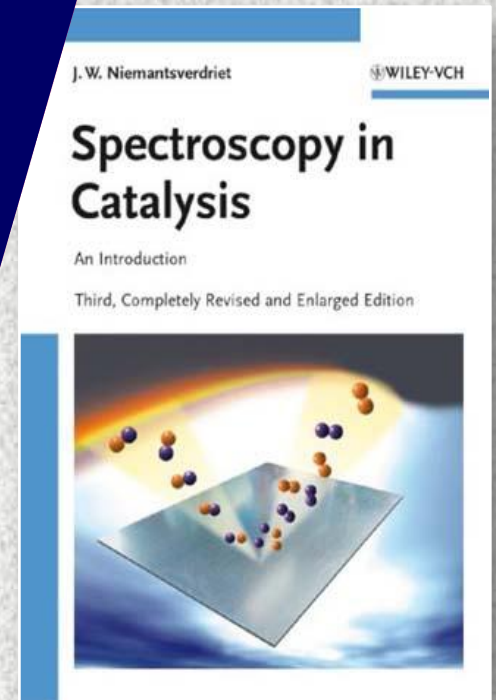


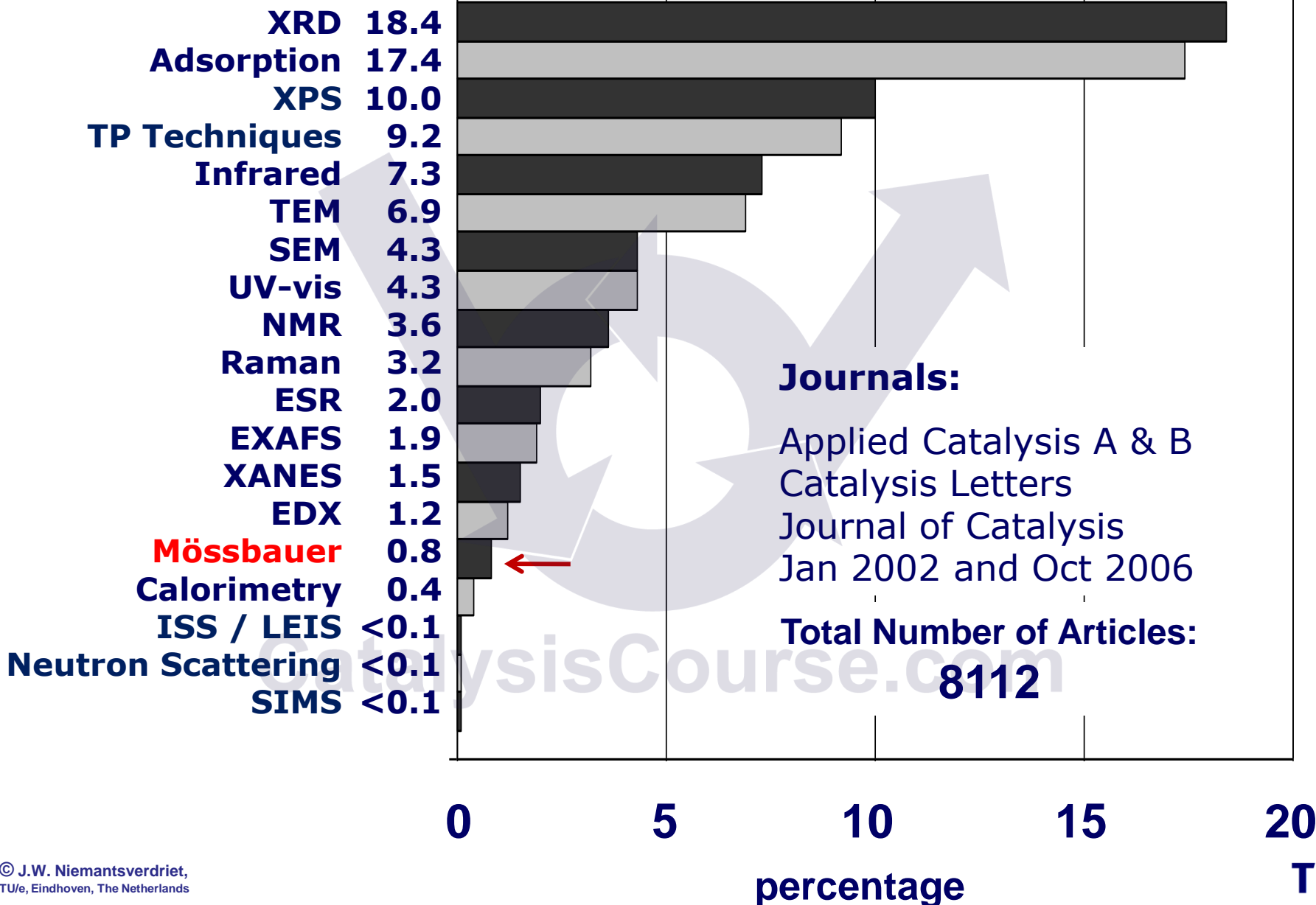
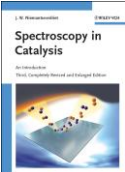
# Characterization of solid catalysts

