Challenges in Catalysis and Dynamics of Surface Chemistry at LCLS II

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Define LCLS **science opportunities** created by the enhanced capabilities and capacity of LCLS-II with focus on:
1. biological sciences, 2. materials science, 3. chemical sciences, and 4. atomic, molecular and optical physics.

In each of the four identified science areas establish a **priority list of desired user experiments** including the ability of placing samples in the beam, preparing the desired state of the sample (e.g. by optical, THz methods), synchronizing the transient states with the x-ray pulses and the required detectors for the x-ray and particle signals from the sample.

Identify important **x-ray beam parameters** to address the envisioned science opportunities, such as photons per pulse, pulse length, 120-Hz-based pulse trains, band width and spectral purity, polarization, special requirements in transverse (diffraction limited) and longitudinal (transform limited) coherence...
Outline

Scientific challenges

→ Chemical energy storage and heterogeneous catalysis
→ Key areas of interface dynamics: Heterogeneous catalysis and charge transfer, non-linear processes

Experimental approaches

→ Current studies of surfaces chemistry at LCLS

Proposed Experiments

→ Future experiments at LCLS II: Excitation and probe schemes
→ Selected problems in catalysis

Technical requirements

→ Dedicated endstation & beam parameters
Key challenge: Storage of renewable energy

Renewable energy replaces fossil fuels only with chemical storage

- Solar refinery
  - methane
  - ammonia
  - methanol
- Hydrogen
  - electrolysis
- Photochemistry
- Solar fuels
  - fossil fuels
- Chemical storage, transportation, trading
- Photovoltaics, electrochemistry, catalysis

...requires advances in photovoltaics, electrochemistry, catalysis,....
Key challenge: Storage of renewable energy

Renewable energy replaces fossil fuels only with chemical storage

Opportunity for ultrafast x-rays:
Element specific probing of chemical reaction dynamics
Spatial resolved imaging of local structures

...requires advances in photovoltaics, electrochemistry, catalysis,...
CO$_2$ chemistry and methanol formation

Selected reactions in the C$_1$/H/O ternary system:

Methanol formation from CO$_2$ (e.g. using Cu-Zn-Alumina catalyst):

\[ \text{CO}_2 + 3 \text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}; \quad \Delta H(300 \text{ K}) = -49.6 \text{ kJ/mol.} \]

CO$_2$ chemistry: Key relevance for chemical energy storage
CO₂ chemistry and methanol formation

Selected reactions in the C₁/H/O ternary system:

Key issues:
Selective control of the reactivity of hydrogen, oxygen and H₂O
Processes must be reliable and efficient on industrial scale

Reactivity of activated oxygen controls overall reaction

Methanol formation from CO₂ (e.g. using Cu-Zn-Alumina catalyst):

\[ \text{CO}_2 + 3 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}; \quad \Delta H(300 \text{ K}) = -49,6 \text{ kJ/mol.} \]

CO₂ chemistry: Key relevance for chemical energy storage
Ammonia synthesis

Pathways for nitrogen fixation:

‘Haber-Bosch’

- Haber-Bosch-Process: N-N bonds are broken first, followed by hydrogenation

- In nature the hydrogenation of the N-N molecule is followed by breaking the bonds

- Why is this different?

- Can we control how the reaction occurs by external parameter?
Simple minded view of heterogeneous catalysis

Heterogeneous catalysis:
- Reduced reaction barrier at the catalyst surface
- Prominent examples:
  - Automotive catalyst
  - Ammonia synthesis (~1.4% of world energy consumption)
  - Future challenge: chemical energy storage and CO₂ conversion

Current understanding:
Basic properties of the dynamics at single crystal surfaces are (fairly) well understood
Catalysis operates on a paradigm of active sites that perform full cycles of chemical reactions. Typically only 1% of catalyst surface contributes to the reaction yield.

Fundamental missing insight concerns the temporal evolution of the whole reaction cycle (not just selected elementary steps) in comparison to simple activating adsorption: Is one active site doing all the reaction or are several sites involved?

