Modern Methods in Heterogeneous Catalysis Research

Axel Knop-Gericke, November 21, 2003

Ion Scattering Spectroscopy (ISS)
Rutherford Backscattering (RBS)
Secondary Ion Mass Spectrometry (SIMS)
Mössbauer Spectroscopy

Outline

Ion scattering (basics)

Rutherford backscattering example

Low Energy ion scattering example

Secondary Ion Mass Spectrometry

Basics of sputter process

Examples

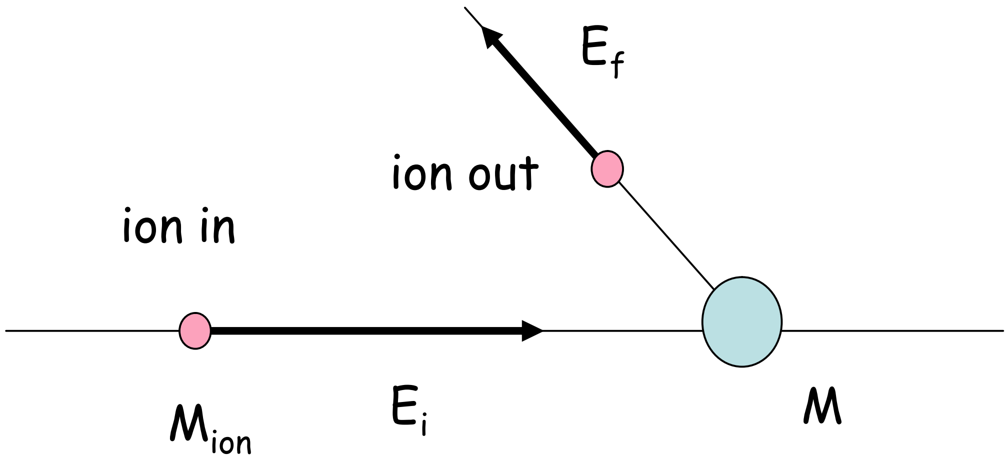
Mössbauer Effect

Mössbauer Spectrocopy

Examples

Summary

Ion Scattering: The Collision Process



$$K_M = \frac{E_f}{E_i} = \left(\frac{\left(M^2 - M_{ion}^2 \sin^2 \Theta\right)^{1/2} + M_{ion} \cos \Theta}{M + M_{ion}} \right)^2$$

K_M: kinematic factor

E_i: energy of the incoming ion

E_f: energy of the scattered ion

M_{ion}: atomic mass of the incoming ion

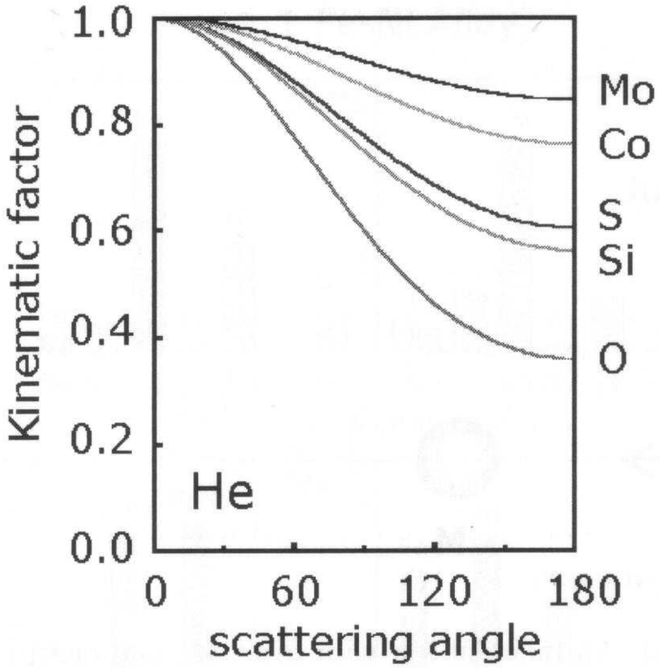
M: atomic mass of the scattering atom in the sample

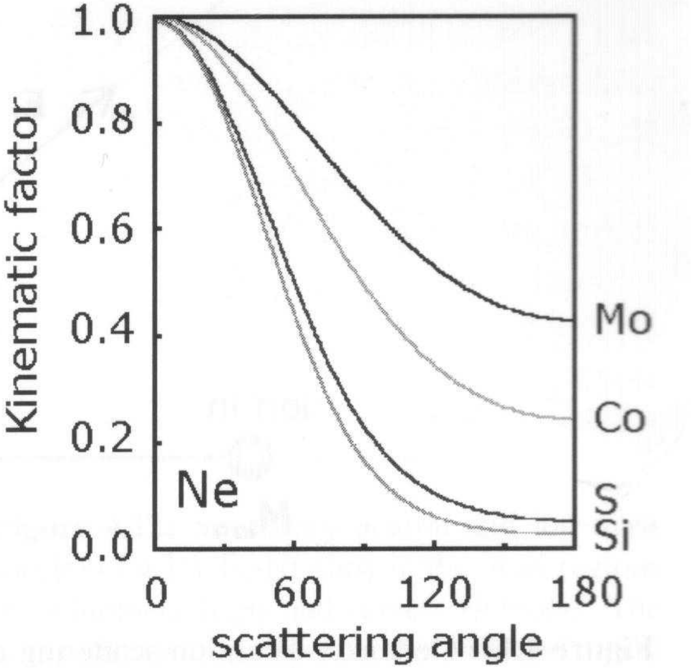
Θ: scattering angle

Ion Scattering: The Collision Process

$$\frac{E_f}{E_i} = \frac{M - M_{ion}}{M + M_{ion}}$$ Θ=90°

$$\frac{E_f}{E_i} = \left(\frac{M - M_{ion}}{M + M_{ion}}\right)^2$$ Θ=180°





Rutherford backscattering spectrometry

Characteristic:

Sample type: thin films and bulk solids

Depth information: 2μm

Latheral resolution: 1 x 1mm

Depth resolution: 1-10 nm

Mass resolution: 1 atomic mass unit for $Z < 40$

Detection limit on Si: N 10^{15} atoms/cm^2
As 10^{11} atoms/cm^2
Au 10^{10}atoms/cm^2

Quantitative Analysis and depth profiling

Rutherford Backscattering Spectrometry

$$s = \frac{Z_{He}^2 Z^2 e^4}{4E_i^2 \sin^4 \frac{\Theta}{2}}$$

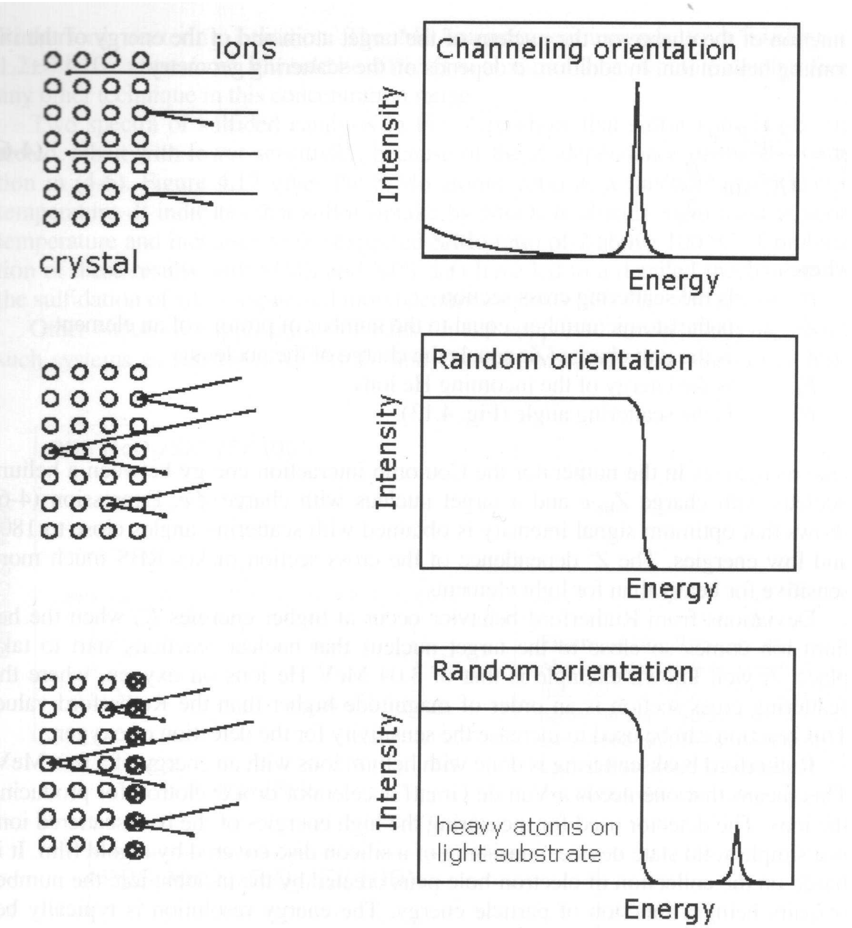
σ : scattering cross section

Z : atomic number, equal to the number of protons of an element

e : unit charge (Ze equals the charge of the nucleus)