## 5. Mössbauer Spectroscopy

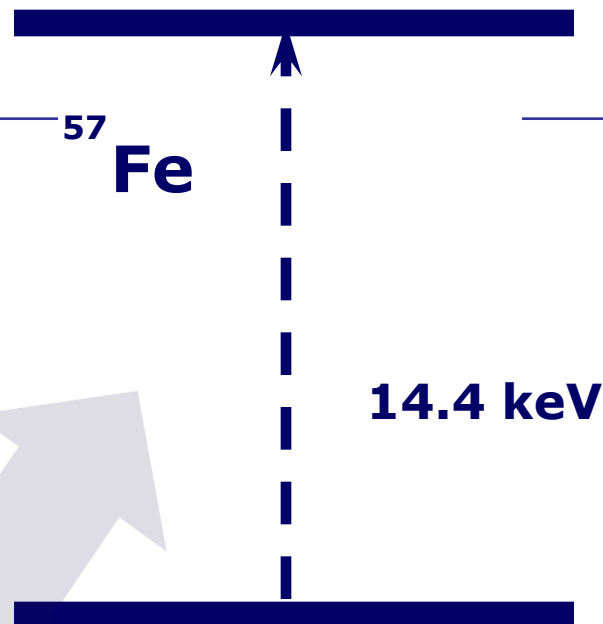
Prof dr J W (Hans) Niemantsverdriet  
Schuit Institute of Catalysis



# How often are techniques used

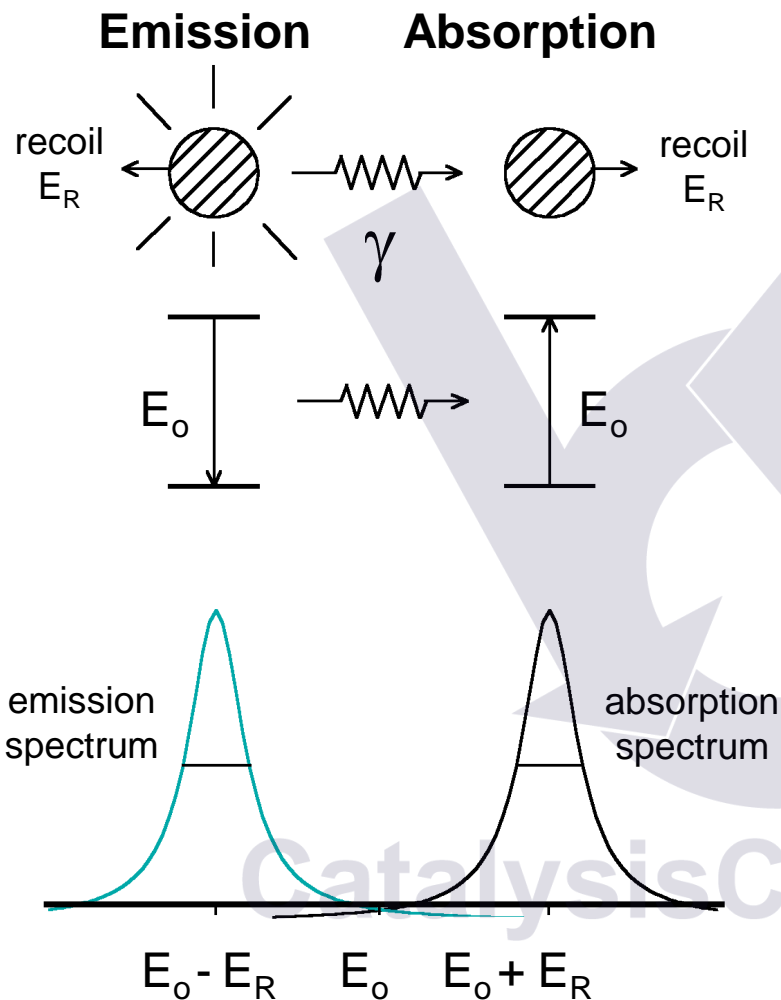


# Mössbauer Spectroscopy



- nuclear technique
- nucleus feels environment via hyperfine interactions
- recoilfree emission and absorption of gamma rays by nucleus
- high penetrating power of gamma rays enables *in situ* investigations