Likewise unexplored is the coupling of structural dynamics of the catalyst (adaptive site) to the elementary processes of a reaction with selectivity channels.
Model approach to heterogeneous catalysis

„Real Catalyst“

relevant length scales:
1 Å– 100 nm

Model Catalyst

Metal Single Crystals

Oxides / Oxide Films

Metals/Oxides Multiple Oxides

Modified Supports

Multiple Components

Poisons Promoters

Nanostructured Oxides

Increasing Complexity

Atomically clean surfaces

Ultrahigh vacuum conditions

Courtesy J. Libuda, Univ. Erlangen-Nürnberg
Key areas in surface and interface dynamics

Heterogeneous catalysis

- Elementary steps and time evolution of surface reactions
- Dynamics of the catalyst and its active sites
- Ultrafast energy transfer on a microscopic level

Interfacial charge transfer

- Dynamics of heterogeneous electron transfer
- Competing processes in photovoltaic/optoelectronic devices: polaron formation, exciton recombination…
- Electrochemistry

Ultrafast x-ray photonics

- Two color x-rays and non-linear optics: interfaces, nanostructures, …
Interfacial electron transfer and photovoltaics

‘Classic’ example: Solar Energy Conversion in the Grätzel Cell  
Nature (1991)

- Photoabsorption in a dye sensitizer
- Charge injection into CB
- Electrochemical redox system

**Electron dynamics:**
- Ultrafast charge transfer
  - \( \tau_{CT} = 25 - 50 \text{ fs} \)
  - \( \tau_{CT} < 3 \text{ fs} \) (LUMO+1)

**Molecular dynamics:**
- Solvent response upon photoexcitation and ET
- Relaxation of molecular structure/conformation

![Diagram of a solar cell](image)

**Diagram Notes:**
- **TiO_2** and **Dye sensitizer**
- **Energy (eV)**
- **CB** and **VB**
- **Electrolyte**
- **Ru-N3 dye**
- **Photoabsorption**
- **Charge injection**
- **Electrochemical redox system**

*References:*
- JCP B 103, 3110 (1999)
Interfacial electron transfer and photovoltaics

Organic-inorganic hybrid systems: light harvesting & optoelectronics

Electron dynamics:
- Ultrafast charge transfer
- Relaxation of molecular structure/conformation
  \[ \tau_{CT} = 25 - 50 \text{ fs} \]
- Ultrafast charge transfer
  \[ \tau_{CT} < 3 \text{ fs} \] (LUMO+1)

Molecular dynamics:
- Solvent response upon photoexcitation and ET
- Competition between charge transfer, transport, and trapping

Key issues:
- Coupling between electronic and nuclear degrees of freedom
- Electron dynamics and solvent response upon photoexcitation and ET
- Competition between charge transfer, transport, and trapping

Notes:
- \( \text{TiO}_2 \) and dye sensitizer
- Energy levels: CB, VB, LUMO, HOMO
- Electron and molecular dynamics
- \( \text{JCP B} 103, 3110 \text{ (1999)} \)
- \( \text{Nature} 418, 620 \text{ (2002)} \)

Dye sensitizer interaction with \( \text{TiO}_2 \) and electrolyte

Energy levels diagram:
- CB (Conduction Band), VB (Valence Band)
- LUMO, HOMO (Light and Heavy Organic Molecules)
- \( E_F \) (Fermi Level)
- Charge transfer process
- \( \text{RuN}_3 \) as an example of a dye sensitizer
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Dynamics of surface reactions

Heterogeneous catalysis:
- Reduced reaction barrier at the catalyst surface

Reaction dynamics:
- Time evolution of elementary steps like adsorption or desorption

Goal: Microscopic understanding of surface reactions
Ultrafast energy redistribution after optical excitation of a metal surface

fs-laser pulse

- monolayer is optical thin
- substrate-mediated excitations dominate


University of Hamburg and CFEL, Stockholm University, Helmholtz-Zentrum Berlin, Fritz Haber Institute, SLAC (LCLS, SIMES, SSRL, SUNCAT)

Surface Science Endstation:
X-ray spectrometer, grazing incidence elliptical grating
XES & fluorescence yield XAS
First LCLS pump-probe experiments: CO on Ru(001)

„A simple experiment“

fs laser induced desorption of CO

Map transient changes of valence electronic structure by x-ray emission spectroscopy (XES) as a function of laser/FEL delay & FEL energy
Photon in – photon out methods: X-ray emission

**x-ray absorption (XAS)**

- Probe chemical state
- Unoccupied valence state

**x-ray emission (XES)**

- Element specific and orbital sensitive map of partial DOS
- Occupied valence state


Resonant inelastic X-ray scattering (RIXS)

Photon Energy

PHOTON IN $h\nu$

XAS

binding energy

$2\pi^*$

PHOTON OUT $h\nu'$

Photon Energy

CO/Ru(001)

Excitation energy (eV)

Emmission energy (eV)

$E = -1.15\text{ps (Before Pump)}$

$E_{\text{F}}$

$O1s$

$4\sigma$

$532.2$

500 510 520 530 540 550

530 531 532 533 534 535

529

CO/Ru(001)
Resonant inelastic X-ray scattering (RIXS)

**Photon IN** $h\nu$

Photon Energy

Excitation energy (eV)

**XAS**

X-ray Absorption Spectroscopy

$2\pi^0$ in XAS

**Photon OUT** $h\nu'$

Photon Energy

**XES**

X-ray Emission Spectroscopy

Emission energy (eV)

Exci...
LCLS pump-probe experiments: CO on Ru(001)

Optical laser excites translations and vibrations, promotes CO into reactive state closer to other reactants.

