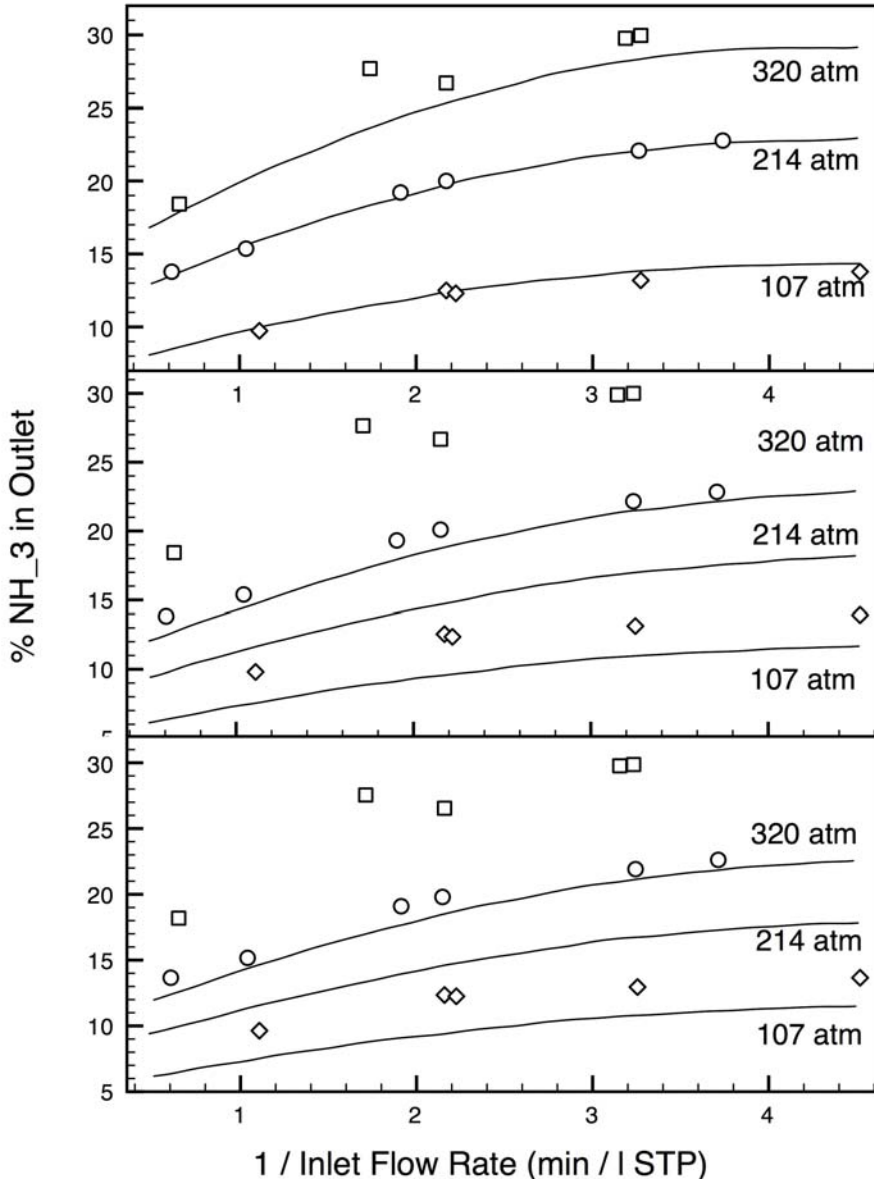


# Elementary steps of ammonia synthesis

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# The result of a model



Norskov et al (1994):

Based on the surface science data of Ertl et al and a microkinetic model (Dumesic et al) it was possible to model the experimental observations (points) by ab-initio models without any fitting (!) of parameters

Models differ slightly in assumptions about hydrogen activation and activation barriers of nitrogen activation: data of Ertl et al:



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# The classical description of a reaction

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Ammonia synthesis from Nielsen et al (1972)

$$r = \frac{k_a^* a_{N_2} - k_b^* (a_{NH_3})^2 / (a_{H_2})^3}{\left[ 1 + k_c^* (a_{NH_3}) / (a_{H_2})^\gamma \right]^{2\alpha}}$$

