Characterization of solid catalysts

9. Surface Science

Prof dr J W (Hans) Niemantsverdriet
Schuit Institute of Catalysis
How to model a catalyst

Particle on a flat support  Single crystal surface

Ultra High Vacuum System for Surface Science

- **LEED**
  Low Energy Electron Diffraction

- **STM**
  Scanning Tunneling Microscopy

- **AES**
  Auger Electron Spectroscopy

- **TPD / TPRS**
  Temperature Programmed Desorption and Reaction Spectrometry

- **RAIRS**
  Reflection Absorption Infrared Spectroscopy
Ultra High Vacuum System for Surface Science

- **LEED**
  Low Energy Electron Diffraction

- **STM**
  Scanning Tunneling Microscopy

- **AES**
  Auger Electron Spectroscopy

- **TPD / TPRS**
  Temperature Programmed Desorption and Reaction Spectrometry

- **RAIRS**
  Reflection Absorption Infrared Spectroscopy
Electrons: particles & waves

\[ \lambda = \frac{\hbar}{\sqrt{2 m_e E_{\text{kin}}}} \]

- \(\lambda\): wavelength of the electrons
- \(\hbar\): Planck's constant
- \(m_e\): mass of the electron
- \(E_{\text{kin}}\): kinetic energy of the electron.
Low Energy Electron Diffraction

$n \lambda = a \sin \alpha$

electrons
Low Energy Electron Diffraction

\[ n \lambda = a \sin \alpha \]
Nitrogen atoms on Rh(100)

LEED of Rh (100) + 0.5 ML N

Rh (100) - c(2x2) N

- Rh atom
- N atom
Nitrogen atoms on Rh(100)

LEED of Rh (100) + 0.5 ML N

LEED represents the reciprocal lattice

\[
\sin \alpha = \frac{n \lambda}{a}
\]

Rh (100) - c(2x2) N

or more precise (\sqrt{2}x\sqrt{2})45°
Surface Science

- **LEED** Low Energy Electron Diffraction
  structure of surfaces; ordered overlayers

- **STM**
  Scanning Tunneling Microscopy

- **AES**
  Auger Electron Spectroscopy

- **TPD / TPRS**
  Temperature Programmed Desorption and Reaction Spectrometry

- **RAIRS**
  Reflection Absorption Infrared Spectroscopy
Surfaces are not perfect...

- terrace sites
- kink sites
- step sites
- adatom
- vacancy
- step vacancy
Scanning Tunneling Microscopy
Tunneling images joint density of states
Tunneling images joint density of states
STM Pt-Rh (100) Surface

50% Pt–50% Rh

but surface:

69% Pt (dark)
31% Rh (bright)

C impurity: black

P.T. Wouda
B.E. Nieuwenhuys
M. Schmidt
P. Varga
Surf Sci 359 (1996) 17
STM images of oxygen atoms on Ru(0001) showing how oxygen atoms order into islands at higher coverages (0.09 and 0.12 ML respectively).

LEED = Low Energy Electron Diffraction

‘collective’ structure information of ordered surface layers on the basis of electron diffraction

needs periodicity

STM = Scanning Tunneling Microscopy

local structure information on the basis of electron tunneling between surface and tip

(‘joint density of states)
Surface Science

- **LEED** Low Energy Electron Diffraction
  structure of surfaces; ordered overlayers

- **STM** Scanning Tunneling Microscopy
  Local ‘structure’ of surfaces via electron density of states

- **AES** Auger Electron Spectroscopy

- **TPD / TPRS**
  Temperature Programmed Desorption and Reaction Spectrometry

- **RAIRS**
  Reflection Absorption Infrared Spectroscopy
Photoemission and Auger Electron Spectroscopy

- Photoelectron
- $E_k$
- $E_b$
- $\varphi$
- X-ray $h\nu$
- Photo emission

CatalysisCourse.com
Photoemission and Auger Electron Spectroscopy

Auger process

core hole

Fermi level

Vacuum level

$E_k$

$L_{2,3} (2p)$

$L_1 (2s)$

$K (1s)$

0

$\phi$

K or 1s

core hole
Auger Electron Spectroscopy

KL \text{ } L_{23} Auger electron

Auger process

E_k

Vacuum level
Fermi level

L_{23} \quad (2p)
L_1 \quad (2s)
K \quad (1s)

Kinetic energy of the Auger electron is fully characteristic of the element it originates from and it is surface sensitive
Auger peaks appear as small ‘bumps’ on the secondary electron spectrum (secondary electrons: suffered non-characteristic energy losses through scattering, etc.)
Auger peaks appear as small ‘bumps’ on the secondary electron spectrum (secondary electrons: suffered non-characteristic energy losses through scattering, etc.).
Example of Auger Electron Spectroscopy

AES of Cu(100) in Methanol Synthesis

- Cu(100), clean
- after MeOH synthesis
- heated to 500 - 550 K
- oxidized at 555 K
- MeOH synthesis

Example of Auger Electron Spectroscopy

If the Auger transition involves valence levels, the peaks may contain chemical information, as in this example of carbon on iridium.