Synchrotron data for the steady state:

Top site

Bridge site

Higher coordination with Ru atoms:

2π* shifts to lower energies (XAS)

dπ-states gain intensity (XES)

Selective excitation in XES enhances or suppresses the signal from the dynamically changing species.
**Discussion: Precursor state of exited CO adlayer**

**Time-resolved RIXS** provides detailed picture of electronic structure changes of a excited adlayer during a surface reaction.

Pronounced transient shifts of binding energies cannot be explained by thermal population of ground state PES.

**Theory** by J. Norskov & coworkers:

*ab-initio* molecular dynamics with full electronic structure „on the fly“

Entropic barrier: Population of precursor state.
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LCLS II should definitely allow performing two-color x-ray experiments:

1) stimulated x-ray Raman spectroscopy

Option of two-color x-ray experiments would open wide area of new scientific opportunities.
LCLS II should definitely allow performing two-color x-ray experiments:
1) stimulated x-ray Raman spectroscopy
2) x-ray pump (resonant excitation) & x-ray probe experiments
3) multi-electron dynamics/double core hole excitation
4) attosecond processes on timescale of core hole lifetime
Proposed experiments: CO$_x$ hydrogenation

**Examples for two color experiment in catalysis:**

- Time of formation of activated oxygen vs. activated methane: “Clock experiments” by excitation of H$_3$COH (or H$_2$CO) and simultaneous element specific probing of oxygen and carbon.

Reactivity of activated oxygen controls overall reaction.
Examples for two color experiment in catalysis:

- Time of formation of activated oxygen vs. activated methane: “Clock experiments” by excitation of H$_3$COH (or H$_2$CO) and simultaneous element specific probing of oxygen and carbon.

- State-selected activation of di-oxygen followed by methane activation with variable delays between 10 fs and 100 ps (x-ray pump – x-ray probe experiment)

- Simultaneous observation of a catalyst atom (e.g. Mg) and carbon or oxygen to elucidate possible catalyst dynamics (x-ray pump – x-ray probe experiment).

- ’Action spectroscopy’: Depletion of reaction intermediates by x-ray pump influences reaction rate or selectivity
Proposed experiments: CO$_x$ hydrogenation

CO$_x$ hydrogenation on Cu-Zn catalyst

- Do surface exposed atoms change their structure during hydrogenation of CO$_2$?

- Time delay between the first hydrogenation to formate and consecutive hydrogenations to methanol with respect to CO bond dissociation?

- Is there a structural dynamics of Zn atoms in comparison to Cu at the reactive site?

F. Studt and J. Nørskov, SLAC Stanford
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Beam parameters

- **Required photon energies** should be >250 eV for C 1s edge (or better >150 eV for S 2p edge)

- **Temporal resolution** as well as jitter between optical laser and x-rays should be better than 10 fs. Control of pulse delay and jitter also for two-color x-ray experiments. (*Self-seeding?*)

- **Excitation schemes** must be extremely versatile: Optical pump with IR, THz, UV… and/or x-ray pump and x-ray probe

- **Diagnostics and reliability** is a key issue

- **Variable polarisation**: from circular to linear polarized (both horizontal and vertical). (*-> no chamber rotation including detectors necessary -> precise alignment*)
Surface science endstation

Current endstation (mobile)  
Anders Nilsson

Electron spectrometer:  
VG Scienta R3000 for XPS

X-ray spectrometer:  
grazing incidence elliptical grating for XES  
fluorescence yield XAS

Needs for LCLS II:  
Dedicated instrument for surface science and catalysis.  
A general RIXS spectrometer will not fulfill the requirements 
Various (non-linear) excitation schemes (e.g. stimulated Raman) will require special geometries  
Features: Sample preparation, high pressure cells...

base pressure: low 10^{-10} torr
Summary

Scientific challenges

- Chemical energy storage as a key challenge
- Key technological areas are heterogeneous catalysis, electrochemistry and photovoltaics

Current experiments at LCLS

- CO desorption probed by time-resolved RIXS

Proposed Experiments

- Two color x-ray experiments would open a new field of opportunities
- Key issue in catalysis: CO_x hydrogenation

Technical requirements

- Dedicated endstation & beam parameters