Fitting to experimental data

3 rate constants

Stoichiometry parameter  $\gamma$

Inhomogeneity parameter (Temkin)  $\alpha$





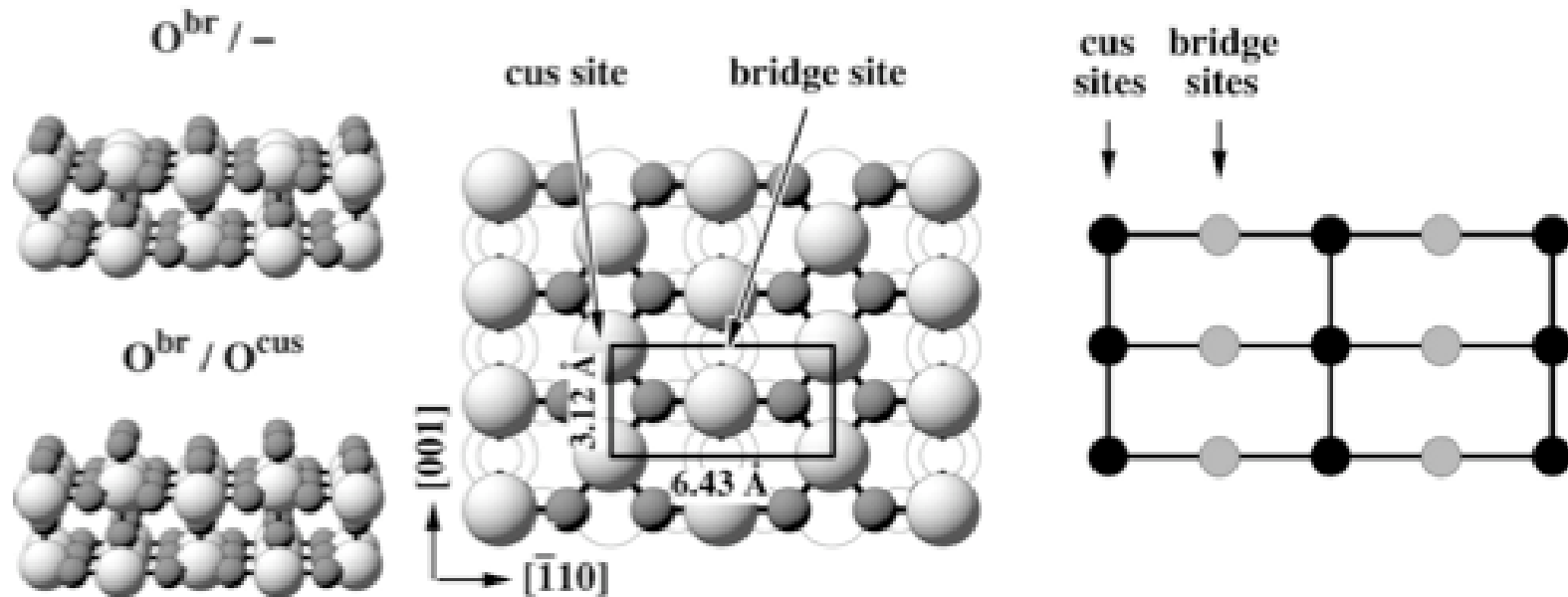
# Gaps

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- Kinetic models should allow to correlate the static observations of model systems to practical reactor performance if:
  - the “mechanism” is known
  - the rds is known
  - the elementary processes in model and real cases are the same
- Until now no exact match (approx. CO oxidation, and ammonia synthesis) and no example of an organic selective reactions (no good models for C-H and C-C re-arrangements)



# CO oxidation over RuO<sub>2</sub>: A model



K. Reuter et al  
H. Over et al

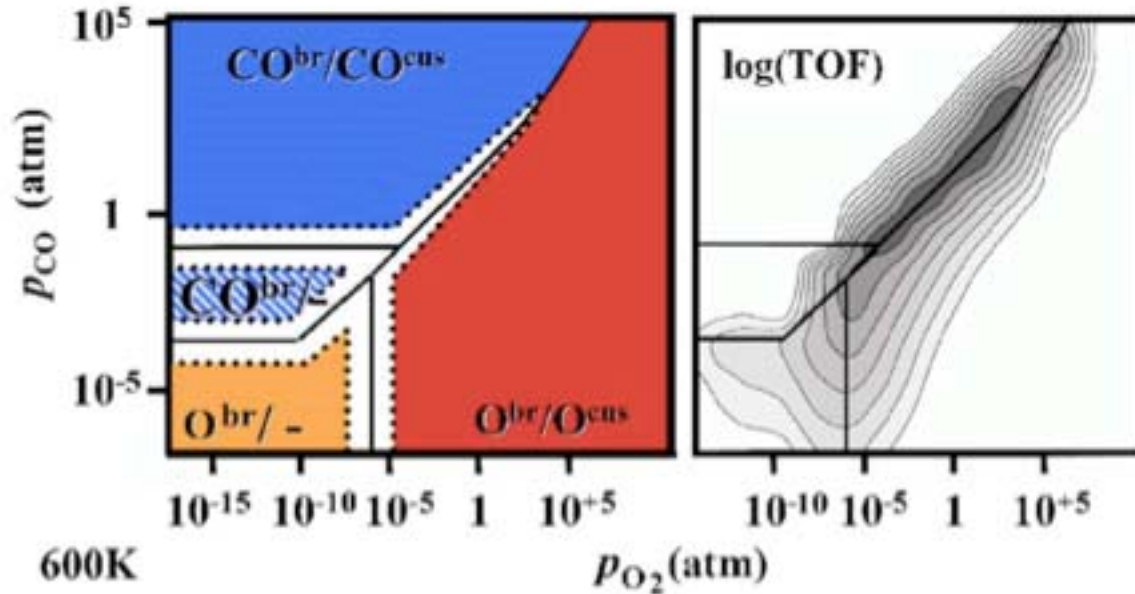
Highly active catalyst as “oxide”  
LEED structure forms basis of theory  
Identification of active sites



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# CO oxidation over RuO<sub>2</sub>: A model



