The relation between model and real systems in heterogeneous catalysis research

Just for curiosity or more?

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Overview

• 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
Why catalysis?

The relevance of catalysis in chemistry, justification of a large scale effort
Catalysis and economics (2004)

- 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
Organic base products

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Demand mtons</th>
<th>Price per ton €</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene</td>
<td>105</td>
<td>510</td>
</tr>
<tr>
<td>propylene</td>
<td>62</td>
<td>437</td>
</tr>
<tr>
<td>butadiene</td>
<td>9</td>
<td>410</td>
</tr>
<tr>
<td>benzene</td>
<td>36</td>
<td>399</td>
</tr>
</tbody>
</table>

There is a huge incentive to replace steam-cracker feedstocks.
The need to find an understanding of catalysis: sustainability of technology

<table>
<thead>
<tr>
<th>Process</th>
<th>Size tons per a</th>
<th>Waste/product</th>
</tr>
</thead>
<tbody>
<tr>
<td>refining</td>
<td>$10^8$</td>
<td>0.1</td>
</tr>
<tr>
<td>Bulk chemicals</td>
<td>$10^6$</td>
<td>5</td>
</tr>
<tr>
<td>Fine chemicals</td>
<td>$10^4$</td>
<td>50</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>$10^2$</td>
<td>50</td>
</tr>
</tbody>
</table>

R. A. Sheldon, 1997

Excluding solvent waste
Why we need catalysis: N/H uncatalyzed is unreactive

![Graph showing partial pressure vs. temperature in Kelvin (K) for p(H)/p0 and p(N)/p0. The graph illustrates the increase in partial pressure with temperature.]
Why we need a catalyst: A Haber Bosch system
Process considerations

Consider the downstream use
Molecular nanostructures

It is the surrounding "mesosotstructure" that makes the active site reactive

Catalysis: a mature science?

• 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)
Why models in catalysis?

The complexity issue, justification of the reductionistic approach
Model systems

- 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)

• 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

• 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

Fe-H

Fe-N

Low pressure static data

Fe(111)

Fe(100), T = 693 K

Fe(110)

N₂ exposure

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Models of catalyst surfaces

Trypsin, an enzyme

Somorjai 1994
The dynamic catalyst

- 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

1.4 nm Ru/C/Ba
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

• 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
Model strategy

- Functional definition
- Structural definition
- complex model systems (dynamical)
- single crystal well-defined (static)
- „practical“ catalyst -reactive-
- In-situ analysis
- choice?
- pragmatic

system descriptor (p,T,[])

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Structure of working catalysts

• 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
There is no evidence of amorphous character in the Mo_{7.5}V_{1.5}NbTeO_{29} or Mo_{6}Te_{2}VO_{24} phases of the active Mo–V–Nb–Te–O\textsubscript{x} catalyst. The catalytic activity is ascribed to the respective microcrystalline phases.

The superior catalytic effectiveness of the Mo_{7.5}V_{1.5}NbTeO_{29} phase stems from the multimetallic/multivalent character of its active sites composed of four different elements, three of which have at least two readily accessible oxidation states each available to them under reaction (redox) conditions.

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.

R.K. Grasselli et al.
Preparation of $\text{Mo}_{1.3} \text{Te}_{0.23} \text{Nb}_{0.125} \text{O}_x$: „Slurry method“

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

NH$_4$VO$_3$ (0.038 mol V)  
(powder)

Te(OH)$_6$ (0.029 mol Te)  
(powder)

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

$\text{MoV}_{0.30} \text{Te}_{0.23}$  
$T = 80^\circ$ C / pH = 5.5

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

Cool down to 40° C

Mo$_{0.30}$V$_{0.23}$Te$_{0.23}$ Nb$_{0.13}$  
(precursor)

275° C  
(10° C/min) / 1 h  
static air

Mo$_{0.30}$V$_{0.23}$Te$_{0.23}$ Nb$_{0.13}$  
(calcined)

600° C  
(2 ° C/min) / 2 h  
He flow

Mo$_{0.30}$V$_{0.23}$Te$_{0.23}$ Nb$_{0.13}$  
(activated)

Spray-drying

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The liquid phase in synthesis

no single molecular species explains the observed spectrum during heating within 13 min to 323 K: vanadyl linkers between Mo oligomers reduction of Mo and/or V

phase separation in solution no 'M1 molecule'

Mo-tellurates Mo-V compounds
Ag: in EO synthesis

• 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)

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

J. Schnadt, A. Michaelides, J. Knudsen, R. T. Vang, K. Reuter, E. Løgsgaard, M. Scheffler, and F. Besenbacher
PRL 2006
Ag nanoparticles: why size can matter

Figure 8.9. Catalyst particle viewed as a crystallite, composed of well-defined atomic planes.

Somorjai 1981
Dynamics: AgO (gaps)
What models in catalysis?