E_i : energy of the incomming He ions

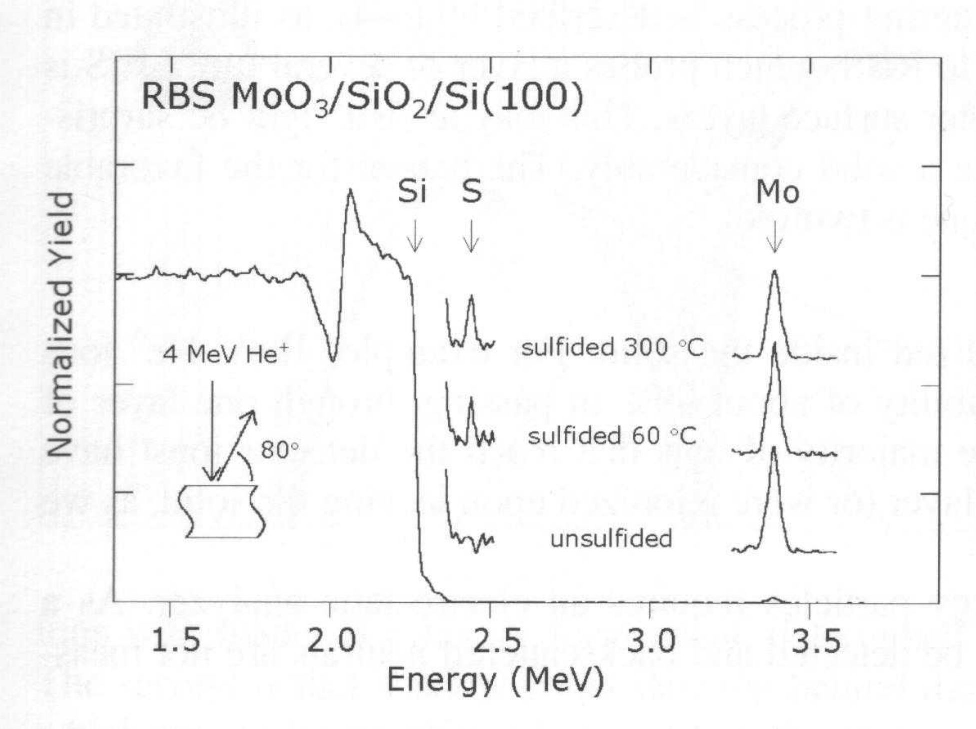
Θ : scattering angle

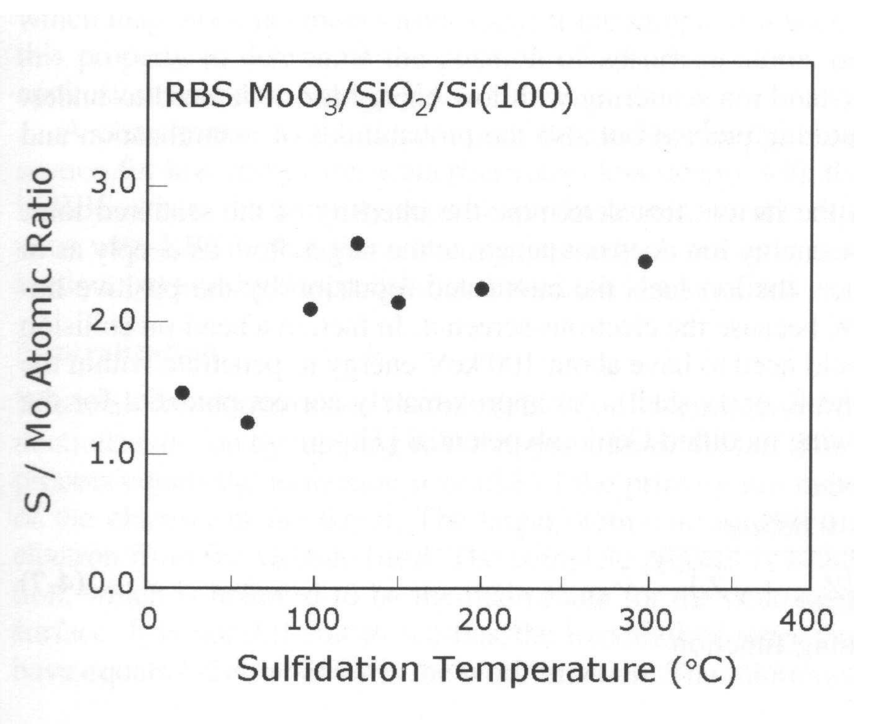


RBS spectra of an $MoO_3/SiO_2/Si(100)$ model catalyst

Molybdenum hydrodesulfurisation catalyst

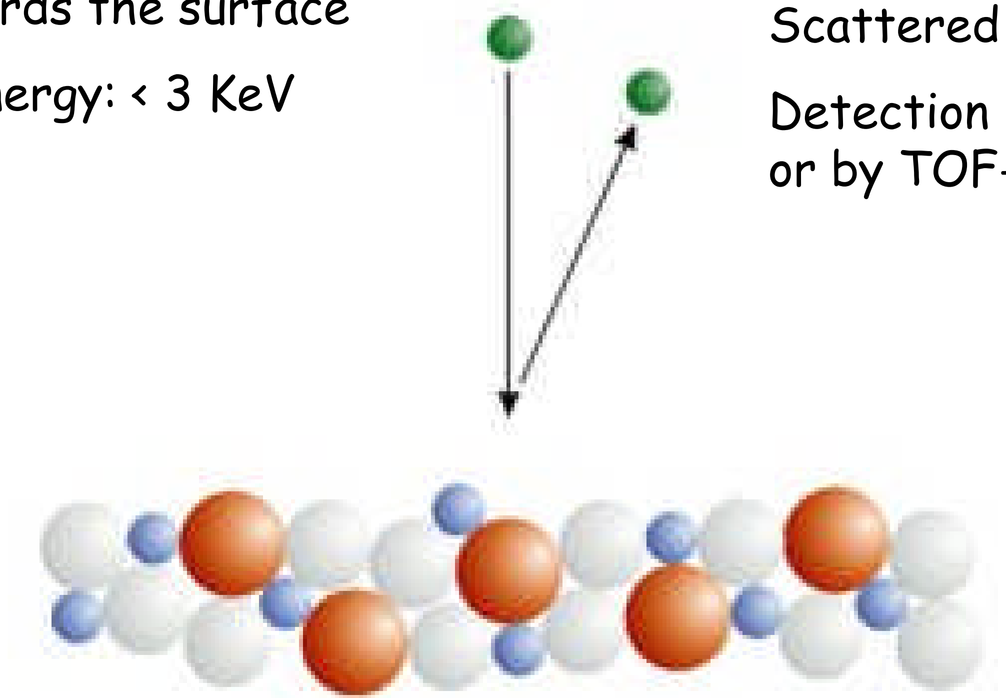
Precursor: $MoO_3/Si(100)$ heated in H_2S/H_2 mixture





Low Energy Ion Scattering (LEIS)

LEIS: mono-energetic noble gas ions are scattered by the atoms in the surface.



Noble gas ions directed towards the surface

Energy: < 3 KeV

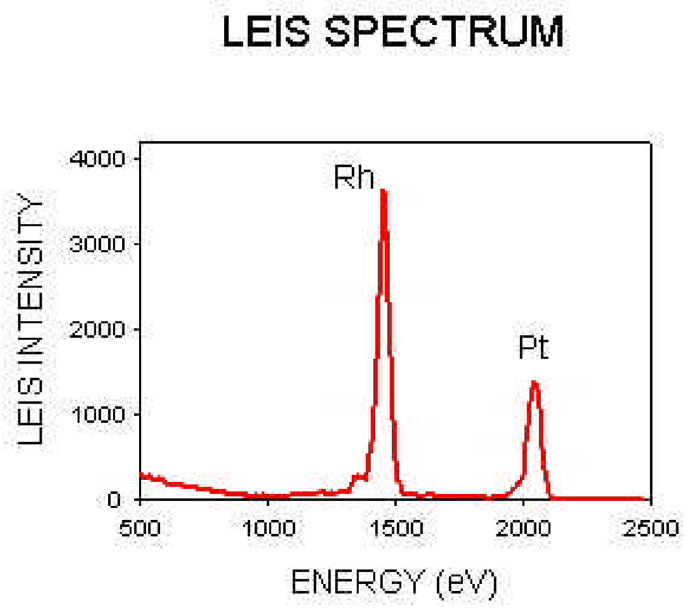
Scattered noble gas ions

Detection by energy analyser or by TOF-MS

surface

Low Energy Ion Scattering (LEIS)

According to the laws of conservation of energy and momentum, the energy of the backscattered ions is characteristic of the mass of the target atoms from which they are scattered. The energy spectrum obtained can thus directly be interpreted as a mass spectrum of the surface atoms.

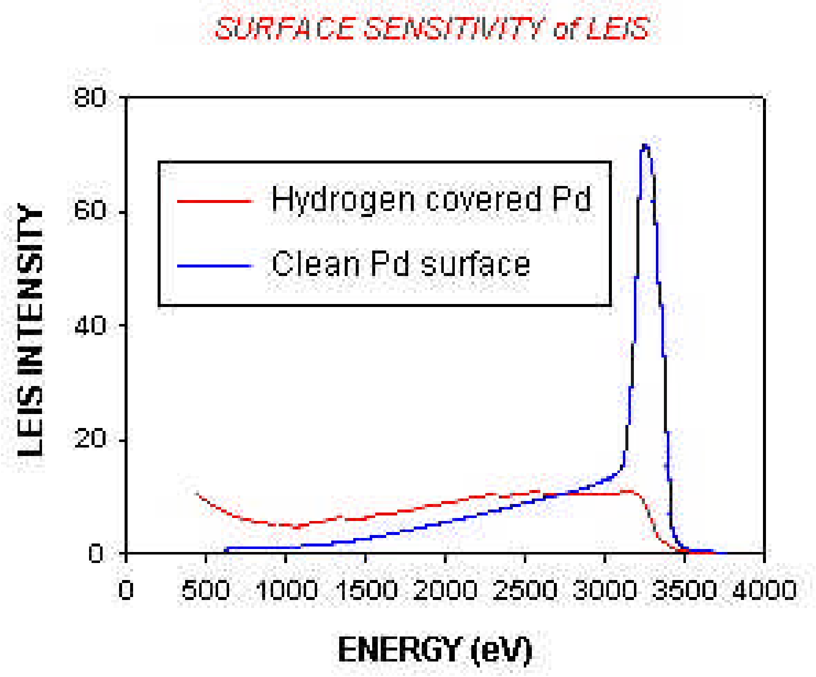


LEIS spectrum obtained from a clean $Pt_{25}Rh_{75}$ (410) surface

The spectrum was obtained using 3 keV Ne^+ ions incident perpendicular to the surface, and was measured using the EARISS analyser.