K. Reuter et al

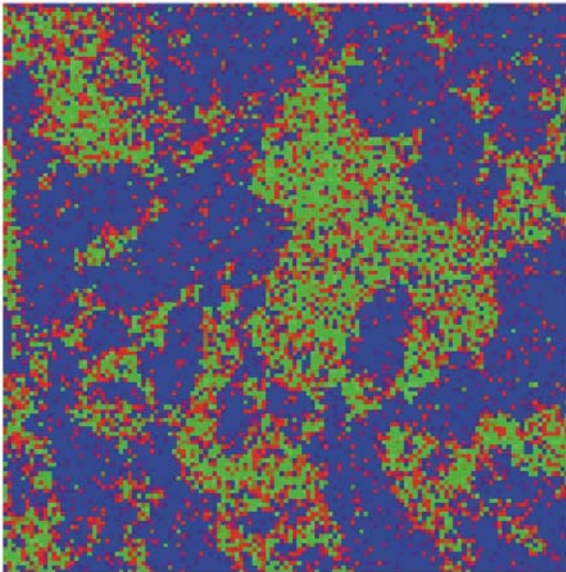
Extensive development of theory  
Predicted phase diagram  
Reactivity study of Jakobi et al  
Excellent quantitative agreement  
Role of co-existence regions



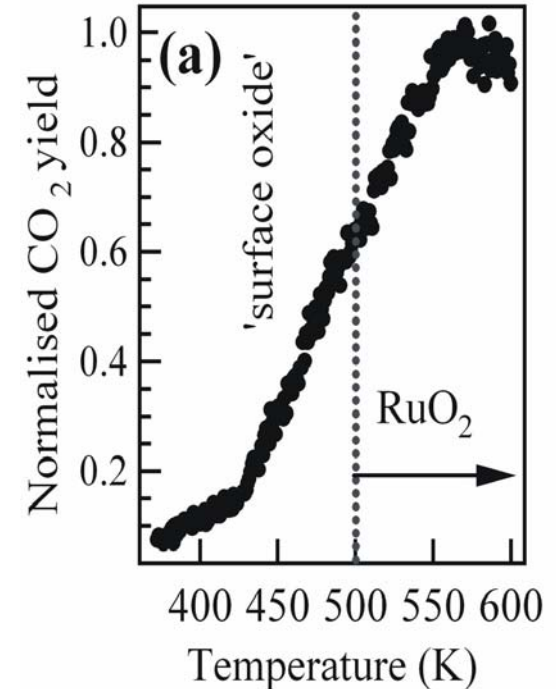
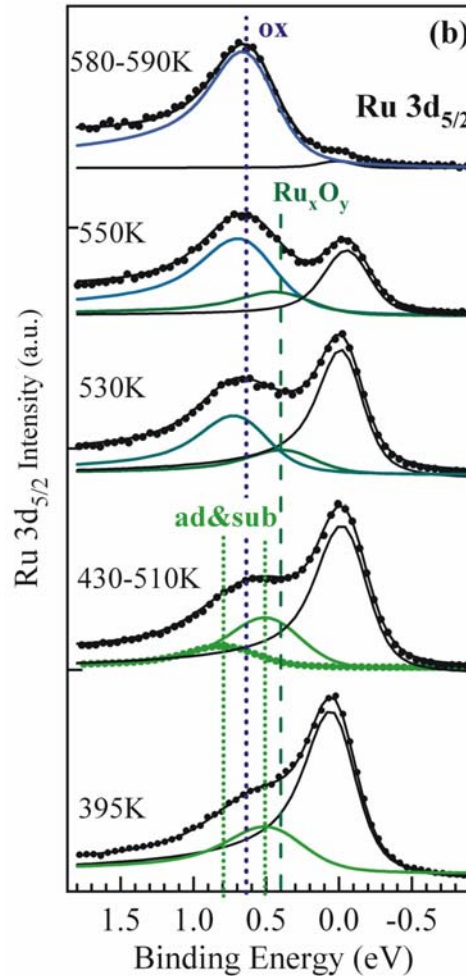
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# What is steady state?



In-situ surface analysis reveals that at steady state conditions a mixture (dynamical) of surface states exists



There is no structure sensitivity nor phase correlation with activity



# Functional material models

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- In complex reactions (selectivity) no numerical models and very little single crystal data except TPRS data (further lecture)
- Minimize chemical complexity of functional catalysts
- Study structural complexity and its dynamics to arrive at elementary steps
- Synthesize models and apply meaningful in-situ techniques, characterize nanostructure
- Examples: nanoparticles on model oxide surfaces (Freund); model oxides with full function for selective oxidation



# Metal particle model system

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benötigt.