# Mössbauer Effect (1957)

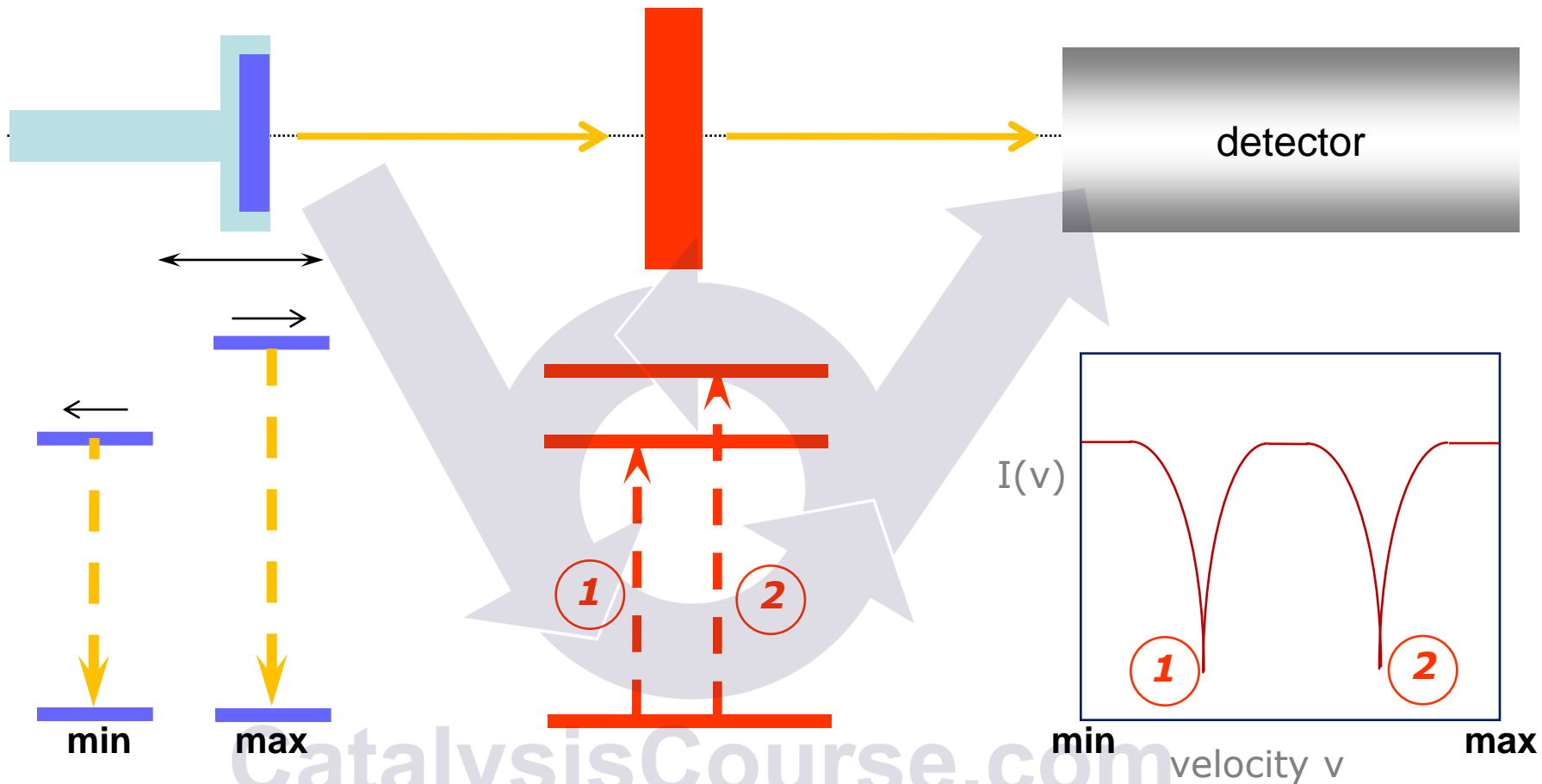


- Resonant absorption only if nuclei (atoms) are fixed in a solid
- Recoil taken up by lattice vibrations (quantized)
- recoil energy < phonon energy:  
**then some absorption events occur without recoil**

*no resonant absorption in free atoms due to the (tiny!) energy loss by recoil*

- **f**: recoil free fraction

# Mössbauer Spectrometer



- single line emitter
- Doppler effect:  