Low Energy Ion Scattering (LEIS)

The information depth LEIS is limited to the outermost atomic layer because the low-energy noble gas ions have a high neutralization probability



Clean Pd surface:

Intense surface peak at 3250 eV

(tail: reionisation of atom scattered at deeper layers)

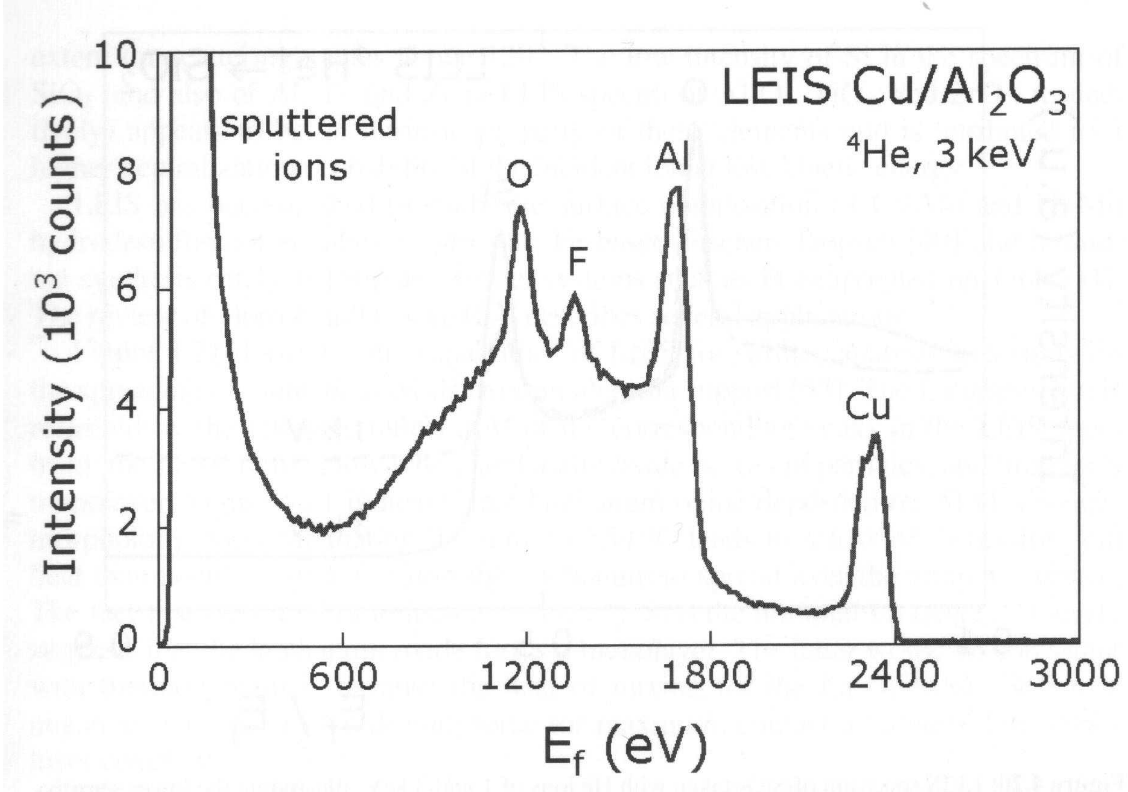
H covered surface:

No peak due to neutralisation by the adsorbed hydrogen atoms

(contribution of sputtered particles ionised when they leave the surface. In this case, the tail at lower energies is dominated by sputtered hydrogen ions)

Low Energy Ion Scattering (LEIS)

LEIS spectrum of an alumina-sopported copper catalyst, Ions: He^+ 3 KeV



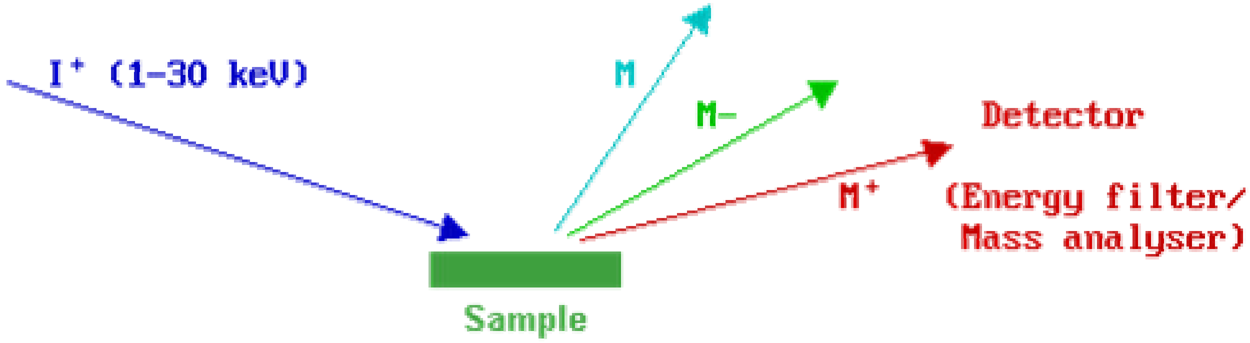
Broadening at lower energies:

The related element is located below the surfce

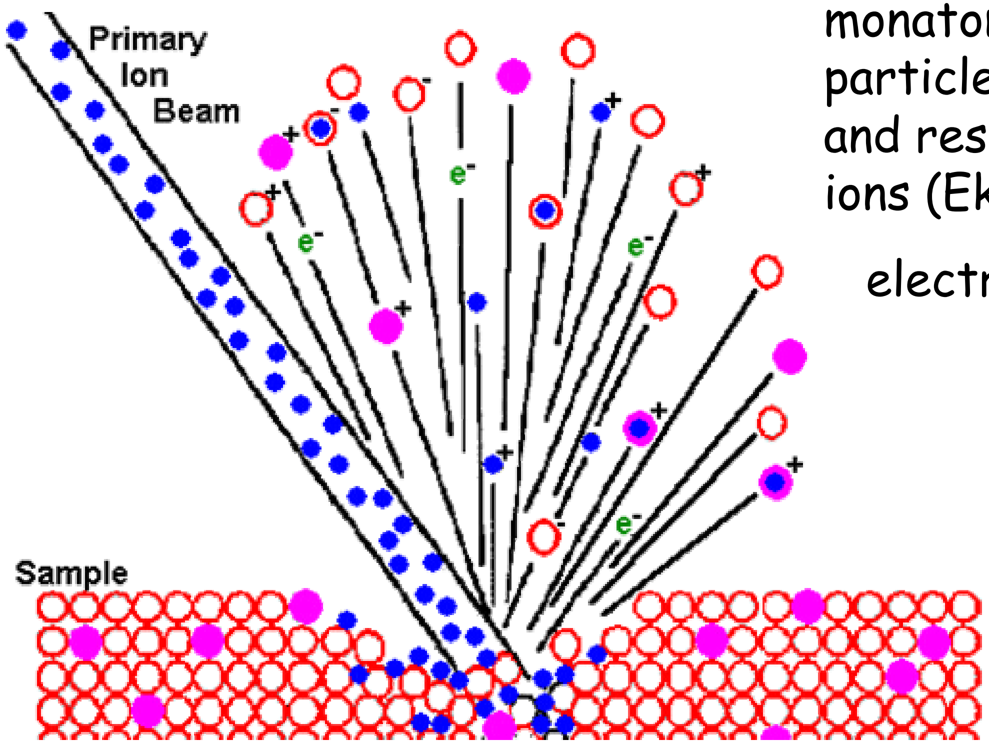
(ions scattered in deeper layer can loose energy due to secondary processes)

Secondary Ion Mass Spectrometry (SIMS)

Bombardment of a sample surface with a primary ion beam followed by mass spectrometry of the emitted secondary ions (quantification is difficult)



Secondary Ion Mass Spectrometry (SIMS)



monatomic and polyatomic particles of sample material and resputtered primary ions (Ekin < 1000 KeV)

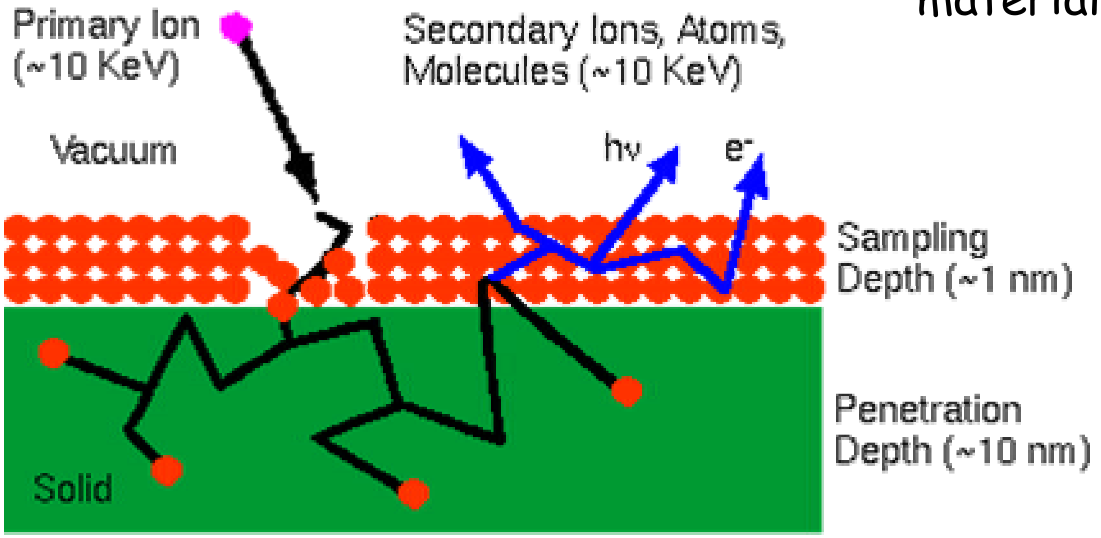
electrons, photons

Primary beam species useful in SIMS include Cs+, O2+, O, Ar+, and Ga+ at energies between 1 and 30 keV. Primary ions are implanted and mix with sample atoms to depths of 1 to 10 nm.

Sputter rates in typical SIMS experiments: 0.5 and 5 nm/s. (depends on primary beam intensity, sample material, and crystal orientation)
The sputter yield is the ratio of the number of atoms sputtered to the number of impinging primary ions. Typical SIMS sputter yields fall in a range from 5 and 15.