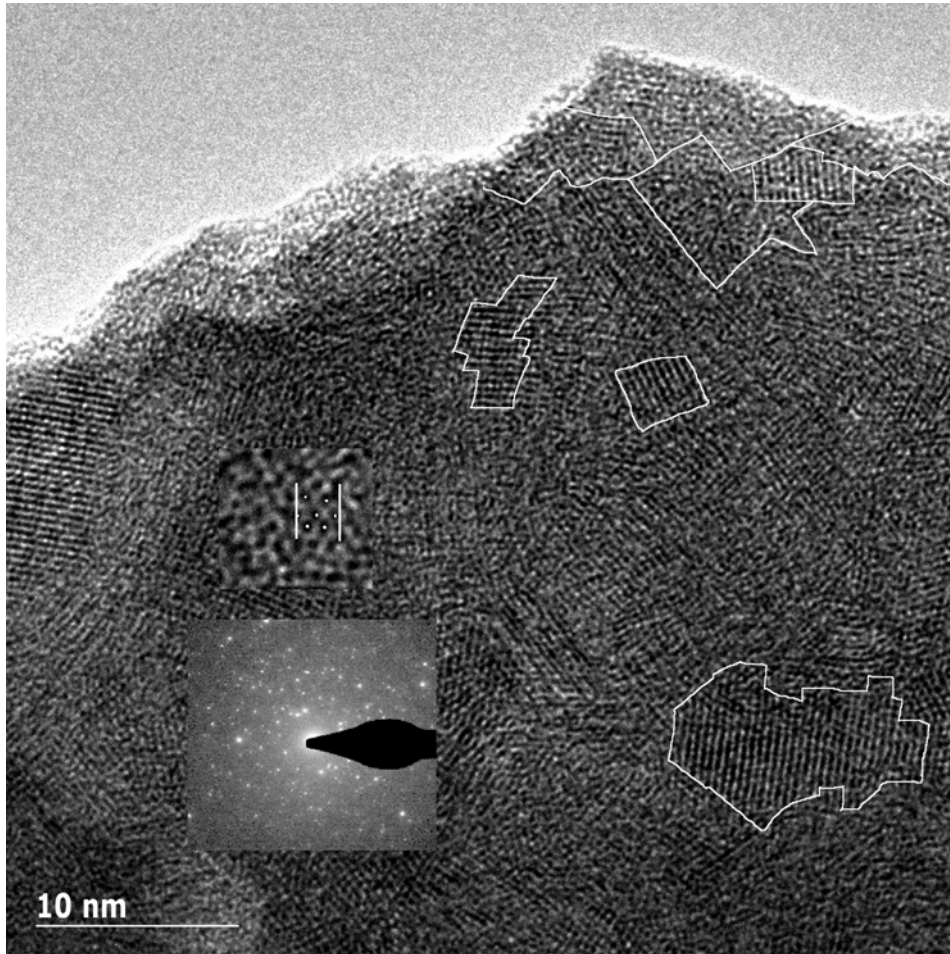
Zur Anzeige wird der QuickTime™  
Dekompressor „TIFF (LZW)“  
benötigt.

Structural  
definition(mesoscopic)  
Indirect structural analysis  
via reactivity (“roughness”)





# Nanostructured Mo-oxide

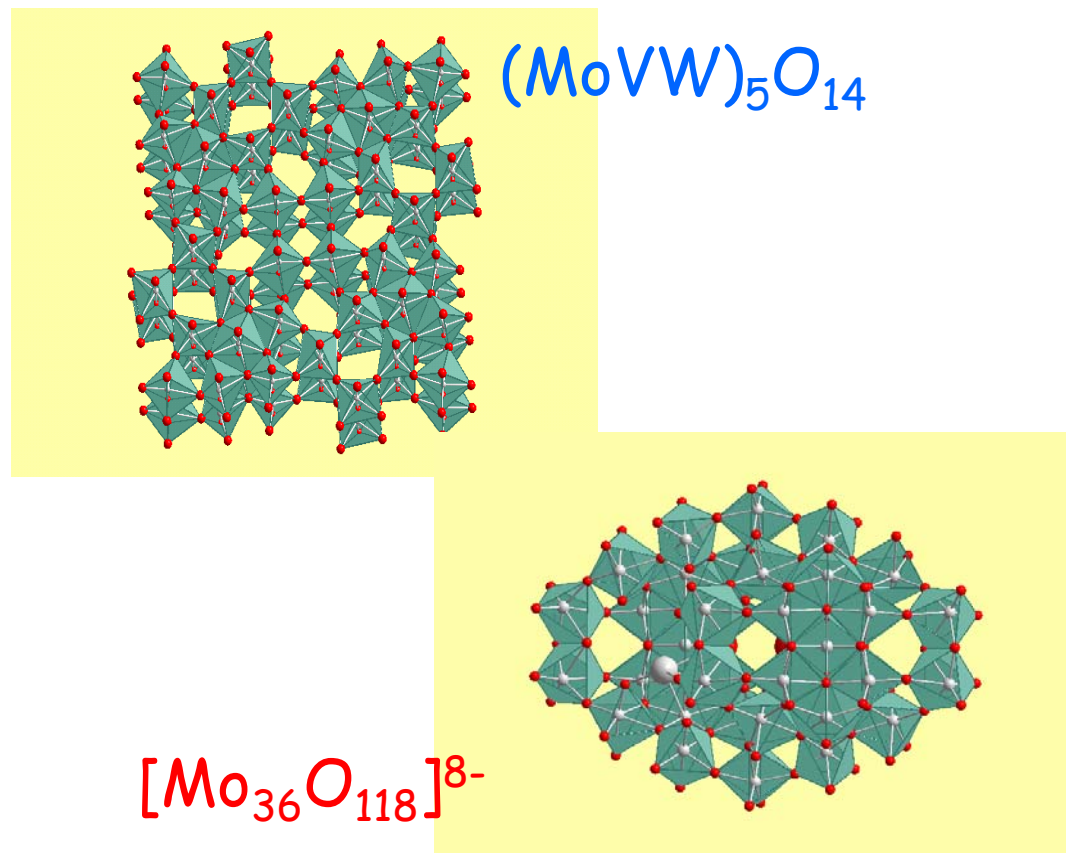
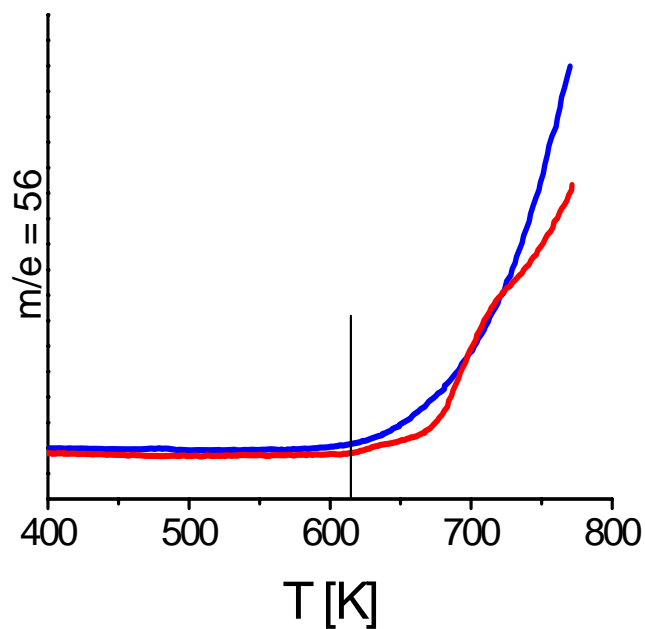