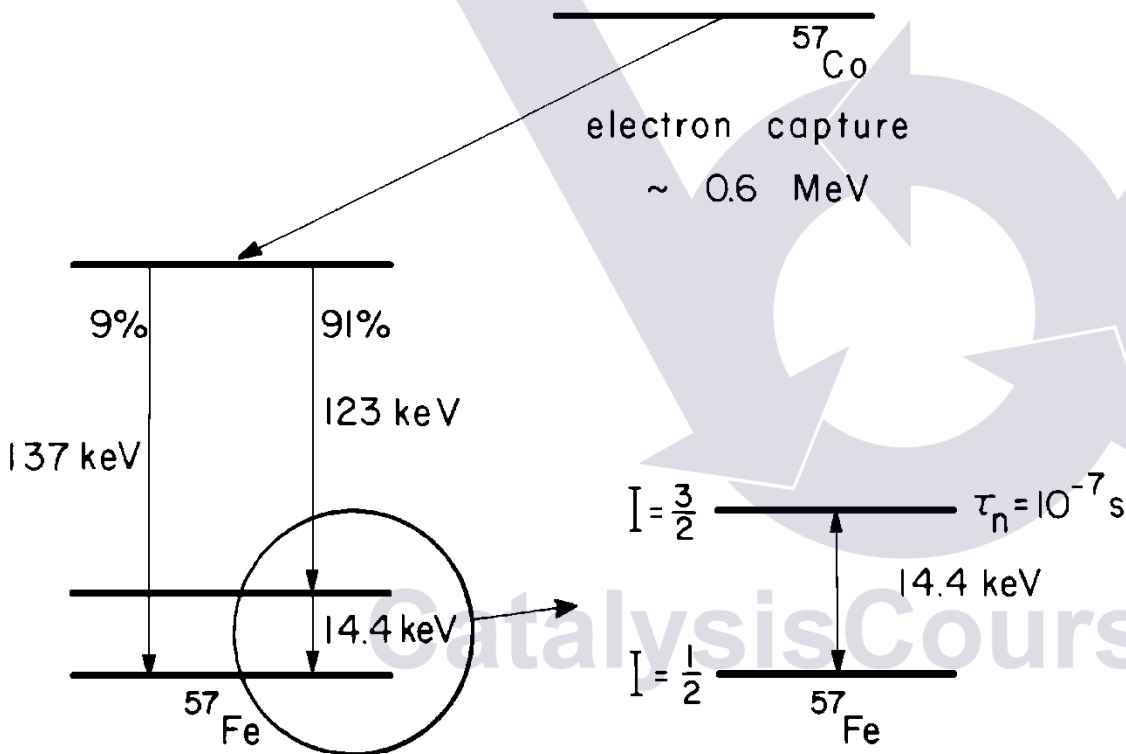
$$E(v) = E_0 (1 + v/c)$$

- absorber with  $^{57}\text{Fe}$

- gamma ray detector,
- transmitted intensity versus velocity

# Mössbauer Spectroscopy in $^{57}\text{Fe}$

## Decay of $^{57}\text{Co}$ to $^{57}\text{Fe}$



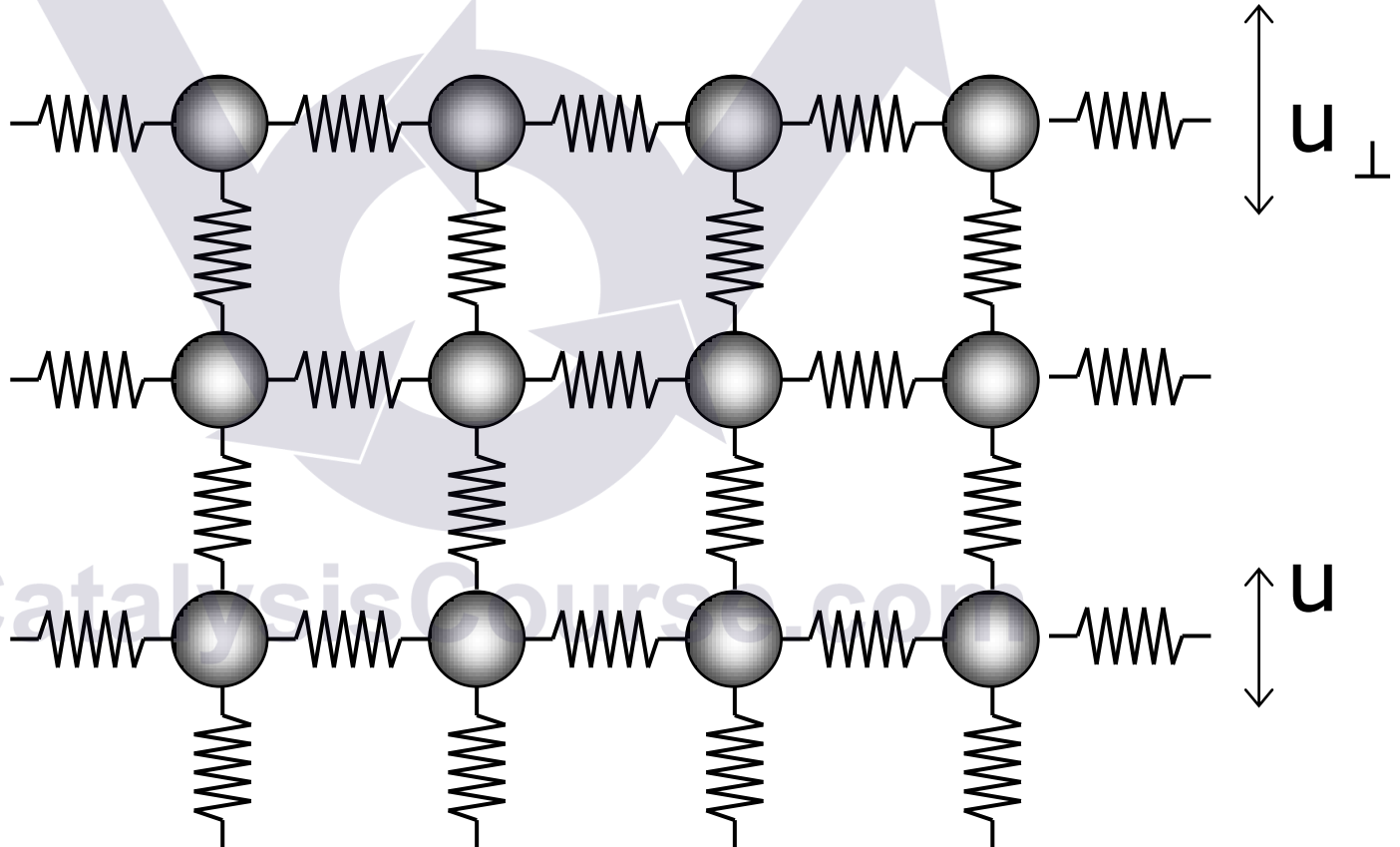
- transition:  
*14.4 keV*
- natural linewidth:  
*4.6 neV*
- hyperfine interactions:  
*1-100 neV*  
are easily resolved!

