Modern Concepts of Heterogeneous Catalysis

Modern motivations

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Modern

• Catalysis is since over a century an enabling science and technology.
• It emerges from synthetic chemistry (catalysts and new molecules) and from physical chemistry (course of a chemical reaction, quantum theory).
• More than 10 Nobel awards were devoted.
• As an independent science still problematic:
• Concepts, models, gaps, “real systems”
Systems: C1 chemistry
Motivation

- Despite its enabling role and several disciplinary attempts:
  - Chemical engineering
  - Surface science and theory
  - Combinatorial chemistry
- Catalysis is still an empirical science.
- Modern motivation: the energy challenge.
- Program:
  - The energy challenge
  - A review over concepts
Structure of a challenge
A sustainable architecture with flexibility

- solar refinery
  - methane
  - ammonia
  - methanol
- hydrogen
- photochemistry
- smart grid
- electricity
- mobility transportation
- heating, process
- combustion
- CO₂
- solar fuels
  - fossil fuels
  - chemical storage, transportation, trading
- hydro wind PV
- biomass
- battery
- power to gas
- electrolysis
Possible realization and critical elements
Dynamics of Pt in OER

Irreversible roughening
Enhanced hydrogen production
Oxidic overlayer pre-requisite for OER
Nature of the Pt “rust” film

Ambient pressure XPS at very high resolution and extreme surface sensitivity:

Pt is covering with a one monolayer film of hydroxide in water leaving divalent Pt.
Alternatives

Electrical current lead

Reaction centre

Mn₃O₄ Hausmannit

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• Problems with switching stability, over-potentials and use of non-sustainable materials.
• OER is the critical reaction.
• Electro-catalysts are dynamical and transform in-situ (learn from chlorine electrolysis).
• Stability and scalability are critical design parameters for second generation systems.
• Lack of solid fundamental understanding of electro-catalytic processes and their material requirements (empirical optimization less likely to be sufficient).
Energy supply: a systemic challenge
Catalysis is the core technology

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RS: Angew. Chem 2011
Power to gas: reaction network of a “simple” hydrogenation

Control variables:
Oxophilicity of active site
Kinetic competition hydrogenation-condensation
Performance: Stable during test (!)

<table>
<thead>
<tr>
<th>Ref</th>
<th>Cat</th>
<th>CO₂ X</th>
<th>CO X</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>1</td>
<td>Ni/Ru</td>
<td>14</td>
<td>1.8</td>
</tr>
<tr>
<td>1</td>
<td>Ru</td>
<td>9.5</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>(Mn,Zn) FeO₄</td>
<td>10</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

- Complex NP can replace noble metals.
- Stability above 24 h is unknown.

1: Sezume et al., Faraday, I (1979)

Performance is not facile,
No complete hydrogen conversion,
Side products unclear
Carbon deposition
Carbon deposition as prime problem

Deposition of carbon limits catalyst performance: loss of active phase through CNT formation.

Protection through carbide formation: labile under reaction conditions: catalyst design allowing for facile carbon dissolution.
Dynamics of Ni under hydrogenation conditions
Summary

- High performance systems contain non-sustainable noble metals.
- Base metal systems insufficient in stability and performance (mind educt purity: CO₂!).
- Complex material dynamics from reaction network activated.
- Gas purification for enduser gas distribution system despite high (90%) selectivity reduces efficiency and drives cost.
- Material and process development needed after verification of fundamental reaction understanding.
Concepts

• Catalysis is a science based on concepts that are partly founded in theory.
• This well-founded part is the result of surface science and of quantum theory and is valid for processes with adsorption / activation as rate-controlling step without selectivity.
• Catalysis is a multi-scale phenomenon and requires thus simultaneous research in several chemical disciplines.
Catalysis is a multi-scale phenomenon

- nano
- meso
- macro

- activity, selectivity
- stability
- conditions
- performance

- elementary steps
- active site
- active mass
- mesostructure
- catalyst formulation
- reactor
- operating process

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Concepts

• The concepts developed differently in the disciplines of catalysis:
  – Homogeneous
  – Heterogeneous
  – Biological.