Sputtering Effects

Collision cascade model



Sputtered material

Series of binary collisions

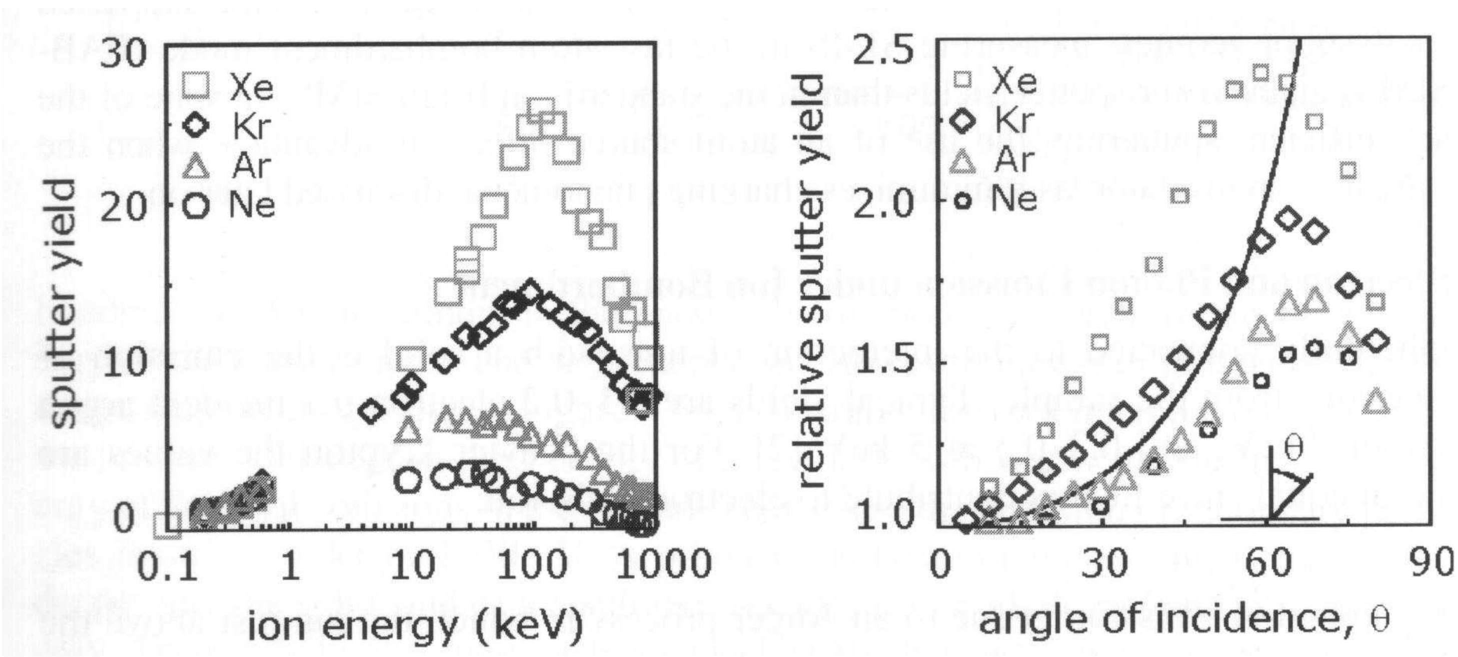
Formation of recoil atoms

Sputter yields

Mass: A heavy ion deposits more energy into the surface and sputters more efficiently than lighter ions

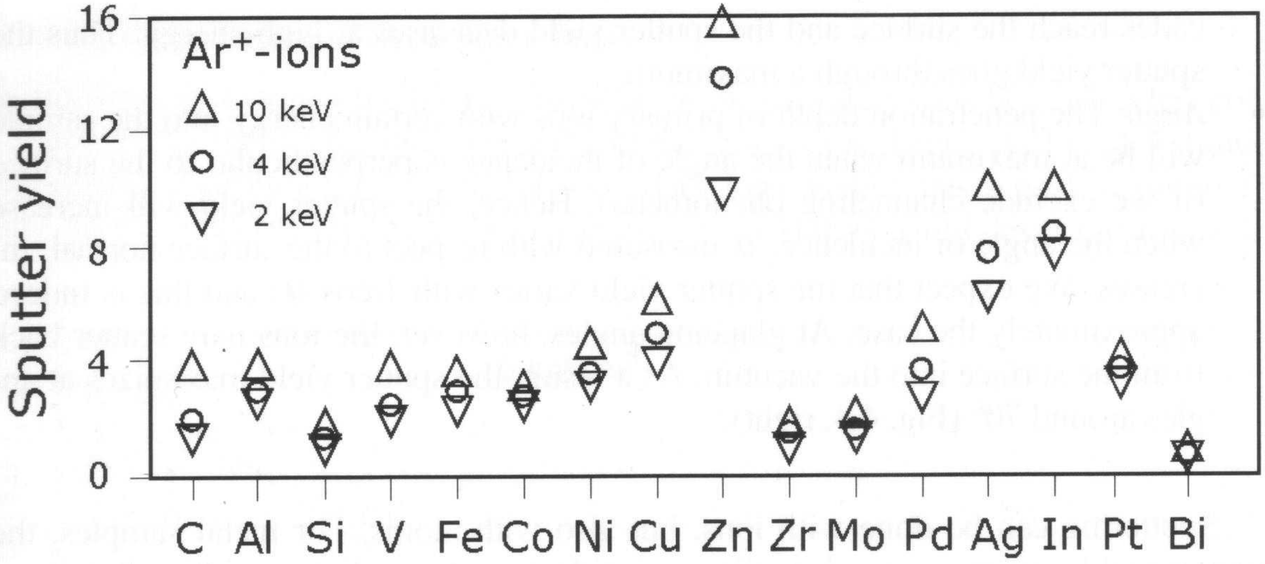
Energy: Increasing the energy of the primary ions initially increases the sputter yield. At higher energy ions penetrate deeper into the solid and dissipate their energy further away from the surface

Angle: penetration depth/energy deposition in a near surface area

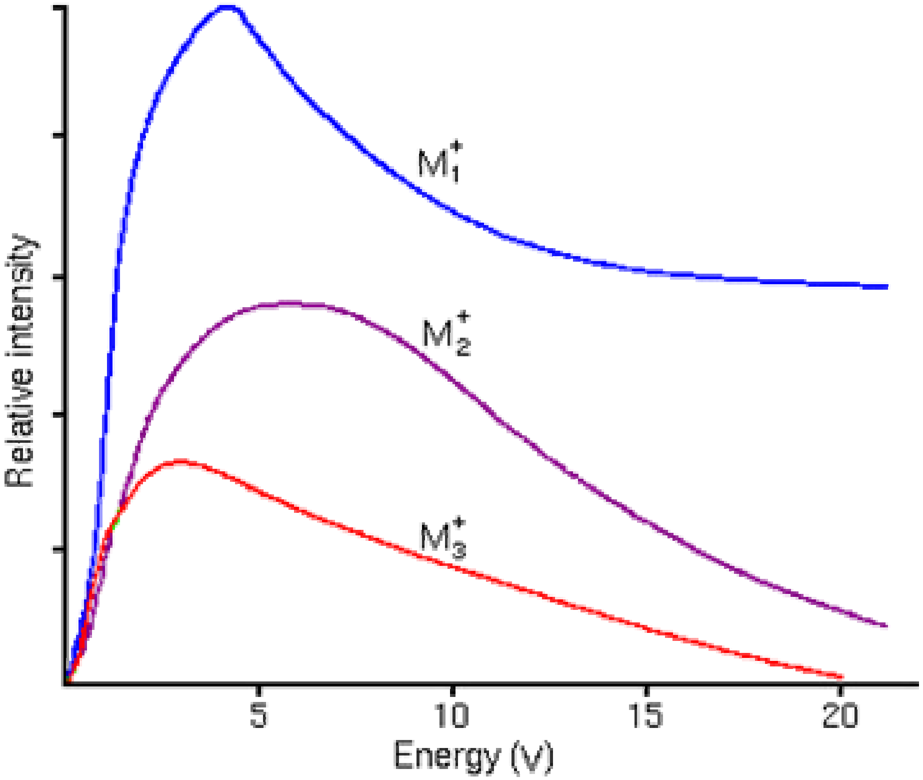


Sputter yield

Sputter yield depends on properties of the sample as well as on those of the incident ion. Sputter yield of the elements vary between 1 and 10. For a given element the sputter yield depends on surface morphology.



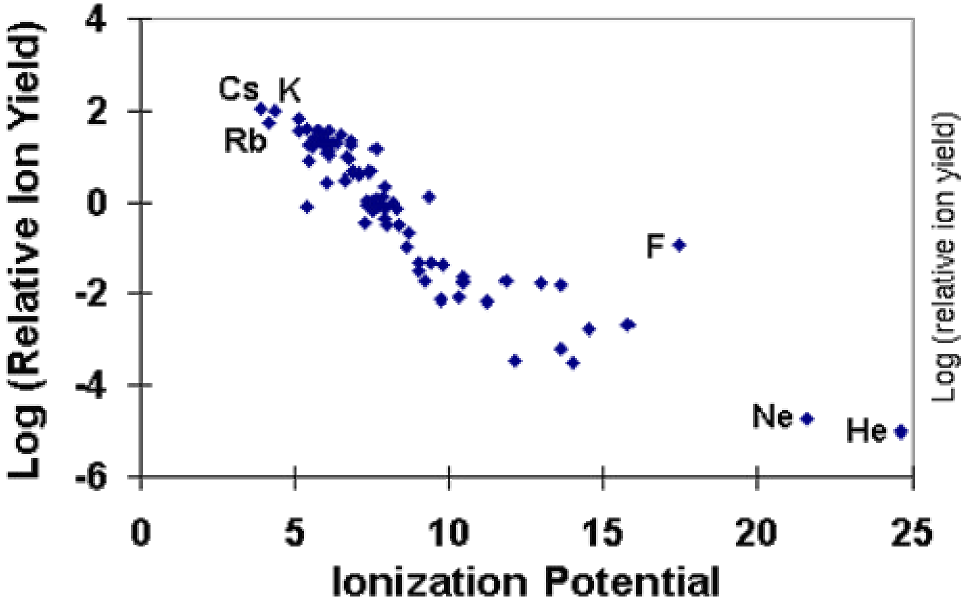
Secondary Ion Energy Distributions

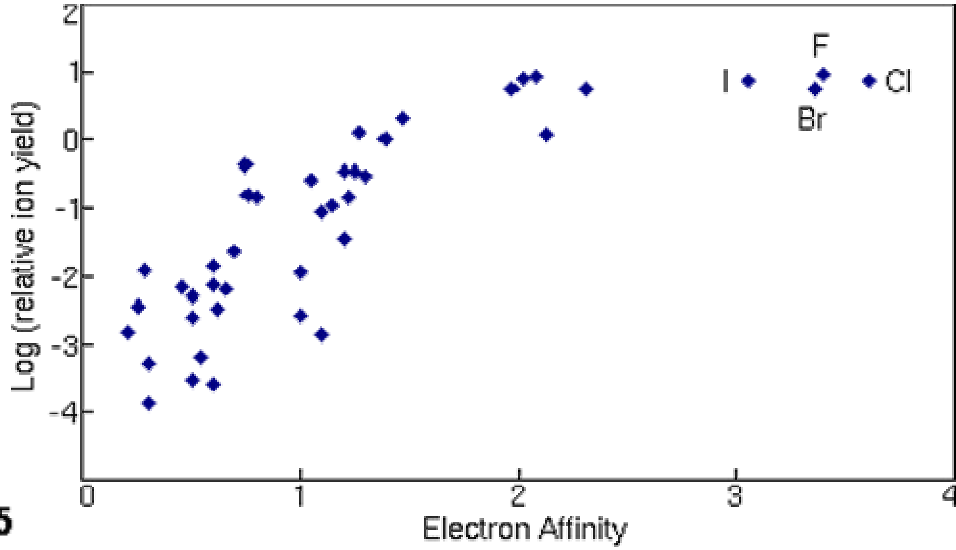


Energy distribution of mono-, di- and triatomic ions

Molecular ions have relatively narrow translational energy distributions because they have kinetic energy in internal vibrational and rotational modes whereas atomic ions have all kinetic energy in translational modes

Secondary Ion yield—Elemental effects





SIMS ionisation efficency = ion yield = fraction of sputtered atoms that become ionised

The ion yields are relative to silicon in a silicon matrix with oxygen sputtering.