Supramolecular phase:  
Nanocrystals of a well-defined  
phase (octahydrate anion of  
 $\text{MoO}_3$ )  
intergrown in  
various relative orientations  
Disordered volume elements  
with glassy structure



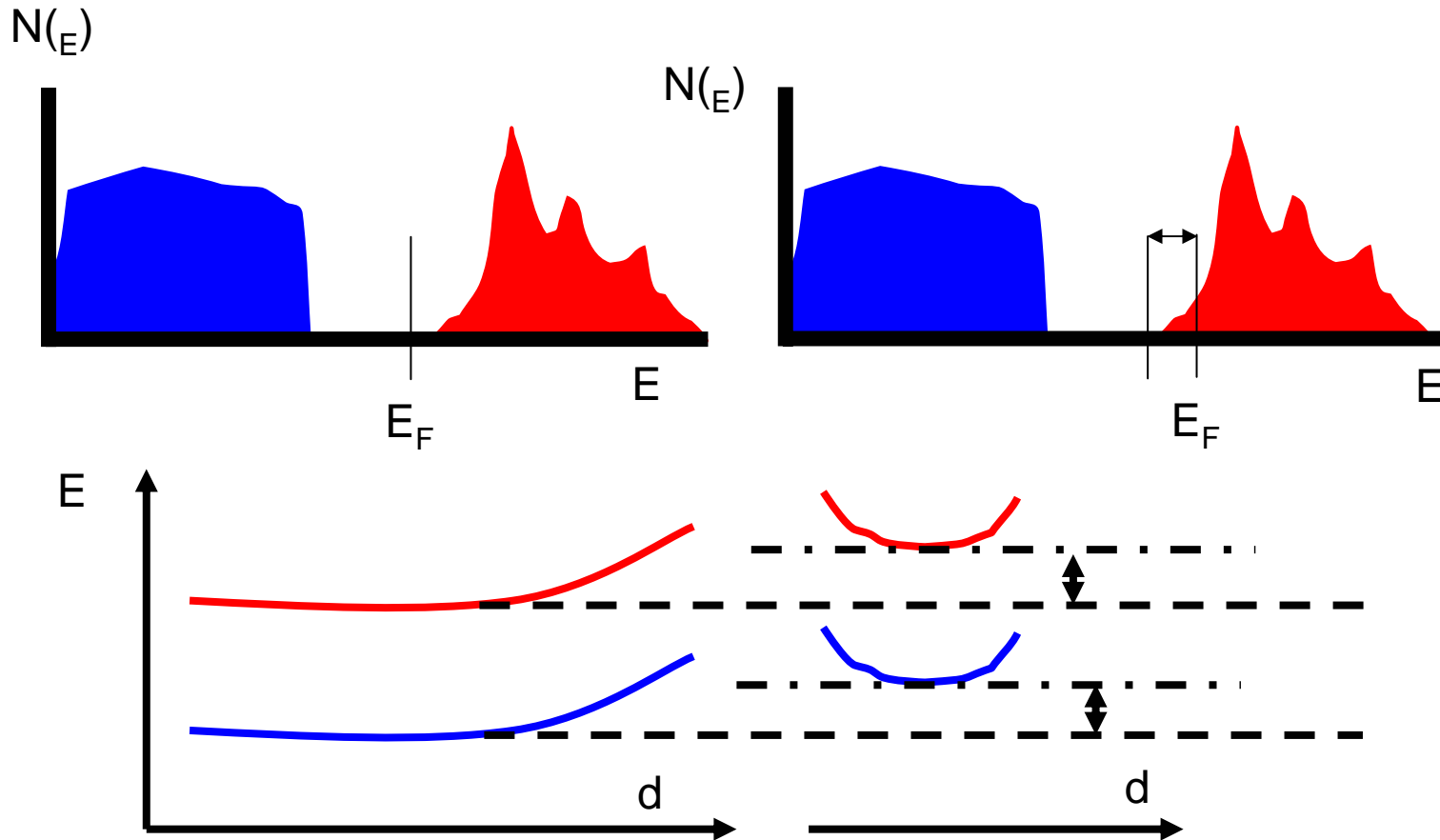
# Catalytic Function

## Chemical vs. Structural Complexity

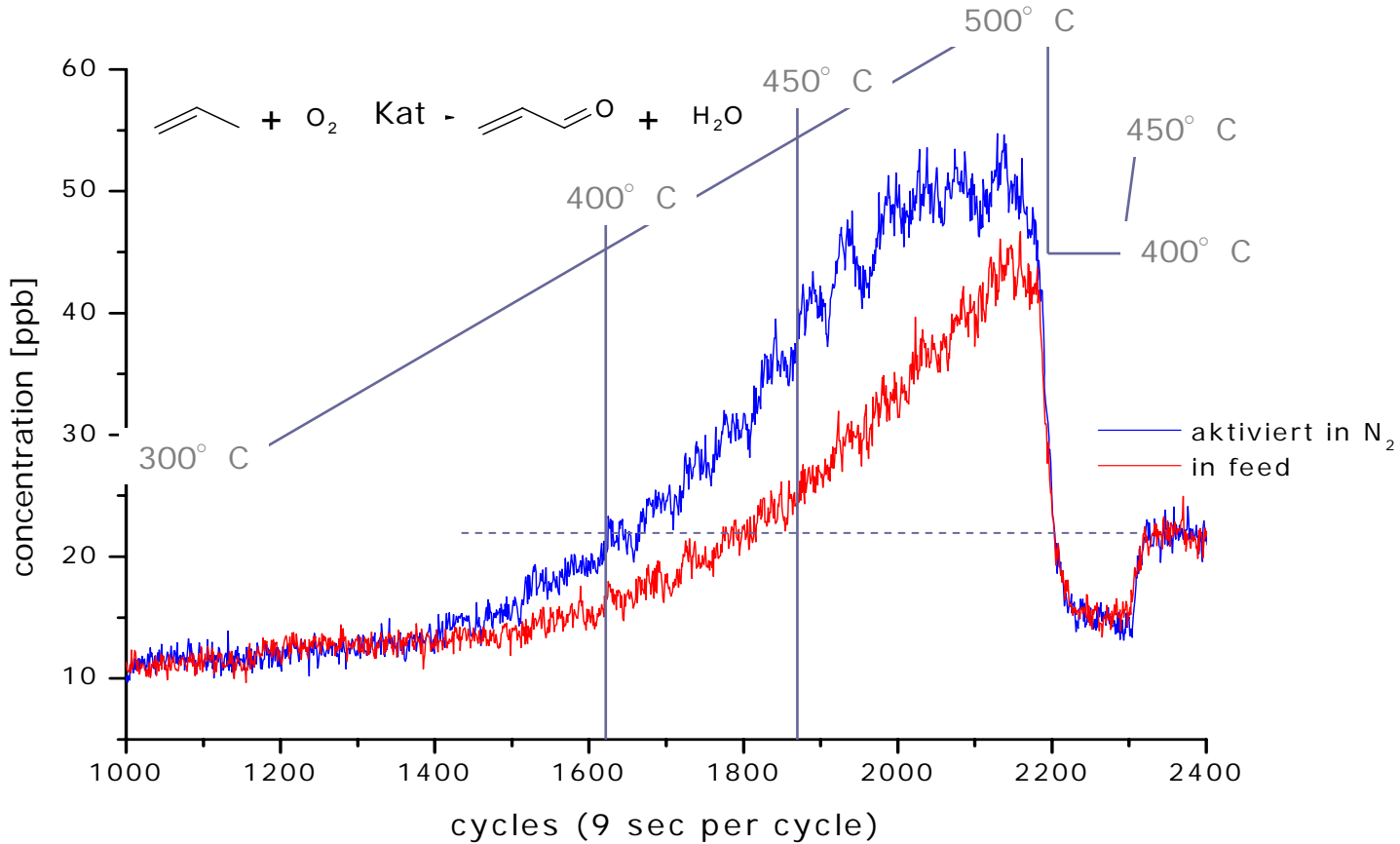




# electronic structure of semiconducting nano-oxides



# The function of nano- $\text{MoO}_3$



on