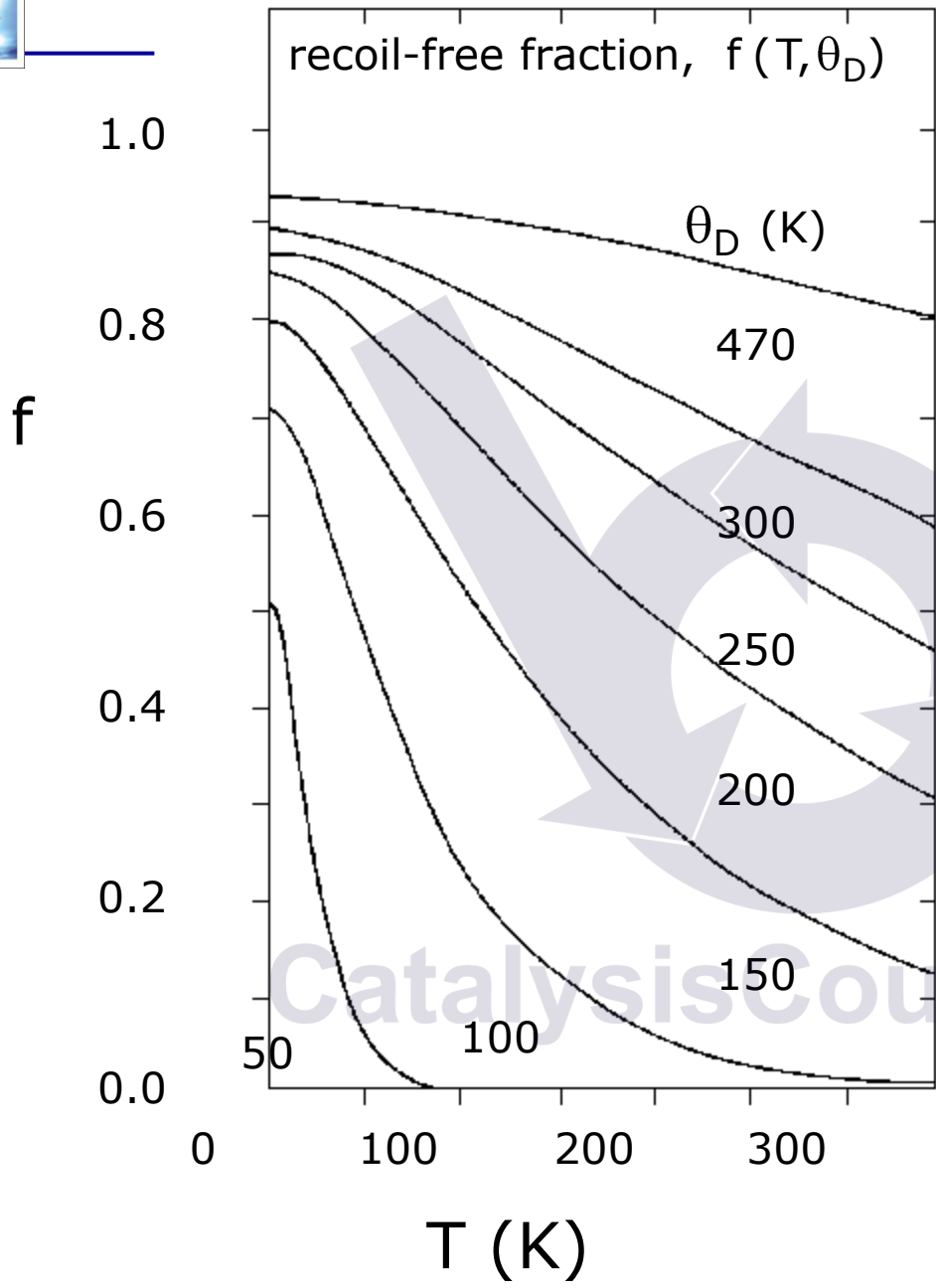
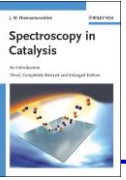
# Mössbauer Intensity: Lattice Vibrations

$$\textit{intensity} = \textit{const} \times n_{Fe} \times f$$

$$f = \exp(-k \langle x^2 \rangle) = f(T, \theta_D)$$

surface





## Debye Temperature, $\Theta_D$

- *high* for *rigid* lattice
- *low* for *soft* vibrations
- can be determined from T-dependence intensity
- surface:  $\sim 50\%$  of bulk value