The correlations of ionization potential with secondary ion yields are not perfect. Variations depend both on the sample matrix and on the element itself. For example, the presence of oxygen in the sample enhances positive ion yields for most elements, but fluorine exhibits anomalously high positive ion yields in nearly all samples.

Theory of SIMS

$$I_S^{+/-} = I_p Y R^{+/-} c^{surf} T$$

$I_S^{+/-}$	intensity of positive or negative ions (expressed as a rate in counts per sec.)
I_p	flux of primary ions
Y	sputter yield of the element, equal to the number of atoms ejected per incident Ion
$R^{+/-}$	probability that the particle leaves the surface as a positive or negative ion
c^{surf}	fractional concentration of the element in the surface layer
T	transmission of the mass spectrometer, typically 10^{-3} for quadrupol and 10^{-1} for a time-of-flight instrument

Application of SIMS on Catalysts

Characterisation of technical catalysts

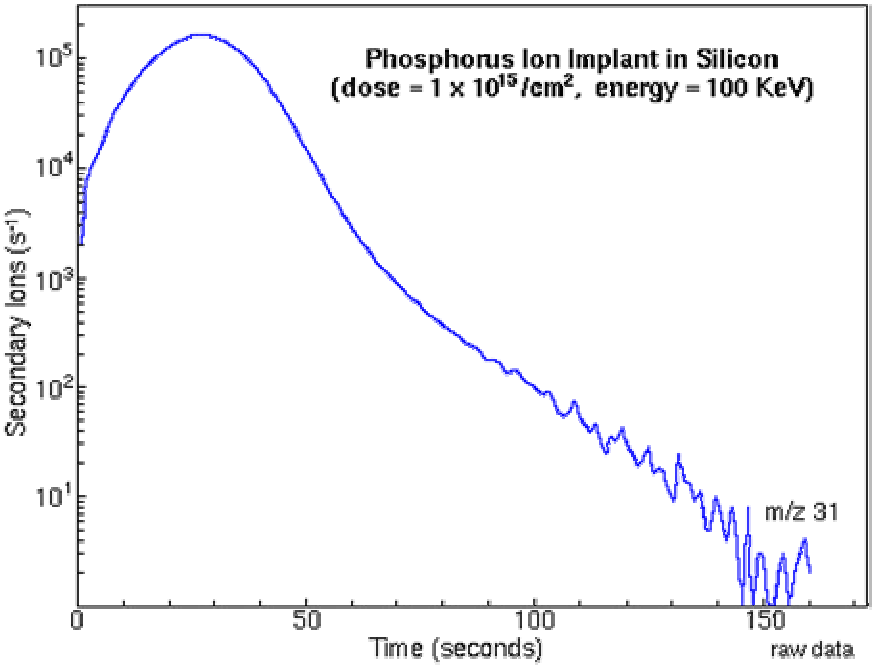
Studies on model systems which both allow for optimum SIMS analysis and realistic simulate aspects of technical catalysts, chosen to adress specific questions

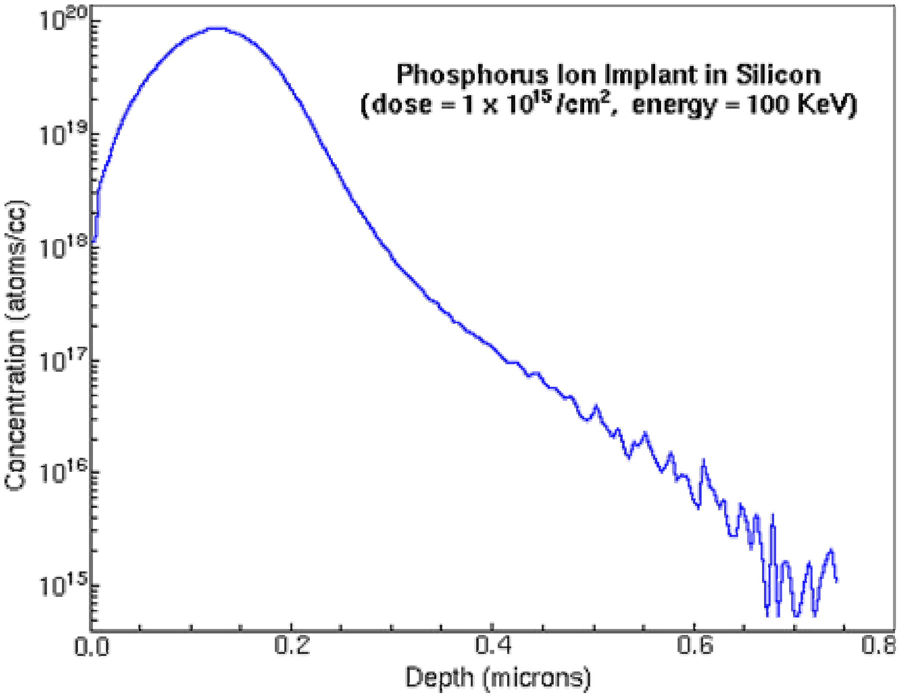
Depth profiling

Surface science studies dealing with adsorption and reaction of gases on single crystal surfaces

Depth Profiling

Monitoring the count rate of selected elements as a function of time leads to depth profiles (Cs^+ ions)



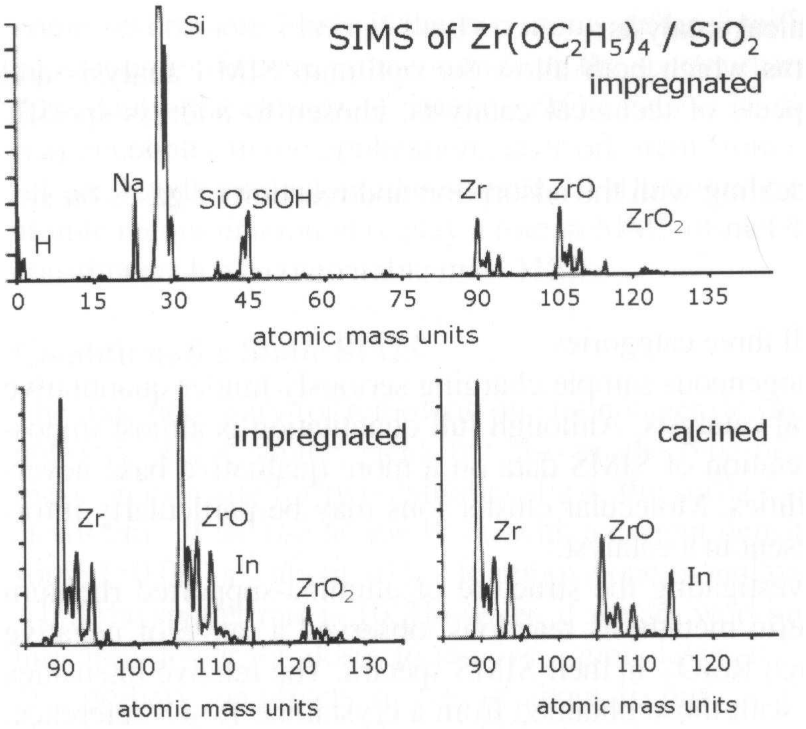


Formation of zirconium dioxide from zirconium ethoxide on silica

ZrO_2 is catalytically active for:

Isomerisation, methanol synthesis and cracking reactions

$Zr(OC_2H_5)_4$ precusor was applied on silica by condensation reaction between ethoxide ligands and OH groups of the support



Fresh catalyst contains $ZrOH^+$

(fragment of zirconium ethoxide)

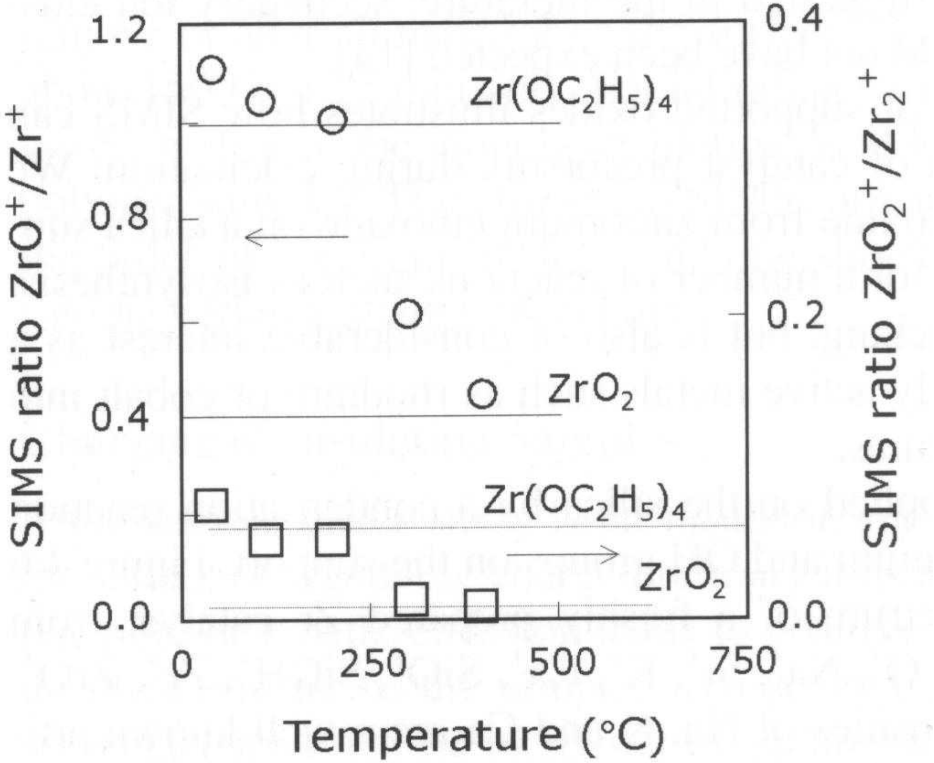
107 amu ($^{90}ZrOH^+$ and $^{91}ZrO^+$)