A.D. van Langeveld and J.W. Niemantsverdriet unpublished data
Ultra High Vacuum System for Surface Science

- **LEED** Low Energy Electron Diffraction
  structure of surfaces; ordered overlayers

- **STM** Scanning Tunneling Microscopy
  Local ‘structure’ of surfaces via electron density of states

- **AES** Auger Electron Spectroscopy
  surface composition

- **TPD / TPRS**
  Temperature Programmed Desorption and Reaction Spectrometry

- **RAIRS**
  Reflection Absorption Infrared Spectroscopy
Temperature programmed desorption
Temperature programmed desorption
Temperature programmed desorption

- amount of adsorbed molecules
- indirect: adsorption sites
- heat of adsorption (!)

more than one adsorbate:
- reaction pathways
- activation energy (!)

Temperature Programmed Desorption

\[ r = - \frac{d \theta_A}{d t} = k_{des} \theta_A^n = \nu ( \theta_A^n ) \theta_A^n \exp \left( - \frac{E_{des} ( \theta_A )}{RT} \right) \]

Rate of desorption

Activation energy

Order

Prefactor

Rate constant

Temperature Programmed Desorption

\[ T = T_o + \beta t \]

Rate of heating
TPD: different desorption orders

Zeroth order

First order

Second order


TPD Analysis Methods

Redhead

$T_{\text{max}}$

relations
$E_{\text{des}} - T_{\text{max}}$
assume:
$\nu = 10^{13} \text{ s}^{-1}$

CAW

$W_{3/4}$
$W_{1/2}$

relations
$E_{\text{des}}, \nu - T_{\text{max}}, W$
extrapolate to zero coverage

Leading edge

In rate vs $1/T$

Construct Arrhenius plot
where coverage is $\sim$constant

TPRS \( \text{CO}_{\text{ads}} + \text{O}_{\text{ads}} \rightarrow \text{CO}_2 \)

**Rate equation (Arrhenius):**

\[
r = k \theta_o \theta_{\text{CO}} = \nu \theta_o \theta_{\text{CO}} e^{-\frac{E_{\text{act}}}{RT}}
\]

**Plot:**

\[\ln \left( \frac{r}{\theta_o \theta_{\text{CO}}} \right) \text{ vs } \frac{1}{T}\]
TPRS $\text{CO}_{\text{ads}} + \text{O}_{\text{ads}} \rightarrow \text{CO}_2$

Rate equation (Arrhenius):
$$r = k \, \theta_o \, \theta_{\text{CO}} = v \, \theta_o \theta_{\text{CO}} \, e^{-\frac{E_{\text{act}}}{RT}}$$

Plot:
$$\ln \left( \frac{r}{\theta_o \theta_{\text{CO}}} \right) \text{ vs } 1/T$$

Slope and intercept:
$$E_{\text{act}} = 103 \pm 5 \text{ kJ/mol}$$
$$v = 10^{12.7 \pm 0.7} \text{ s}^{-1}$$

Ultra High Vacuum System for Surface Science

- **LEED** Low Energy Electron Diffraction
  structure of surfaces; ordered overlayers

- **STM** Scanning Tunneling Microscopy
Local ‘structure’ of surfaces via electron density of states

- **AES** Auger Electron Spectroscopy
surface composition

- **TPD / TPRS** Temperature Programmed Desorption and Reaction Spectrometry
adsorbate coverage, reaction kinetics, activation energies

- **RAIRS** Reflection Absorption Infrared Spectroscopy

---

TU/e Technische Universiteit Eindhoven
University of Technology
Adsorption: loss of rotational degrees of freedom and lowering of CO stretch frequency
The IR Frequency of Adsorbed CO

or why CO is such a popular molecule in surface science

Gas phase CO: 2143 cm\(^{-1}\)
Linear CO: 2000 - 2130 cm\(^{-1}\)
Bridged CO: 1880 - 2000 cm\(^{-1}\)
Triple CO: 1800 - 1880 cm\(^{-1}\)
4-fold CO: below 1800 cm\(^{-1}\)

four factors contribute to shift:

- mechanical coupling (+ 30 cm\(^{-1}\))
- image dipole (-25 to -50 cm\(^{-1}\))
- dipole-dipole coupling (+ 10 to 30 cm\(^{-1}\))
- chemisorption bond (backbonding)
Several ways to perform vibrational spectroscopy

- Transmission
- Diffuse Reflection
- Attenuated Total Reflection
- Reflection Absorption
- Raman Scattering
- Sum Frequency Generation
- Electron Energy Loss
Dipole-dipole coupling between CO molecules increases the frequency.
Ultra High Vacuum System for Surface Science

- **LEED** Low Energy Electron Diffraction
  structure of surfaces; ordered overlayers

- **STM** Scanning Tunneling Microscopy
  Local ‘structure’ of surfaces via electron density of states

- **AES** Auger Electron Spectroscopy
  surface composition

- **TPD / TPRS** Temperature Programmed Desorption and Reaction Spectrometry
  adsorbate coverage, reaction kinetics, activation energies

- **RAIRS** Reflection Absorption Infrared Spectroscopy
  vibration modes, adsorbate identification
Download the handout for this lecture from www.catalysiscourse.com

Read more about

surface science techniques in Spectroscopy in Catalysis: An Introduction, Third Edition

J. W. Niemantsverdriet

Copyright 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
ISBN: 978-3-527-31651-9

gives many examples and references to the literature