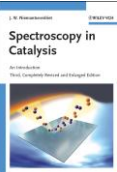
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# Hyperfine Interactions

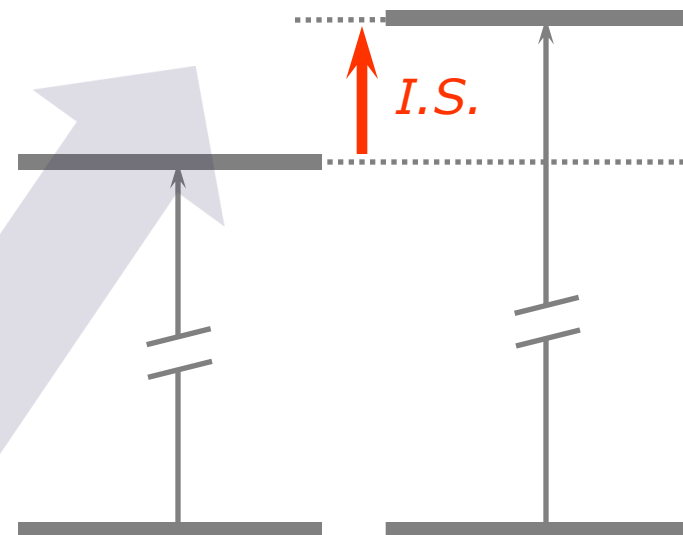
- Isomer Shift:  
***oxidation state***
- Quadrupole splitting:  
***local symmetry***
- Magnetic Splitting:  
***nuclear magnetic field***

# Hyperfine Interactions



## Isomer Shift:

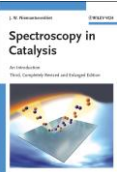
- Coulomb interaction nucleus - s-electrons
- Information on



***oxidation state***

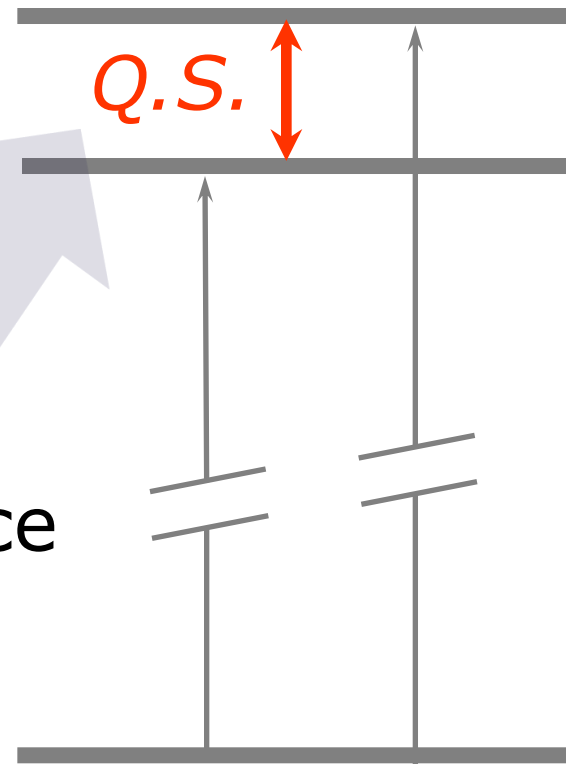
CatalysisCourse.com

# Hyperfine Interactions



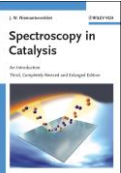
## Quadrupole Splitting:

- nuclear quadrupole moment  
electric field gradient (EFG)
- EFG: due to electrons and lattice
- Information on