111 amu ($^{94}ZrOH^+$)

After calcination at 400°C in air ZrO range resembles that of Zr

Formation of zirconium dioxide from zirconium ethoxide on silica

Comparison of SIMS with spectra obtained from zirconium oxide and zirconium ethoxide



T<200°C: zirconium ethoxide, T>300°C: zirconium oxide

SIMS spectra of a $MoO_3/SiO_2/Si(100)$ model catalyst

Molybdenum sulfide catalysts for hydrodesulfurisation (HDS)

Removal of sulfur from heavy oil fractions

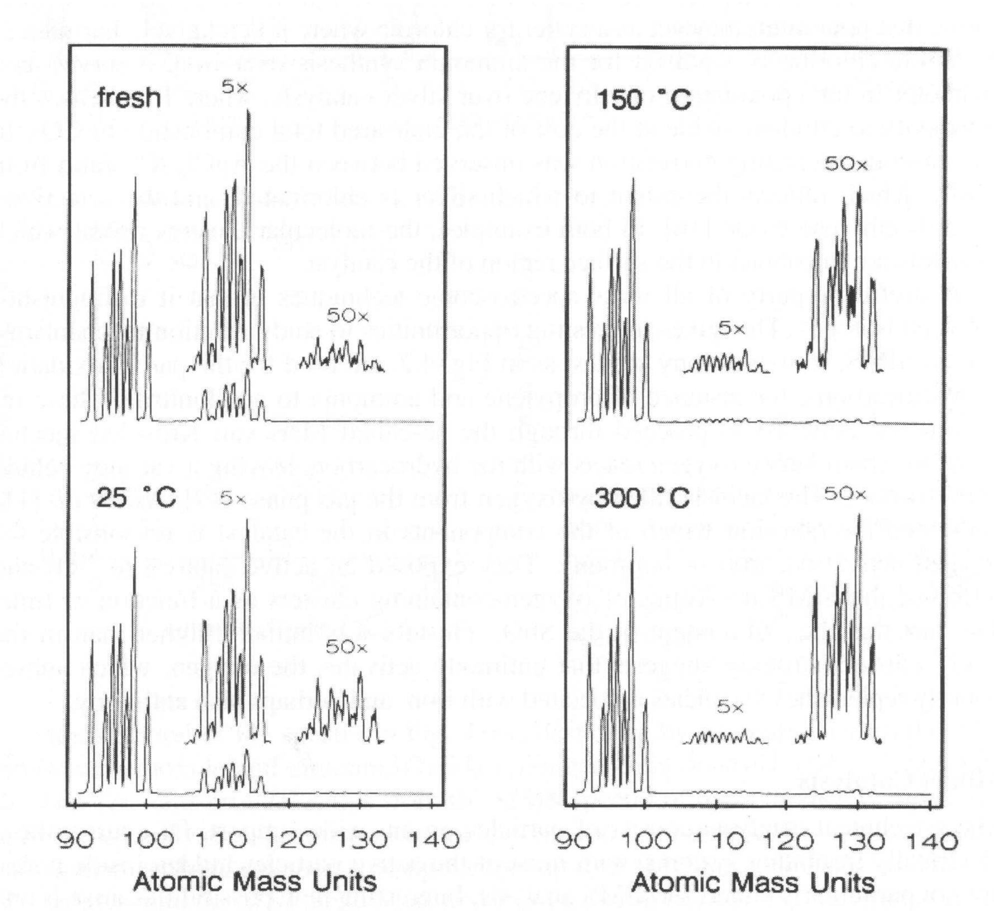
Promoter: Co, Ni ; activation: sulfidation in H_2S –H_2 mixture

Mo^+: 92-100 amu

MoO^+:108-116 amu

MoS^+, MoO_2^+:

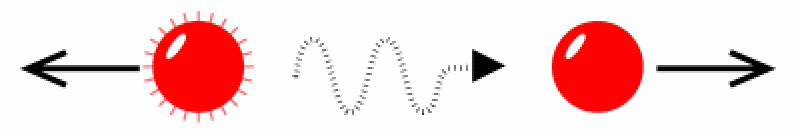
124-132 amu



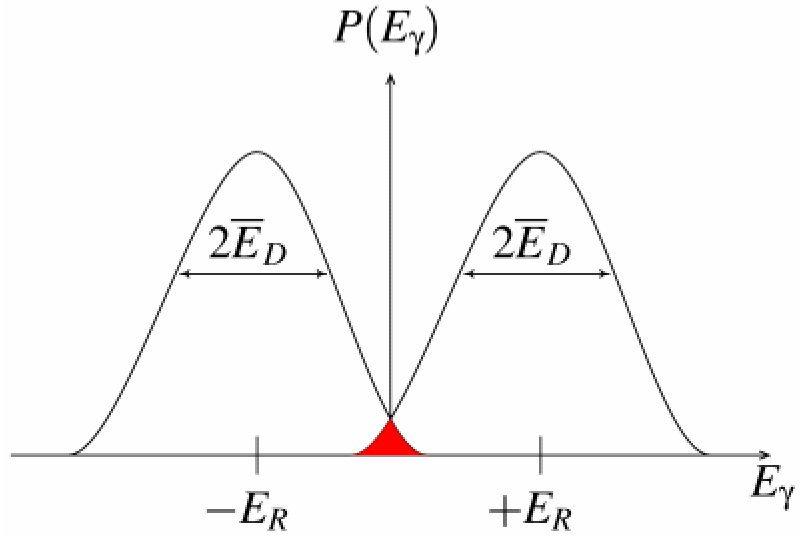
Sulfidation of the catalysts starts at 25°C

Mössbauer Effect

Recoilless gamma ray absorption and emission discovered by Rudolph Mössbauer in 1957 (Nobel-Price in Physics in 1961)



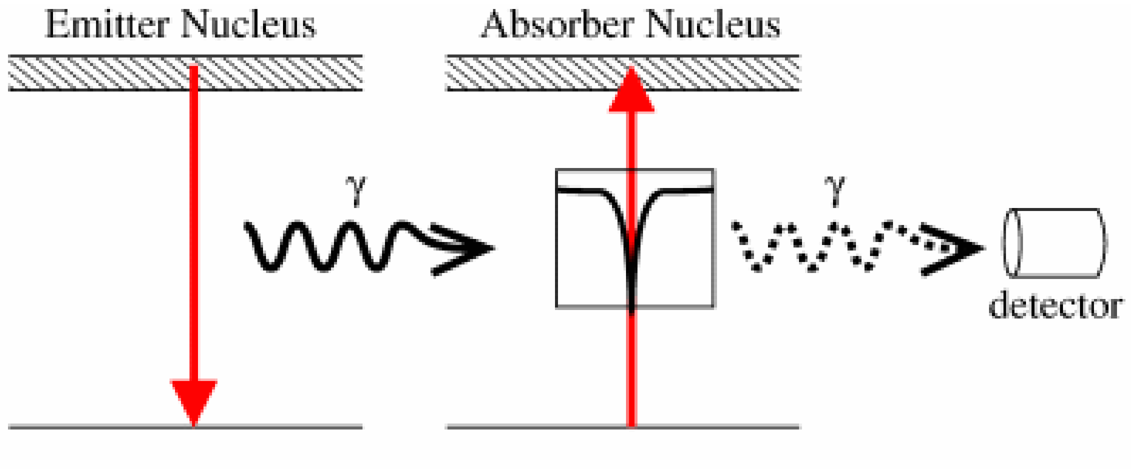
Recoil of free nuclei in emission or absorption of a gamma-ray



Resonant overlap in free atoms. The overlap shown shaded is greatly exaggerated

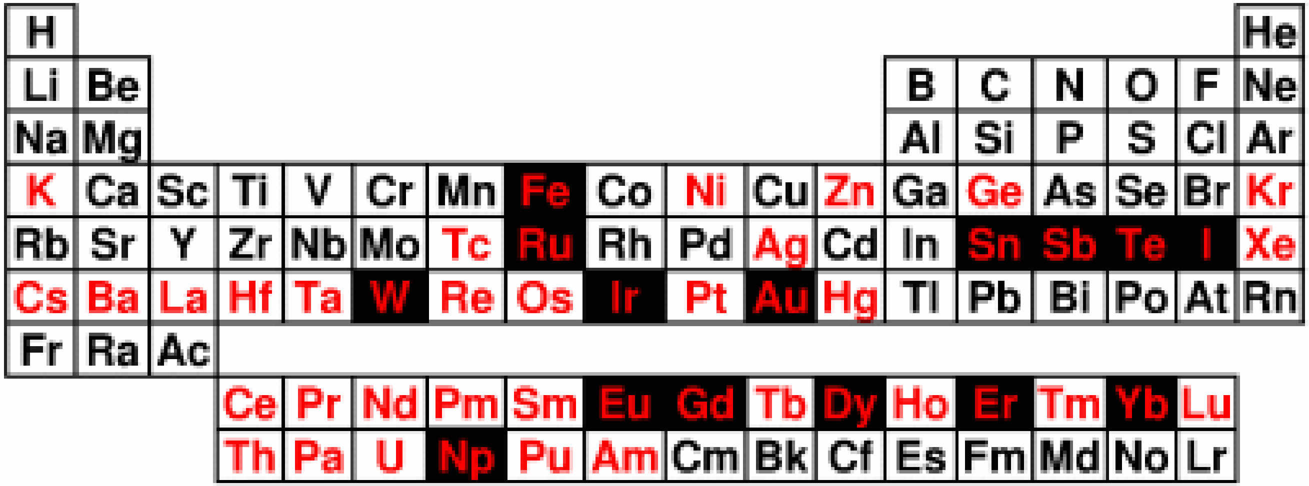
Mössbauer Effect

Recoil-free emission or absorption of a gamma-ray when the nuclei are in a solid matrix such as a crystal lattice



Simple Mössbauer spectrum from identical source and absorber

Mössbauer Effect



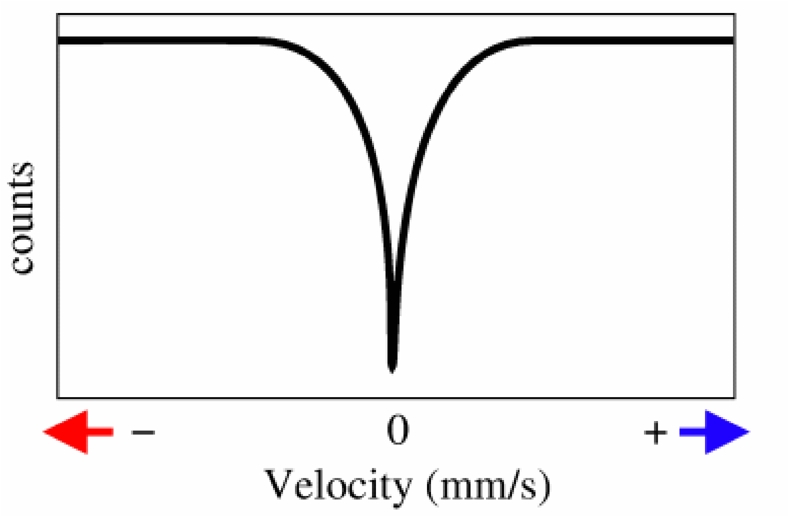
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Elements of the periodic table which have known Mössbauer isotopes (shown in red font). Those which are used the most are shaded with black

For the most common Mössbauer isotope, ^{57}Fe, this linewidth is 5×10^{-9}ev. Compared to the Mössbauer gamma-ray energy of 14.4keV this gives a resolution of **1 in 10^{12}**!!!!

