Operando Electron Microscopy

in catalysis

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Outline

- Why electron microscopy?
- Why operando experiments?
- Operando electron microscopy
- Limitations
- Example

### Industrial Catalysis

**Industrial sector** | **Production/ton y⁻¹**
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Petrochemicals | $10^6$-$10^8$
Bulk chemicals | $10^4$-$10^6$
Fine Chemicals | $10^2$-$10^4$
Specialities/pharmaceuticals | $10$-$10^3$

- annual worldwide value of chemicals (incl. petrochemicals) produced by catalytic reactions is about US$ 2–4 trillion
- 80-90% of chemical conversion require catalysts
- 2004: global market for catalysts: US$ 13 billion

→ **Found by empirical optimization**

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Renewable natural energy sources are replenished at a higher rate than they are consumed.

- Demand on catalyst systems of different complexity will rise dramatically.
- Can not be compensated by empiricism

→ Transit to renewable energy sources requires transfer to knowledge based catalyst tailoring

→ The function of the interface has become important (activation vs. deactivation).
The performance of a solid depends on the structure of the interface that forms under reaction conditions. It (mainly) depends on
- the real structure of the interface (→ handle for synthesis group)
- the dynamics of the interface under „working“ conditions, i.e. the local chemical potential
Functional Interfaces – research examples –

Solid-solid interfaces [1]

Solid-liquid interfaces [2]

Solid-gas interfaces [3]

The importance of the real structure - the averaging gap in catalysis -

- The real structure alters the local chemistry
- Less than 1% of the accessible surface area can be active

S.W. Chee et al. Chem. Rev. 2023, DOI: 10.1021/acs.chemrev.3c00352.
The complexity of catalysts

**Model systems for ammonia synthesis**

**Norskov:** model that is based on Ertl’s experimental work and derived under the assumption of homogeneous surface states: $\text{N}_2$ dissociation on 111 surfaces is the rate determining step.


**When does complexity start?**
The complexity riddle – When does it start? -

MgO

Oxidative coupling of methane: $2 \text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + 2 \text{H}_2\text{O}$

Corner atoms at single atomic steps are slightly off-centered

The surface structure of Isostructural complex oxides

Oxidative dehydrogenation of ethane

\[ \text{C}_2\text{H}_6 + 0.5\text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \]

- Isostructural molybdenum and vanadium based oxides exhibit different surface structures:
  \( \rightarrow (\text{Mo,V})\text{O}_x \): defective surfaces
  \( \rightarrow (\text{Mo,V,Te,Nb})\text{O}_x \): smooth surfaces
- The different surface structures affect the catalytic performance of the oxides in the selective oxidation of small alkanes:
  \( \rightarrow (\text{Mo,V})\text{O}_x \): more active
  \( \rightarrow (\text{Mo,V,Te,Nb})\text{O}_x \): more selective

Untangling the structural complexity would not have been possible without aberration corrected (S)TEM.

L. Masliuk et al. submitted.
Untangling the local chemistry of a solid

S.W. Chee et al. Chem. Rev. 2023, DOI:10.1021/acs.chemrev.3c00352.
A catalyst is a functional material that continually consumes and produces active sites under reaction conditions.

The working structure of a heterogeneous catalyst is influenced by chemical dynamics:

- Irreversible: transformation
- Reversible: dynamic

Actuator: local chemical potential, i.e., the gradient of the chemical potential along the interface.

Handles for reactor engineers to set the correct flow conditions.
Healing of Surface Defects during ODE

Healing of surface defects plays an essential role for selectivity in oxidation reactions.

L. Masliuk, et al, to be submitted.
The (local) chemical potential

μ_A > μ_B: transformation of substance A into substance B, or transport from place A to place B
μ_A = μ_B: no transformation, no transport, chemical equilibrium
μ_A < μ_B: transformation of substance B into substance A, or transport from place B to place A.

\[ \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{V,T,p,n_j,pH;n_i \neq n_j} \]
On the influence of the local chemical potential on the structure

Catalysis induced dynamics and frustrated phase transition

Differences of the surface structure compared to the bulk.

X. Li et al. Chemical Science 2019, 10, 2429-2443.
S.W. Chee et al. Chem. Rev. 2023, DOI:10.1021/acs.chemrev.3c00352.
Frustrated phase transition

Optimal working structure forms under reaction conditions, e.g. strain, polyhedra distortions, sub-surface chemistry, surface states, structural bulk changes, redox transition

Figure 3. Images of the (a) Cu$_2$O(110), (b) Cu$_2$O(110) with interstitial oxygen, and (c) CuO(110) surfaces.

M. Greiner at al. JACS 2017, 139, 11825-11832.
Insights into fixed bed reactors – The local chemical potential at work

Pt coated $\alpha$-Al$_2$O$_3$ foam during methane oxidation

- Carbon deposits can be observed
- Different morphology

MoO$_x$ coated $\gamma$-Al$_2$O$_3$ spheres during ethane oxidation

FHS: ceramic front heat
GP: Gas phase before and after the catalyst bed.