Mo-  
Si (111)  
on and



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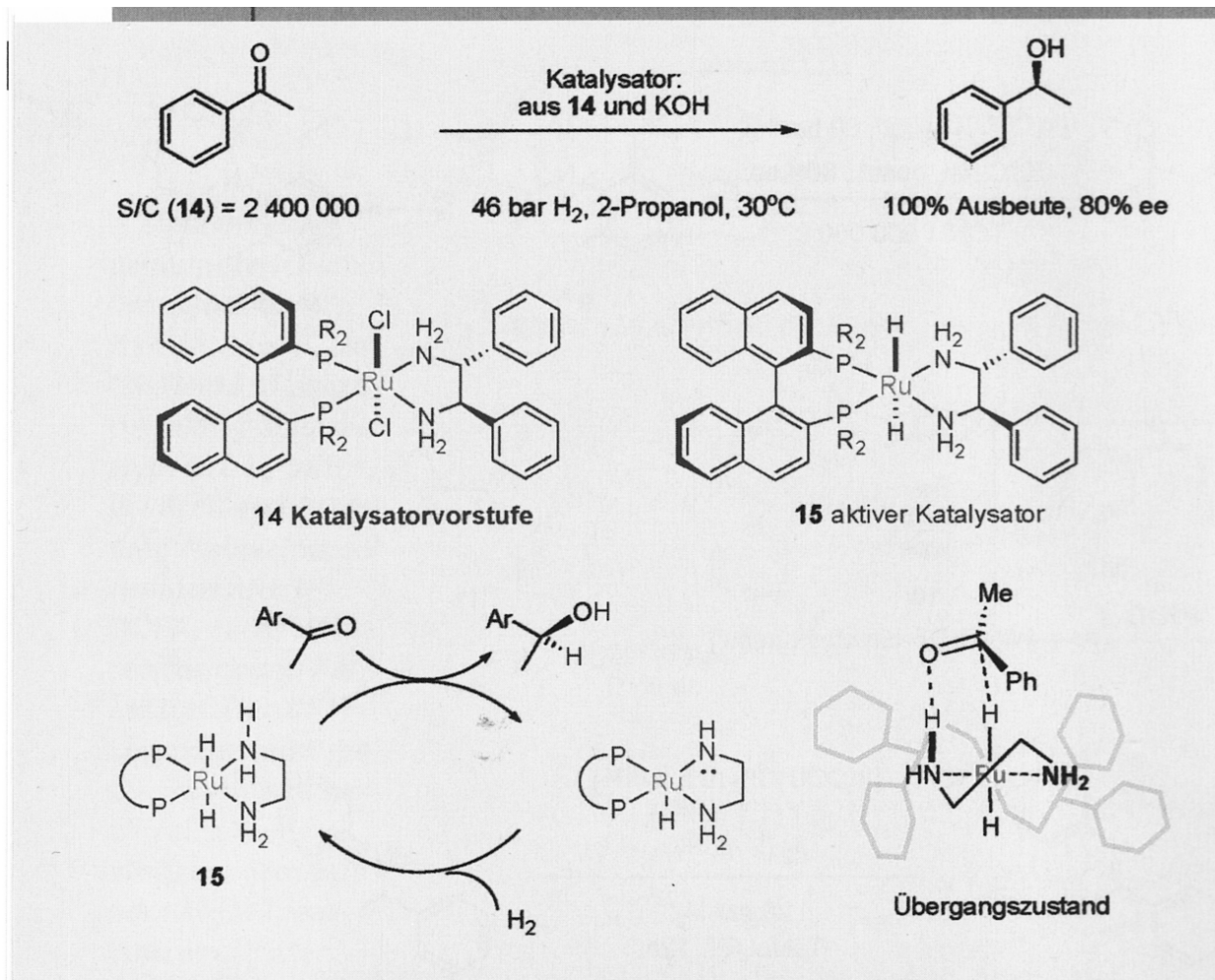
# Qualitative models “concepts”

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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
- Leads to guidelines for catalyst development without a *knowledge* base