CatalysisCourse.com  
***local symmetry***

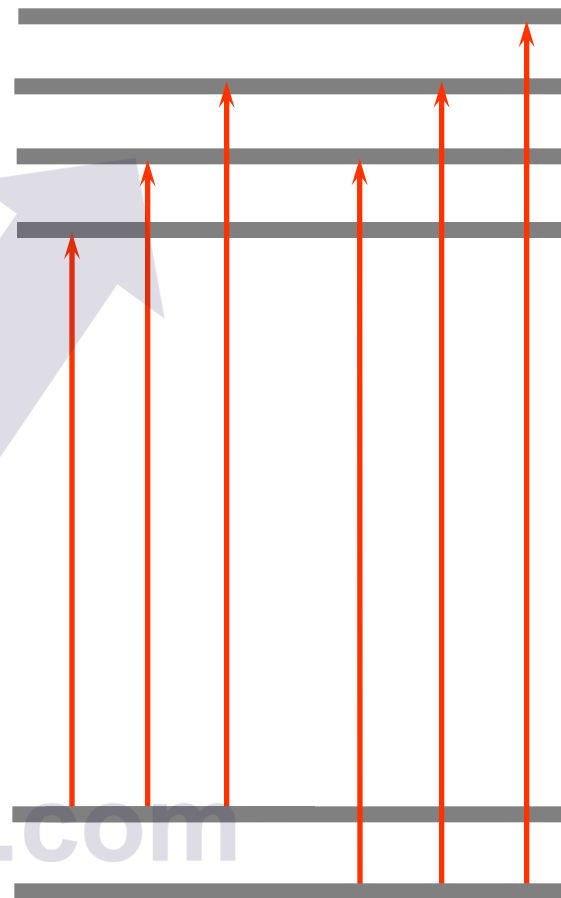
# Hyperfine Interactions

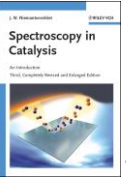


## Magnetic Splitting:

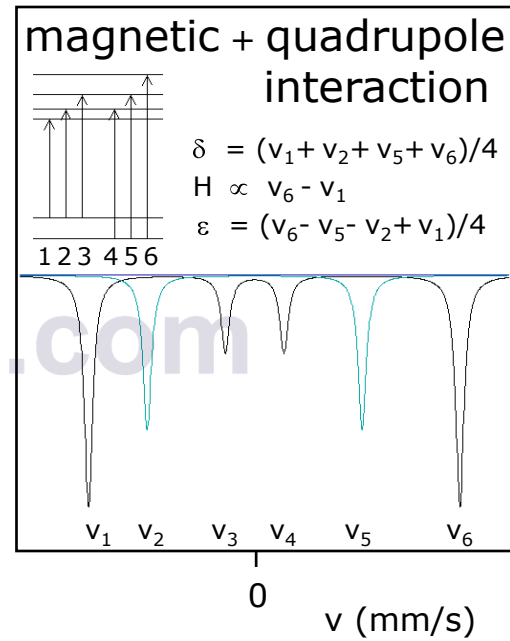
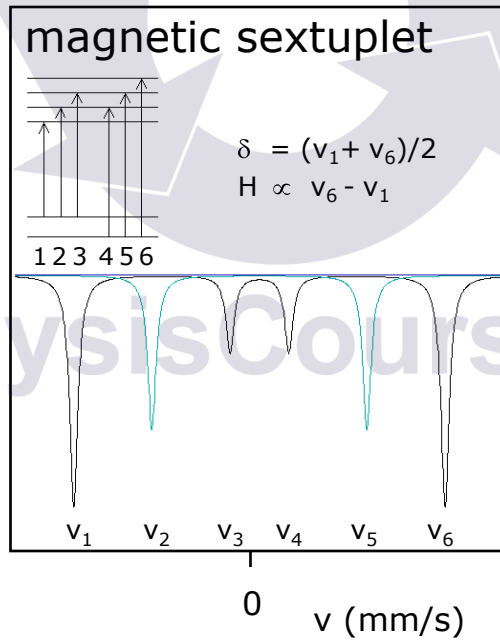
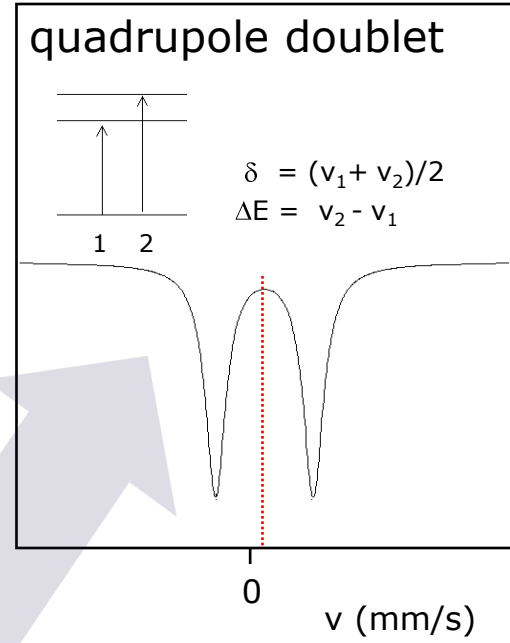
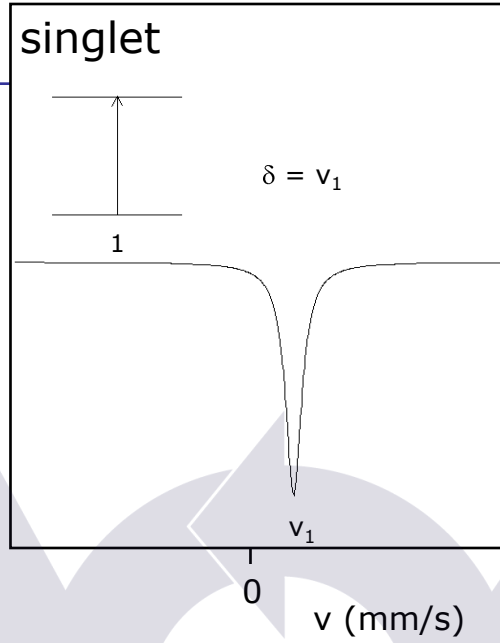
- nuclear magnetic moment  
magnetic field at nucleus  
(Zeeman Effect)
- Information on