The importance of *operando* measurements in heterogeneous catalysis research

The interaction of solids with gases:
- Complex reaction networks
- Stoichiometric reaction
- Sorption processes

„The *operando* methodology combines *structure and activity measurements in a single experiment*, using a reaction cell that meets the requirements for both, a catalytic reactor and an *in situ* cell.“

*ideally under technical conditions"
## Structural averaging operando techniques

### Table 1. Existing in situ/operando techniques in catalysis with maximum operating conditions in all modes

<table>
<thead>
<tr>
<th>Technique</th>
<th>Window/capillary material</th>
<th>Maximum reported working conditions</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR</td>
<td>KBr/ZnSe/MgF₂/CaF₂/silicon/ diamond/germanium/KRS-5</td>
<td>850&lt;sup&gt;7&lt;/sup&gt;</td>
<td>200&lt;sup&gt;8&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>XAS</td>
<td>quartz/glass/beryllium/sapphire/ polyimide/carbon/aluminum</td>
<td>850&lt;sup&gt;9&lt;/sup&gt;</td>
<td>250&lt;sup&gt;10&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Raman</td>
<td>quartz/sapphire/alumina</td>
<td>800&lt;sup&gt;11&lt;/sup&gt;</td>
<td>200&lt;sup&gt;12&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>UV-vis</td>
<td>quartz/sapphire</td>
<td>800&lt;sup&gt;13&lt;/sup&gt;</td>
<td>300&lt;sup&gt;14&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>EPR</td>
<td>quartz</td>
<td>550&lt;sup&gt;15&lt;/sup&gt;</td>
<td>20&lt;sup&gt;16&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>XRD</td>
<td>sapphire/quartz</td>
<td>1,100&lt;sup&gt;17&lt;/sup&gt;</td>
<td>35&lt;sup&gt;17&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>NMR</td>
<td>zirconia/glass</td>
<td>250&lt;sup&gt;18&lt;/sup&gt;</td>
<td>400&lt;sup&gt;18&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

Operando experiments in catalysis

Ethylene epoxidation over Cu$_2$O

How about spatial distribution?

M. Greiner at al. JACS 2017, 139, 11825-11832.
Operando electron microscopy

Where do changes occur?

Stimuli:
Gas Reactants (Composition and Pressure), Temperature

Response:
Converted Products, Heat Transfer

Before Reaction → During Reaction → After Reaction

S.W. Chee et al. Chem. Rev. 2023, DOI:10.1021/acs.chemrev.3c00352.
Heterogeneous Catalysis on the local scale
Heterogeneous Catalysis on the macroscale
Heterogeneous catalysis is a multiscale phenomenon

Scale-bridging microscopy line up

The essence of catalysis:
- Ensemble property
- Real structure of a catalyst
- Synergistic effects
- Transport phenomena

**Operando SEM**
- Imaging
- (EDX)

**Operando TEM**
- (S)TEM imaging
- Electron diffraction

**Identical location TEM**
- (S)TEM imaging
- Electron diffraction
- EELS
- EDX

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2Ag + Cl₂ → 2AgCl @ 7 mbar

Environmental TEM

Fig. 2. Effect of scattering of electrons on gas molecules in a differential pumped EFTEM. (a) Scattering of electrons on gas molecules (indicated by hatched lines) takes mainly place between the first set of pressure limiting apertures, which extend the focal length of the objective lens. (b) Normalized image intensity (without a specimen present) measured on a pre-GIF Ultrascan CCD camera, plotted as a function of gas pressure for Ar at three different acceleration voltages. The data points have been fitted to exponential functions.

Figure 4. Gold nanoparticles supported on a graphene substrate. The images are (from left to right) recorded in vacuum ($10^{-4}$ Pa), and in 290 Pa and 430 Pa of hydrogen, respectively.
Closed cell systems – room temperature –

I.M. Abrams et al. Science 1944, 100, 273-274.


Figure 3
View of the installed apparatus. Two tubes connect the valves at the objective lens with the box mounted on the left side of the microscope. The box contains a membrane pressure gauge with a reference vacuum (measuring range 0.1 to 50 Torr), a gas storage tank (capacity 1 liter), five valves and the necessary connections for evacuating, filling, and flushing with gas. The indicated flow scheme facilitates the use of the apparatus.
Closed cell -room temperature-

$$2Ag + H_2S \rightarrow Ag_2S + H_2$$ @RT

Closed cell systems – room temperature –


Fig. 14. Growth process of plate shaped Cu crystal which is formed by the reduction of CuI at 700°C in hydrogen gas of 100 Torr.
Closed cell systems –first operando experiments-

Fig. 3. Au cluster during annealing at 350 °C, in H₂ (4 mbar). The weak contrast is due to the drift.