- Generic concepts of catalyst function from a large body of such information (see textbook Thomas and Thomas)



# The molecular phenomenology



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

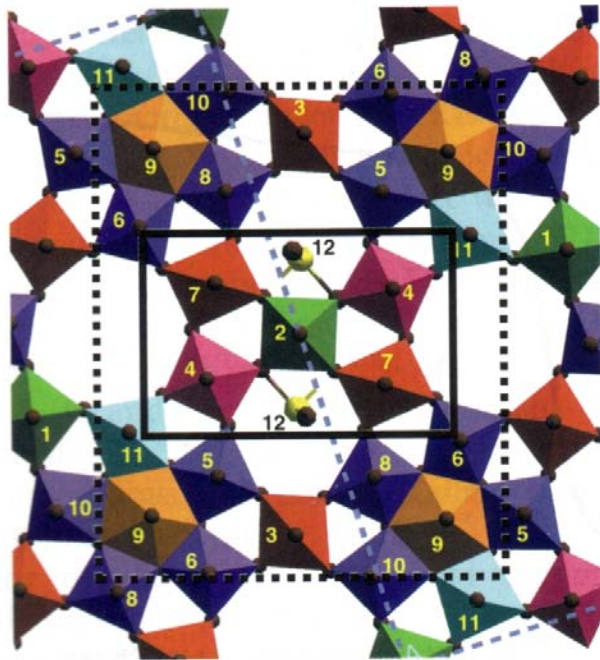
Enantioselective hydrogenation



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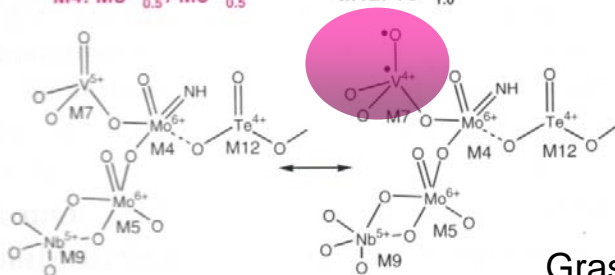
# The heterogeneous analogy



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?