This exceptional resolution is of the order necessary to detect the hyperfine interactions in the nucleus.

Fundamentals of Mössbauer Spectroscopy



Simple spectrum showing the velocity scale and motion of source relative to the absorber

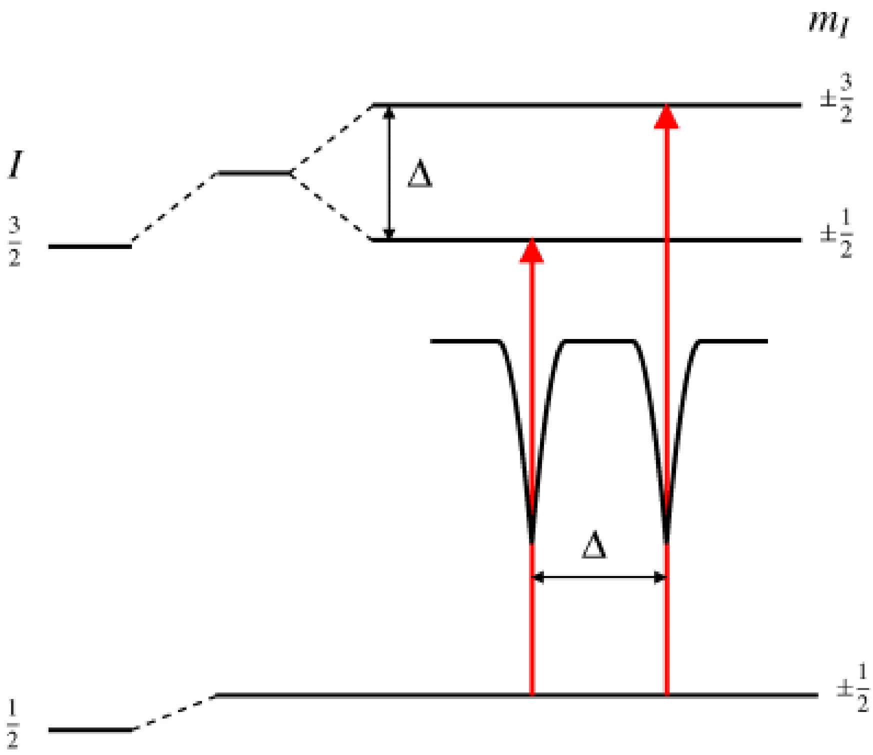
(Doppler-Effect)

The energy levels in the absorbing nuclei can be modified by their environment in three main ways: by the **Isomer Shift**, **Quadrupole Splitting** and **Magnetic Splitting**.

Isomer shift of common iron compounds

Compound	**δ (mm/s)**
α-Fe_2O_3	0,43
α -FeOOH	0,35
Fe_3O_4	0,63
FeO	1,08
FeS_2	0,28
α -Fe	0,00
Θ-Fe_3C	0,19
SNP	-0.26

Quadrupole Splitting



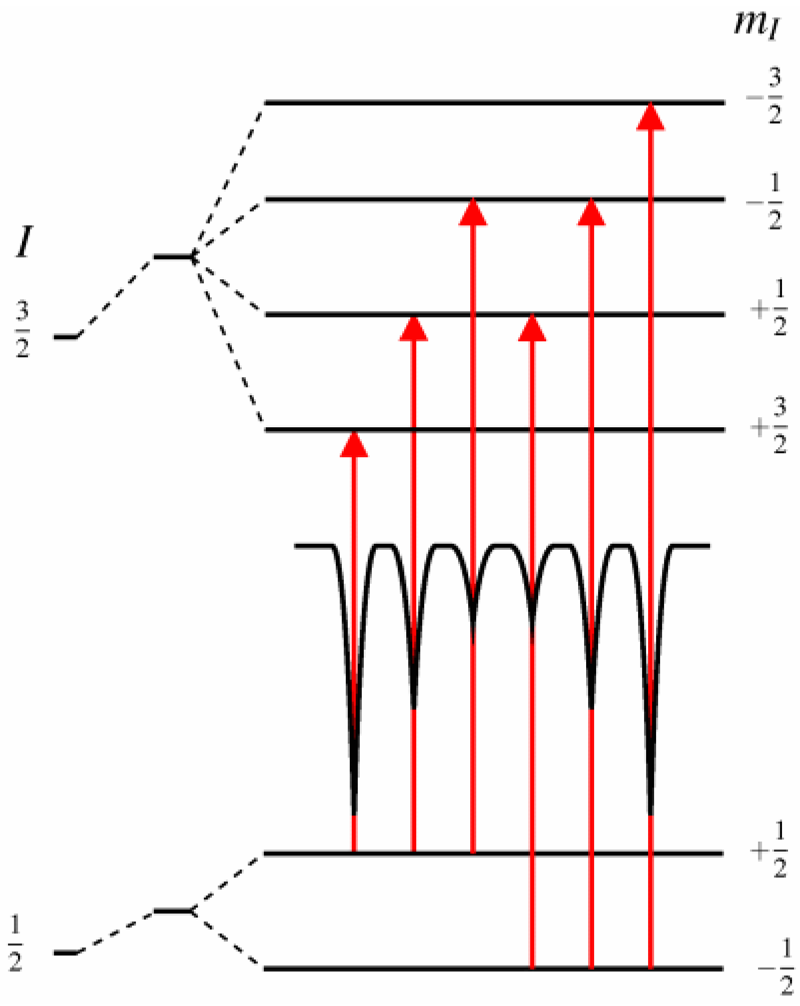
In the case of an isotope with a $I=3/2$ excited state, such as ^{57}Fe or ^{119}Sn, the excited state is split into two substates $m_I=\pm1/2$ and $m_I=\pm3/2$.

Nucleii with $I > \frac{1}{2}$ have non-spherical charge distribution

➡ Nuclear quadrupole moment Q

In the presence of an asymmetrical electric field (produced by an asymmetric electronic charge distribution or ligand arrangement) this splits the nuclear energy levels.

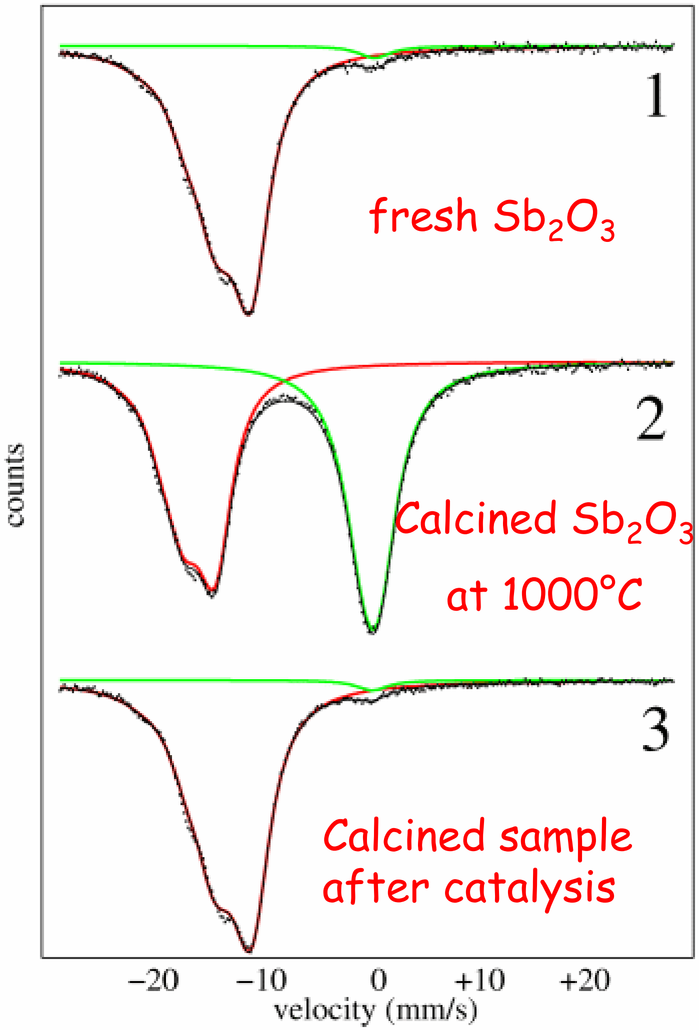
Magnetic Splitting



In the presence of a magnetic field the nuclear spin moment experiences a dipolar interaction with the magnetic field ie Zeeman splitting

This magnetic field splits nuclear levels with a spin of I into (2I+1) substates. This is shown in the figure for ^{57}Fe. Transitions between the excited state and ground state can only occur where m_I changes by 0 or 1. This gives six possible transitions for a 1/2 to 3/2 transition.

Sn-Sb-O catalyst



Sn-Sb-O catalyst are used for selective oxidation of olefines

What is the antimon charge state?