Surface science is not the only model strategy required
Numerical models

• Microkinetics with a set of elementary steps derived from surface science experiments
• Identification of the rds from energetics
• Ab-inito calculation of critical steps and their transition states
• Incorporation of experimental values fro 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

\[ \text{N}_2 + \text{cat} \rightarrow \text{N}_2 \text{ (ads)} \quad (1) \]

\[ \text{N}_2 \text{ (ads)} + \text{cat} \rightarrow 2\text{N(ads)} \quad (3) \]

\[ \text{H}_2 + 2\text{cat} \rightarrow 2\text{H(ads)} \]

\[ \text{N(ads)} + \text{H(ads)} \rightarrow \text{NH(ads)} + \text{cat} \quad (4) \]

\[ \text{NH(ads)} + \text{H(ads)} \rightarrow \text{NH}_2\text{(ads)} + \text{cat} \quad (6) \]

\[ \text{NH}_2\text{(ads)} + \text{H(ads)} \rightarrow \text{NH}_3\text{(ads)} + \text{cat} \quad (8) \]

\[ \text{NH}_3\text{(ads)} \rightarrow \text{NH}_3 + \text{cat} \quad (11) \]
The result of a model


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:
The classical description of a reaction

Ammonia synthesis from Nielsen et al (1972)

\[ r = \frac{k^*_a a_{N_2} - k^*_b \left( a_{NH_3} \right)^2 / \left( a_{H_2} \right)^3}{\left[ 1 + k^*_c \left( a_{NH_3} \right)/ \left( a_{H_2} \right)^\gamma \right]^{2\alpha}} \]

Fitting to experimental data
3 rate constants
Stoichiometry parameter \( \gamma \)
Inhomogeneity parameter (Temkin) \( \alpha \)
Gaps

• 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$_2$: A model

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

K. Reuter et al
H. Over et al
CO oxidation over RuO$_2$: A model

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

- 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

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

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

Bäumer et al, 100x100nm
Nanostructured Mo-oxide

Supramolecular phase:
Nanocrystals of a well-defined phase (octahydrate anion of MoO$_3$)
intergrown in various relative orientations
Disordered volume elements with glassy structure
Catalytic Function
Chemical vs. Structural Complexity

\[ \text{m/e} = 56 \]

\[ T \, [\text{K}] \]

\[ (\text{MoVW})_5\text{O}_{14} \]

\[ [\text{Mo}_{36}\text{O}_{118}]^{8-} \]
electronic structure of semiconducting nano-oxides
The function of nano- MoO$_3$

<table>
<thead>
<tr>
<th>Temperature, (K)</th>
<th>Mo average valence</th>
</tr>
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<tbody>
<tr>
<td>373</td>
<td>5.94</td>
</tr>
<tr>
<td>473</td>
<td>5.96</td>
</tr>
<tr>
<td>573</td>
<td>5.98</td>
</tr>
<tr>
<td>673</td>
<td>6.0</td>
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**Absorption Energy**

<table>
<thead>
<tr>
<th>Temperature, (K)</th>
<th>Absorption Energy, (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>0.0</td>
</tr>
<tr>
<td>473</td>
<td>1.0</td>
</tr>
<tr>
<td>573</td>
<td>2.0</td>
</tr>
<tr>
<td>673</td>
<td>3.0</td>
</tr>
<tr>
<td>773</td>
<td>4.0</td>
</tr>
</tbody>
</table>

**In-situ EXAFS**

*in-situ confocal RAMAN microscopy*

Spin-coating of Mo-isopropoxide onto Si (111)

Controlled activation and oxidation

Temperature (°C): 300, 400, 450, 500

<table>
<thead>
<tr>
<th>Concentration [ppb]</th>
<th>cycles (9 sec per cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1000</td>
</tr>
<tr>
<td>20</td>
<td>1200</td>
</tr>
<tr>
<td>30</td>
<td>1400</td>
</tr>
<tr>
<td>40</td>
<td>1600</td>
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<td>50</td>
<td>1800</td>
</tr>
<tr>
<td>60</td>
<td>2000</td>
</tr>
<tr>
<td>70</td>
<td>2200</td>
</tr>
<tr>
<td>80</td>
<td>2400</td>
</tr>
</tbody>
</table>

**Acrolein (m/e = 56)**
**CO$_2$ (m/e = 44)**
**H$_2$O (m/e = 18)**

10 % propene + 10 % O$_2$

<table>
<thead>
<tr>
<th>Temperature, (°C)</th>
<th>Concentration [ppb]</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>10</td>
</tr>
<tr>
<td>400</td>
<td>20</td>
</tr>
<tr>
<td>450</td>
<td>30</td>
</tr>
<tr>
<td>500</td>
<td>40</td>
</tr>
</tbody>
</table>

aktiviert in N$_2$
in feed

Konvektive Reaktion auf den Becher

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Qualitative models “concepts”

- 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

Enantioselective hydrogenation

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

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
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
Epilogue

Properties and status of models in catalysis
Models: Necessity

• Any catalytic reaction is to 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

• 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

- 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

• 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