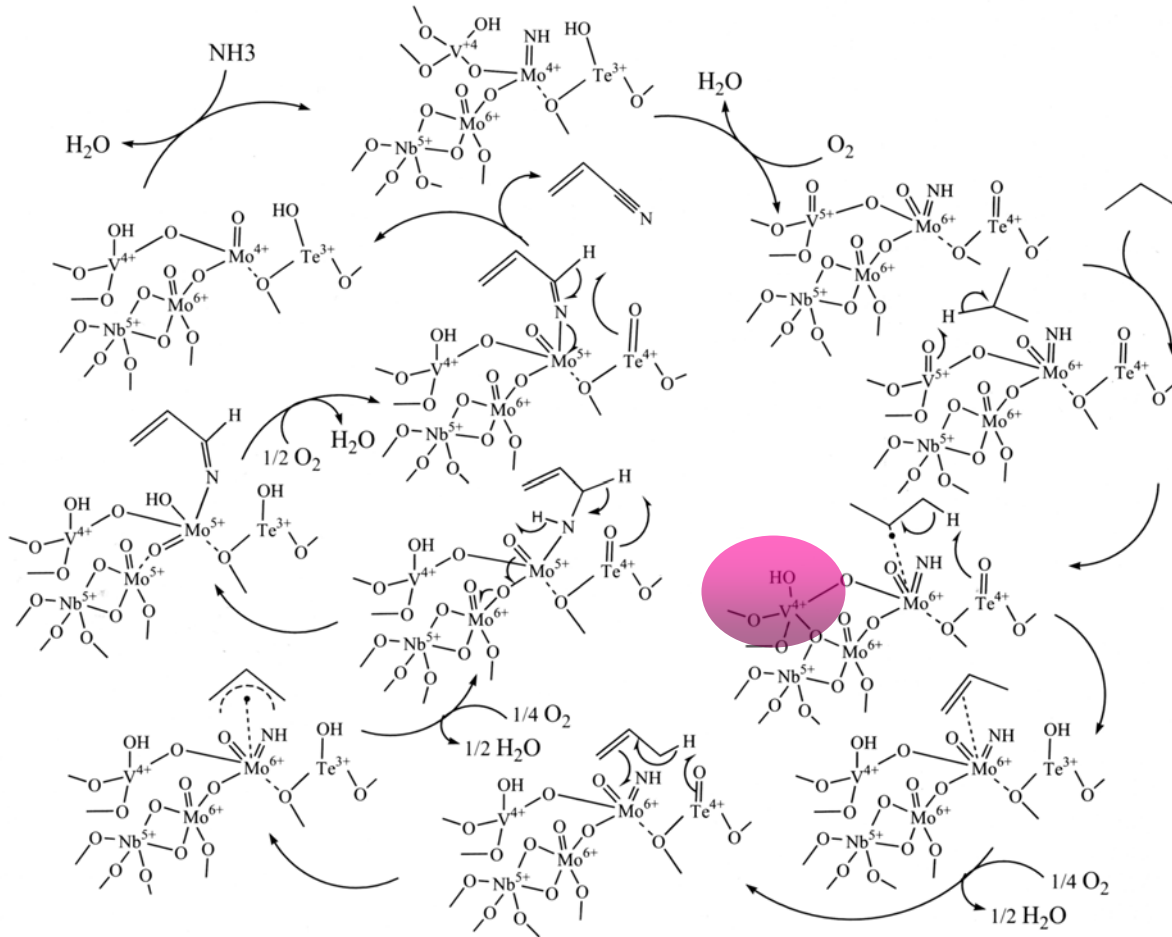
Grasselli et al



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# The heterogeneous analogy



Some critical intermediates and the configuration of the active sites were found to be not impossible form 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



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# Epilogue

Properties and status of models in catalysis





# Models: Necessity

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- Any catalytic reaction is too complex to be understood on “real systems”
- Multi-scale issues, structural dynamics and transport dynamics inhibit disentangling of reaction network
- Only in-situ analysis of real systems can 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





# Model properties

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- Models are structurally and chemically well-defined
- Models allow in-situ analytics
- Models allow to determine their surface structure “where are which atoms”
- Models are slow in their function allowing to isolate individual reaction steps
- Models should not need structure-distorting activation steps such that their definition is lost
- Models perform the desired reaction, no proxys



# Model types

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- No model for any complete catalyst function
- Models on atomic scale; single crystal approach and multi-scale theory
- Only limited function as mesoscopic effects “surrounding, molecular-molecular interaction
- For these dimensions no models so far (beginning in enzymes and 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 (photosystem II, but Wacker reaction)
- 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