Fresh: isomer shift indicates Sb3+ (Sb_2O_3)

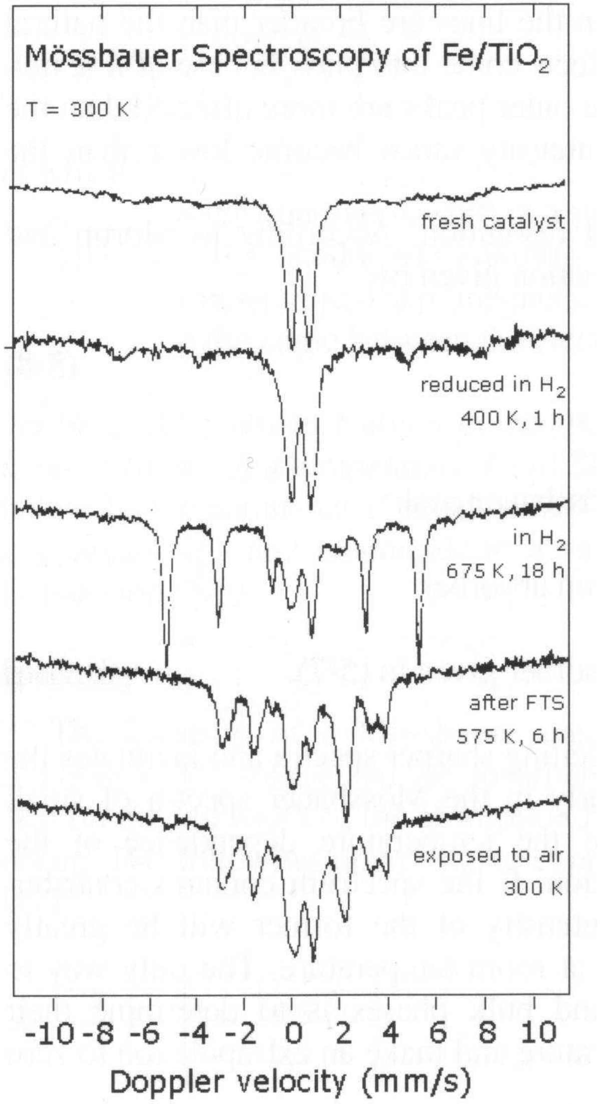
Calcined: Sb3+ and Sb5+ (Sb_2O_4, Sb_6O_{13})

Used sample: Sb3+

Sn:

One single line of identical isomer shift. No change in charge of tin during all parts of the process

Fe/TiO$_2$ – phase identification



Fe/TiO$_2$ is used for Fischer-Tropsch synthesis

Freshly imprgnated: iosomer shift of 0.37 mm/s, quadrupol splitting of 0.82 mm/s (highly asymmetric environment)

Well dispered Iron oxide or oxyhyoxied

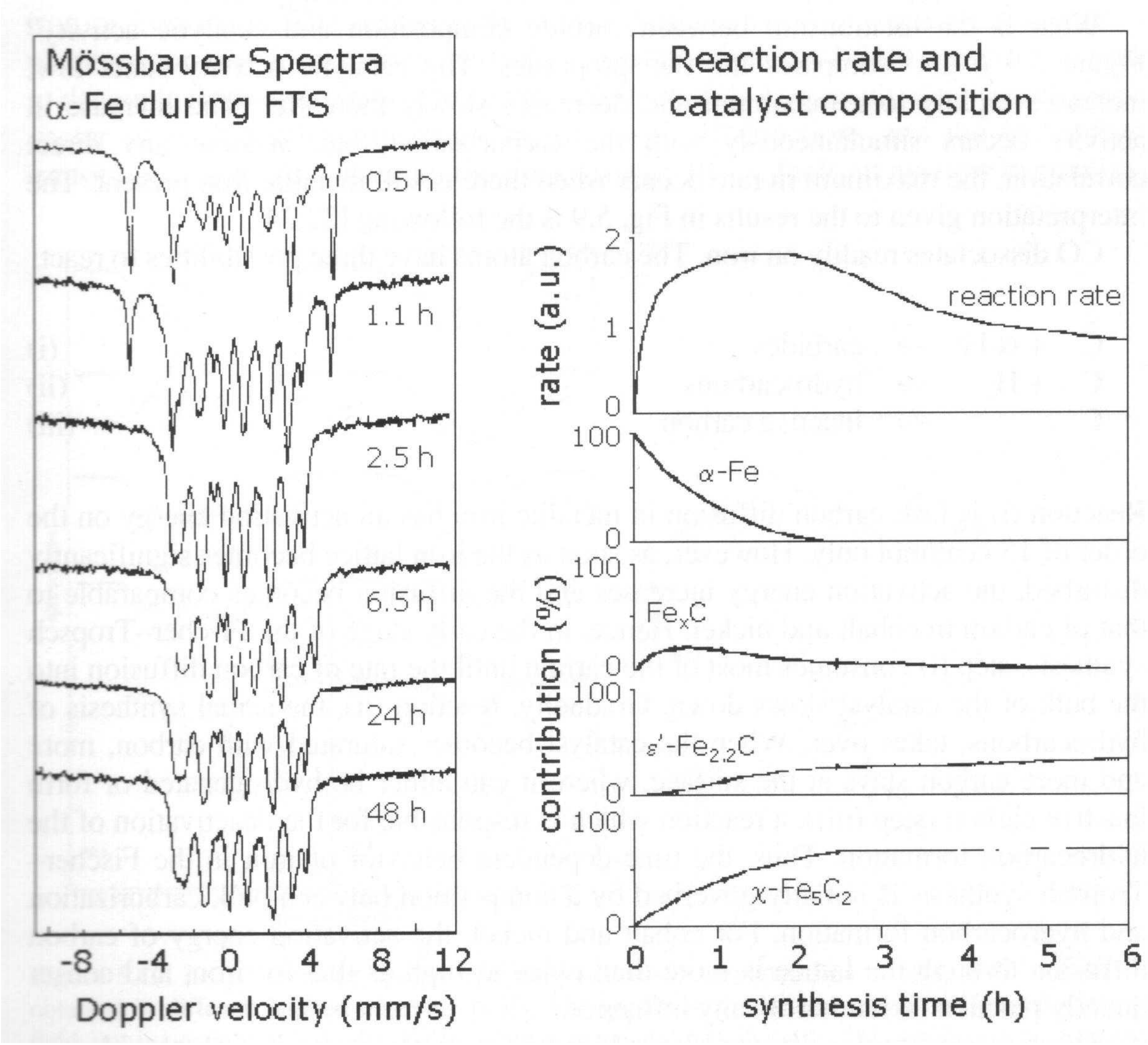
Reduction at 675 K: metallic iron (sextet) + unreduced iron (Fe2+ and Fe3+ center)

FTS: spectrum changes entirely: Fe$_5$C$_2$ (Hägg carbide) and a few Fe2+ center

Exposed to air: carbide phase is stable, part of the iron oxidised.

In situ studies are required!!

Mössbauer Spectra of α-Fe used in Fischer-Tropsch synthesis



Fischer-Tropsch-Synthesis

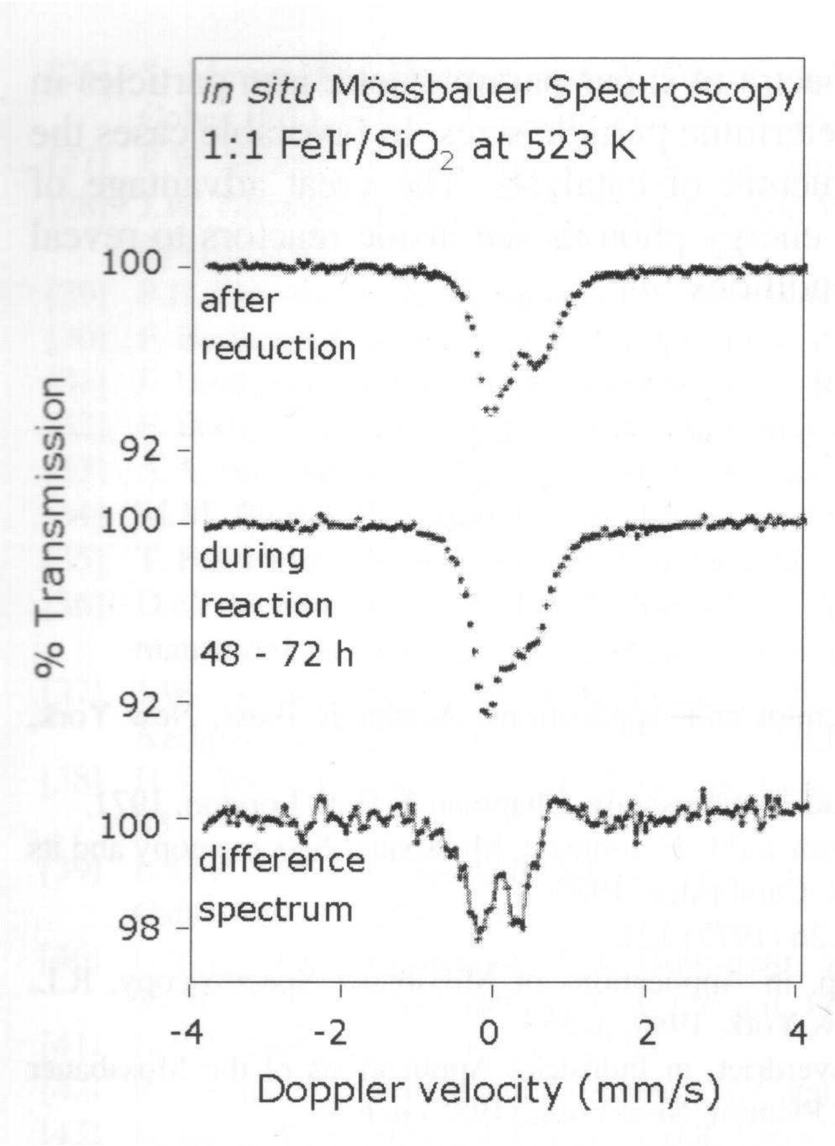
$CO + H_2$, 240°C

C + α-Fe —> carbides

$C + H_2$ —> hydrocarbons

C —> inactive carbon

In situ Mössbauer Spectroscopy



Fe-Ir catalysts for methanol synthesis from CO and H_2

First 10-50h:
Main product: methane

after reduction: Fe-Ir particles and unreduced iron in contact with the support

Spectrum changed in steady state

Difference spectrum:

Formation of an iron carbide in the superparamagnetic state

Summary

Method	Source	Information depth	What is detected	information
RBS (quantitative)	Protons, deuteron, alpha-particles of a few MeV	Several µm	Protons, deuteron, alpha-particles	Buried layers, Depth profiles
LEIS (quantitative)	Ions (He+, Ne+…) 100eV-10KeV	Topmost layer (neutralisation)	ions	Chemical composition surfaces
SIMS (quantitative analysis is difficult)	ions	Topmost layer (Static) depth profile (dynamic)	ions	Depth profiles
MS (can be applied in situ)	Gamma ray	bulk	Gamma ray	Identification of phases Determination of oxidation state Kinetics of bulk transformations