• Common to all: catalysis is a kinetic effect and cannot modify thermodynamic limits.

• Consequence: catalysts are non-equilibrium systems.

• They contain only few functional sites in a matrix of stabilizing species!
Heterogeneous catalysis

• Two concepts for active sites:
  – Mean field approximation: all sites are equal and all geometric sites are active (Langmuir model).
  – Active sites are embedded in non-active surface sites allowing adsorption (checkerboard model, Taylor model).

• All theory and most model systems operate with the Langmuir model, Taylor model mostly qualitative: CO oxidation, gold catalysis: “perimeter models”.

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Activity and selectivity

• Catalyst quality according to yield per unit
  – Mass: well measurable
  – Total surface area: more realistic
  – Active surface area: sometimes possible
  – Active site most desired: not countable (tof concept)

• No absolute measure possible for any catalyst today!!

• Selectivity is fraction of atoms (!!) from feed that are found in the desired product:
  – Analytical accuracy and definition ambiguities.
Catalytic activity in what units?

CO oxidation over 2% Pd/Fe$_2$O$_3$
Basic concepts

• Catalysts bring together reactants by adsorption.
• At special high energy sites ("active sites") adsorbates can react (exchange atoms in molecular entities).
• Catalysts operate cyclically recuperating the active site.
• Excessive strength of adsorption kills catalyst by poisoning the active site.
The standard model (Langmuir, Taylor, Ertl)

- A heterogeneous catalyst can be approximated by a single crystal surface.
- No compound of the catalyst with its reactants.
- The terminating atoms are all equal and active.
- Adsorption strength may change this: perimeter of islands in CO oxidation; (dynamics).
- Surface atoms can be defined precisely with atom co-ordinates.
- They can be studied by surface science structural tools.
Function of a catalyst: Static SM

Adsorbate structure dynamical (chemical waves), Bulk is “irrelevant”, no chemical transformations sub-surface
Application: energy storage
A catalytic reaction is given by the ability of a catalyst to activate reactants:

- Optimum between strength of adsorption and heat of reaction: the Sabatier (Tamaru) principle.
- Modern version the “vulcano” trend.
- Concept allows predictions of catalytic reactivity from simplified theories.
- Offering the chance to “test” many catalysts by computation rather than by experimental screening.
- Reduction of the search space for potent catalysts.
Example: CO methanation

Table 3
Metal contents in the different supported catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Re</th>
<th>Fe</th>
<th>Co</th>
<th>Ru</th>
<th>Rh</th>
<th>Ni</th>
<th>Ir</th>
<th>Pd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal load (wt%)</td>
<td>1.64</td>
<td>0.64</td>
<td>2.12</td>
<td>1.87</td>
<td>1.71</td>
<td>3.47</td>
<td>1.51</td>
<td>1.34</td>
<td>1.14</td>
</tr>
</tbody>
</table>

Fig. 9. Activities of different supported transition metals as a function of molecular CO chemisorption energies.
What do we design?

Is there a way to pre-define the correct electronic structure?

Stability and decomposition kinetics
Fundamental gap: complexity

- We consider individual mechanistic processes.
- Desire for single molecule spectroscopy (SPM).
- We observe $10^{17}$ ($10^{10}$ planets of humans) simultaneous events:
  - Can there be a unique relation?
  - Statistics: distribution of properties leads to distributions of reaction pathways:
    - Beware of using the term "mechanism".
    - In homogeneous systems the distribution of properties is much narrower.
Model systems

• are “real” (contrast to high performance 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).
Model reactions
Structure effects

Pentenes to pentane

Hydrogenation in the presence of subsurface H [Pd particles]

No hydrogenation without subsurface H [Pd(111)]

Freund, Shaikhutdinov et al., Angew. Chem. 2003

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Active sites

• The central concept in all types of catalysis.
• Act as coordination centres allowing to exchange adsorbates (fragments) and electrons (oxidation state).
• Are modified during chemical bond rearrangement.
• In a catalytic cycle they are regenerated into their most active initial state.
• Adaptivity required as mostly the reaction product is more reactive than the starting species: selectivity through autogenous partial deactivation.
Selective oxidation:
Coupling of transformation and material
It is inadequate to concentrate on the “reaction”