+ conversion detection

A brief history on closed cell and MEMS development

1959
- First integrated circuit

1962
- First silicon pressure sensor by Honeywell

1991
- First proposal for SiN windows in EM by Heide [48]

1992
- Closed cell with SiN windows for in situ atmospheric SEM from Green et al. [49]

1994
- Deep reactive ion etching (DRIE)

1995
- Microfabricated packed-bed reactor by Losey et al. [32]

2000
- Modern MEMS heating chip by Allard et al. [53]

2003
- Modern MEMS liquid cell from Zheng et al. [58]

2008
- Modern MEMS gas cell by Creemer et al. [58]

2009
- Monolithic MEMS gas cell for high operating pressure by Creemer et al. [81]

2014
- MS conversion data acquired alongside in situ TEM experiment: first operand experiment by Vendelbo et al. [23]
Closed cell system – MEMS based

https://crozier.engineering.asu.edu/
S.W. Chee et al. Chem. Rev. 2023, DOI:10.1021/acs.chemrev.3c00352.
Closed cell system – catalyst loading on a MEMS chip -

Heater spiral (400 x 400 µm²)

Thin SiN windows (~50 nm): add additional contrast

Courtsey: Dr. M. Boniface, FHI
Technical Conditions include Reaction Cells

Almost any analytical technique can be equipped with in situ/operando technology.

Comparison of different reactors for the same catalytic measurements

S.W. Chee et al. Chem. Rev. 2023, DOI:10.1021/acs.chemrev.3c00352.
Aberration corrected FEI Titan
Pressure: up to 1 bar
Temperature: up to 1000°C
Home built gas feeding station
QMS Mass Spectrometer (detection of conversion from µg amounts of sample and bad space hourly velocity)

denssolutions.com
Gas-beam-sample interaction – i.e. beam damage –

Cleaning of carbon deposits @ RT

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S.W. Chee et al. Chem. Rev. 2023, DOI:10.1021/acs.chemrev.3c00352.
The influence of electron beam on function and structure of the functional materials

Change of the function 
BaTiO$_3$

Threshold values for damaging CNTs

Structure growth (Au/MgO) in the presence of Water vapor

Particle shrinkage and coalescence in air Pt/Al$_2$O$_3$

Water in the electron microscope

S.W. Chee et al. Chem. Rev. 2023, DOI:10.1021/acs.chemrev.3c00352.
M. Boniface et al. Topics in Catalysis 2020, 63, 1623-1643.
### Comparative Assessment of different operando EM techniques

<table>
<thead>
<tr>
<th>Technique</th>
<th>Relative Strengths</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETEM</td>
<td>• High spatial resolution (subnanometer)</td>
<td>• Limited liquid-phase options</td>
</tr>
<tr>
<td></td>
<td>• Moderately high temporal resolution (subsecond)</td>
<td>• Low pressure</td>
</tr>
<tr>
<td></td>
<td>• Spectroscopy possible</td>
<td>• Beam damage</td>
</tr>
<tr>
<td></td>
<td>• High temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Conversion detection possible</td>
<td></td>
</tr>
<tr>
<td>ESEM</td>
<td>• Transport process and macroscale phenomena</td>
<td>• Low pressure</td>
</tr>
<tr>
<td></td>
<td>• Moderate spatial resolution (nanometers)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• High temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Conversion detection possible</td>
<td></td>
</tr>
<tr>
<td>Quasi in situ TEM (gas)</td>
<td>• Atomic resolution</td>
<td>• Possible artifact formation during cooling and change of environment</td>
</tr>
<tr>
<td></td>
<td>• Spectroscopy possible</td>
<td>• No real-time information</td>
</tr>
<tr>
<td></td>
<td>• Flexible devices for different application</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Only “limited” beam effect</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Conversion detection possible</td>
<td></td>
</tr>
</tbody>
</table>

#### Gas phase

- · Ambient pressure
- · High spatial resolution (subnanometer)
- · Moderately high temporal resolution (subsecond)
- · Spectroscopy possible
- · High temperature
- · Conversion detection possible

#### Liquid phase

- · Moderate spatial resolution (nanometer)
- • Beam damage (very low electron fluxes and doses required)
- · Moderately high temporal resolution (subsecond)
- · Limited spectroscopy options
- · Relevant environment of electrolyte and applied potentials
- · No conversion detection

#### Quasi in situ
Can we see active sites?

Cu/ZnO/Al₂O₃ for methanol synthesis

Is it that trivial?

Can we see active sites?

Pt@CeO$_2$

Can we see active sites?

- No, we can’t.
- Structural complexity and diversity that can exist under reaction conditions
- Frustrated phase transition
- Metastable and transient states
- Changes of bulk and morphology

S.W. Chee et al. Chem. Rev. 2023, DOI:10.1021/acs.chemrev.3c00352.
Microsc. Microanal. 2020, 26, 220.
Example -CO Oxidation over Pt nanoparticles-

**CO Oxidation**

\[ 2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2 \]

Surface reconstruction\(^1,^2\)

Morphology changes\(^3\)


Conclusion

- Operando electron microscopy as an important tool to study the local dynamics of heterogeneous catalysts.

- There are limitations, e.g. beam damage and seeing active sites.

- The outcome can complement structural averaging data that might be needed to finalize the puzzle.
Thank you very much for your Attention!