Characterization of solid catalysts

1. Introduction

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Schuit Institute of Catalysis
How does a catalytic reaction proceed?

A + B → P

Answer: via a cycle of elementary reaction steps in which molecules react in a complex formed with sites on the catalyst, which are regenerated at the end of the cycle.
What is a catalyst?

Catalysts

- increase the rate of a reaction
- without being consumed in the process

- offer alternative, energetically favorable pathways for reactions
- enable reactions to occur under industrially achievable conditions
- allow selective production routes without or with less undesirable byproducts
- are the work horses of the chemical industry
- are the key enablers for sustainable (green)production

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length and time scales in catalytic processes

- **microscopic**: catalytic surface, catalytically active particles on a support
- **mesoscopic**: shaped catalyst particles
- **macroscopic**: catalyst bed in a reactor

Supported catalyst

Metal – support combination determines
• particle morphology
  • crystal planes exposed
  • steps, kinks, etc
  • type of interface with support
• degree of reduction
• particle size
• stability against sintering
• involvement of support in reactions
Requirements of a successful catalyst

• High activity per unit volume in the reactor
• High selectivity at high conversion; no byproducts
• Long life time
• Regenerable
• Reproducible preparation & activation
• Thermal stability (no sintering)
• High mechanical strength
• High attrition resistance

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Aims of Catalyst Characterization

Fundamental research:
- composition & structure
- of the catalytic surface
- under reaction conditions
- in atomic detail

Applied research:
- identification of properties that discriminate between poor and successful catalysts
Catalyst Characterization

What do we want to know about a supported catalyst?

- **Composition**
  - XPS, XANES, XRD
  - ICP, AAS

- **Surface Composition**
  - LEIS, XPS, SIMS

- **Particle size**
  - Electron Microscopy
  - H₂ chemisorption
  - XRD line broadening

- **Surface Area**
  - Total: BET
  - Metal: H₂ or CO chemisorption
  - Pore size distribution:
    - Hg porosimetry

- **Morphology**
  - Particles: TEM
  - Overall: SEM

- **Adsorbed Gases**
  - FTIR, DRIFTS, TPD

- **Structure**
  - XRD
  - XPS, EXAFS, TEM

- **Degree of Reduction**
  - TPR, XPS, XANES

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Things that Matter in a Supported Catalyst:

**Structural Parameters**
- Particle orientation and size
- Particle shape and structure: facets, edges, corners, steps, defects
- Structure of particle-support interface
- Type and site of catalyst poisons
- Type and site of catalyst promoters
- Structure of support surface and support defects

**Kinetic Effects**
- Restructuring effects (particle reshaping structural flexibility)
- Confinement effects (limited number of surface and bulk sites, coverage fluctuations)
- Communication effects (surface diffusion between different sites)
- Geometric effects (specific sites, e.g., edges, corners, facets, site blocking effects, structural effects of promoters...)
- Electronic effects (electron confinement, electronic support / promoter interaction...)
- Support effects (adsorption, diffusion, reaction on support / promoter)
‘All’ Characterization Techniques can be derived from:

- Energy
- Intensity
- Spatial configuration
- Time structure
- Temperature
- ......
### How often are techniques used

<table>
<thead>
<tr>
<th>Technique</th>
<th>Percentage</th>
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<tbody>
<tr>
<td>XRD</td>
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<tr>
<td>Adsorption</td>
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<td>XPS</td>
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<td>SIMS</td>
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**Journals:**
- Applied Catalysis A & B
- Catalysis Letters
- Journal of Catalysis
  - Jan 2002 and Oct 2006

**Total Number of Articles:** 8112
## In situ or under vacuum?

<table>
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<tr>
<th>reaction conditions</th>
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<tr>
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<td>XRD, TP techniques</td>
<td>Infrared TP techniques</td>
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<td>Infrared and Raman</td>
<td>STM, AFM</td>
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<td>EXAFS, XANES, AFM</td>
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<tr>
<td>vacuum</td>
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Download the handout for this lecture from [www.catalysiscourse.com](http://www.catalysiscourse.com)

Read more in

Spectroscopy in Catalysis: An Introduction, Third Edition

J. W. Niemantsverdriet

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NB CHAPTER ONE AVAILABLE ON WEBSITE COURSE FOR FREE

gives many examples and references to the literature

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