- **educts to products**
  - Activation fast
  - Desactivation slow

- **active site to de-activated site**
  - Fast reaction, "synthesis"
  - Cyclic activation, fast

- **matrix re-structuring**
  - Stabilization lifetime

Reaction dynamics Paralleled by Material dynamics

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Reaction pathway catalyst

Dynamics and adaptation

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Reaction networks: 
A catalyst activates it all!
Dynamics vs stability

Activation energy for propane consumption

<table>
<thead>
<tr>
<th>Absolute Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
</tr>
<tr>
<td>20.0</td>
</tr>
<tr>
<td>40.0</td>
</tr>
<tr>
<td>60.0</td>
</tr>
<tr>
<td>80.0</td>
</tr>
<tr>
<td>100.0</td>
</tr>
<tr>
<td>120.0</td>
</tr>
</tbody>
</table>

H₂O / O₂ / propane

0 / 0 / 3

T = 973 K

MoVTcNb 8612 sieve fraction

GHSV = 5000 h⁻¹

T = 350 - 390 °C
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 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
The mean field approximation is a upper bound for modelling active sites.

Courtesy of F. Studt and J. Nørskov, SLAC Stanford
Macrokinetic descriptions: transport and atomistic processes?

(1): CH₄ + 2 O₂ → CO₂ + 2 H₂O
(2): 2 CH₄ + 0,5 O₂ → C₂H₆ + H₂O
(3): CH₄ + O₂ → CO + H₂O + H₂
(4): CO + 0,5 O₂ → CO₂
(5): C₂H₆ + 0,5 O₂ → C₂H₄ + H₂O
(6): C₂H₄ + 2 O₂ → 2 CO + 2 H₂O
(7): C₂H₆ → C₂H₄ + H₂
(8): C₂H₄ + 2 H₂O → 2 CO + 4 H₂
(9): CO + H₂O → CO₂ + H₂
(10): CO₂ + H₂ → CO + H₂O

Fig. 3 Transition from the kinetic regime to the diffusion-controlled regime of a heterogeneous catalytic fluid-solid reaction carried out on a porous catalyst.

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Modern: The generic innovation

- We can follow the dynamics of catalysts.
- In-situ (not “operando”) spectroscopy.
- Precison structural analysis (high-energy sites).
- Allow catalysts to respond to the chemical potential of the reactants:
- Catalysts activate themselves!!
- Do not attempt to design active structures too reactive as activation will damage the system.
A research approach (both for models and high performance systems)

- inorganic chemistry
- design concept
- synthesis
- kinetic test
- structural dynamics
- in-situ function
- model

**structural parameters:**
- phase purity, morphology, texture
- XRD (LEED)
- EM
- EXAFS
- BET
- SPM

**intrinsic reaction parameters:**
- activation energy, rates
- chemisorption calibrmetry
- IR
- TDS

**changes in structural parameters:**
- phase purity, morphology, texture

**surface dynamics:**
- adaptive sites, minority species, electronic structure
- surface-bulk coupling
- spectroscopy

**qualitative concept:**
- active site, reaction parameters
- compare to theory
- plausibility of reaction sequence

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Summary

coordination chemistry

ligands

reactive site

active element

reactants incorporation

compound

roughness

termination

metal-support interaction

strain, epitaxy

transport

reaction conditions

Composition, T_p

nanostructure

solvents

cocatalysts

support
Conclusions

• We understand concepts of catalysis such as active sites, adsorption, checkerboard structures.
• We have quantitative models for simple cases where no selectivity occurs and where dynamics does not change structure in the window of relevant parameters.
• The chemical complexity of active sites in demanding reactions and the absence of a general model that couples properties of catalyst and reactants are missing for a design of catalysis.
• More empirical work is less useful than conceptual work mapping out the essence of complexity.
• A theory is emerging allowing to solve these issues.
Dem Anwenden muss das Erkennen vorausgehen

Max Planck

Thank You