***magnetism***



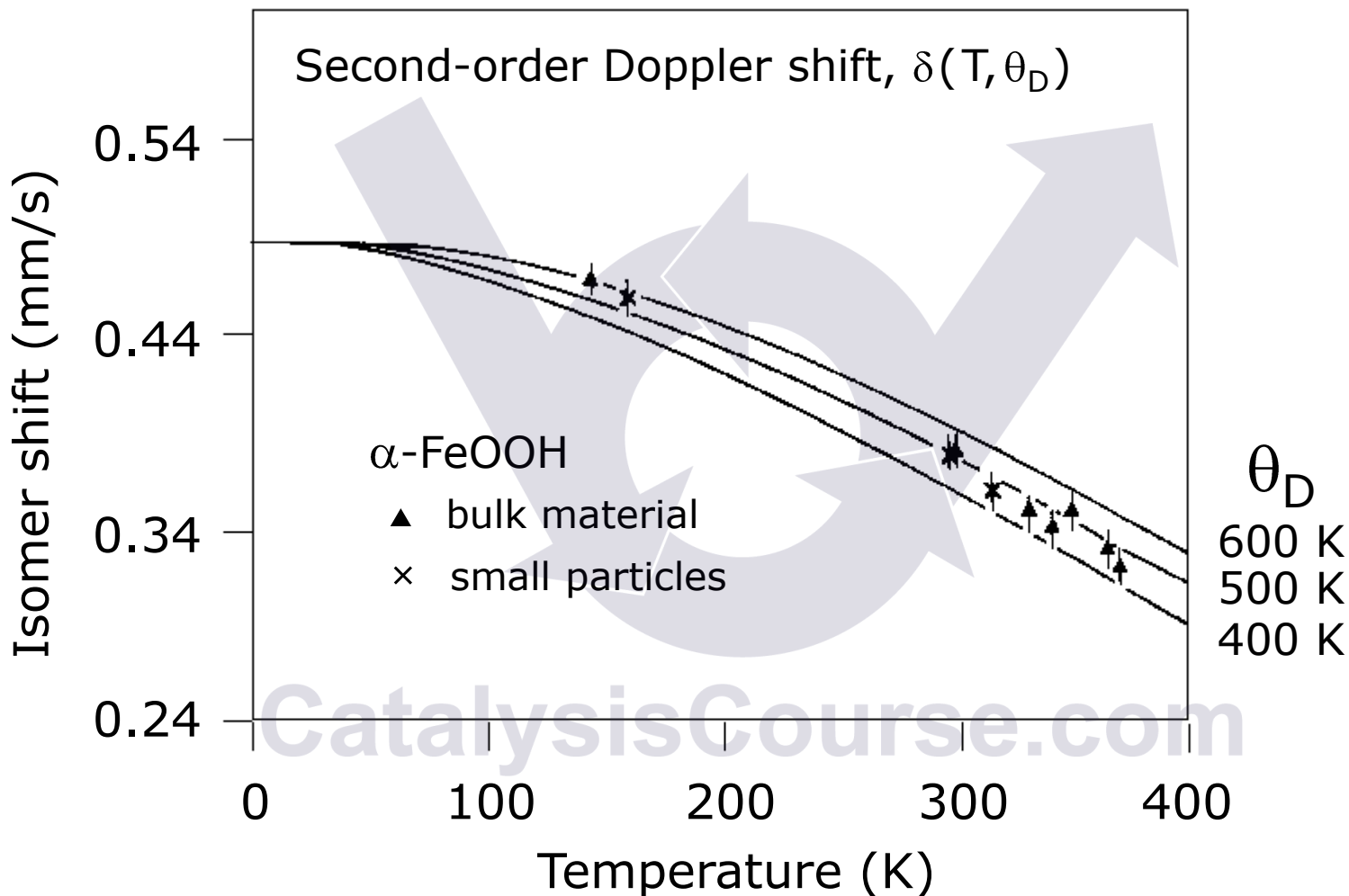


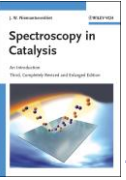
The most common types  
of Mössbauer spectra  
from iron compounds



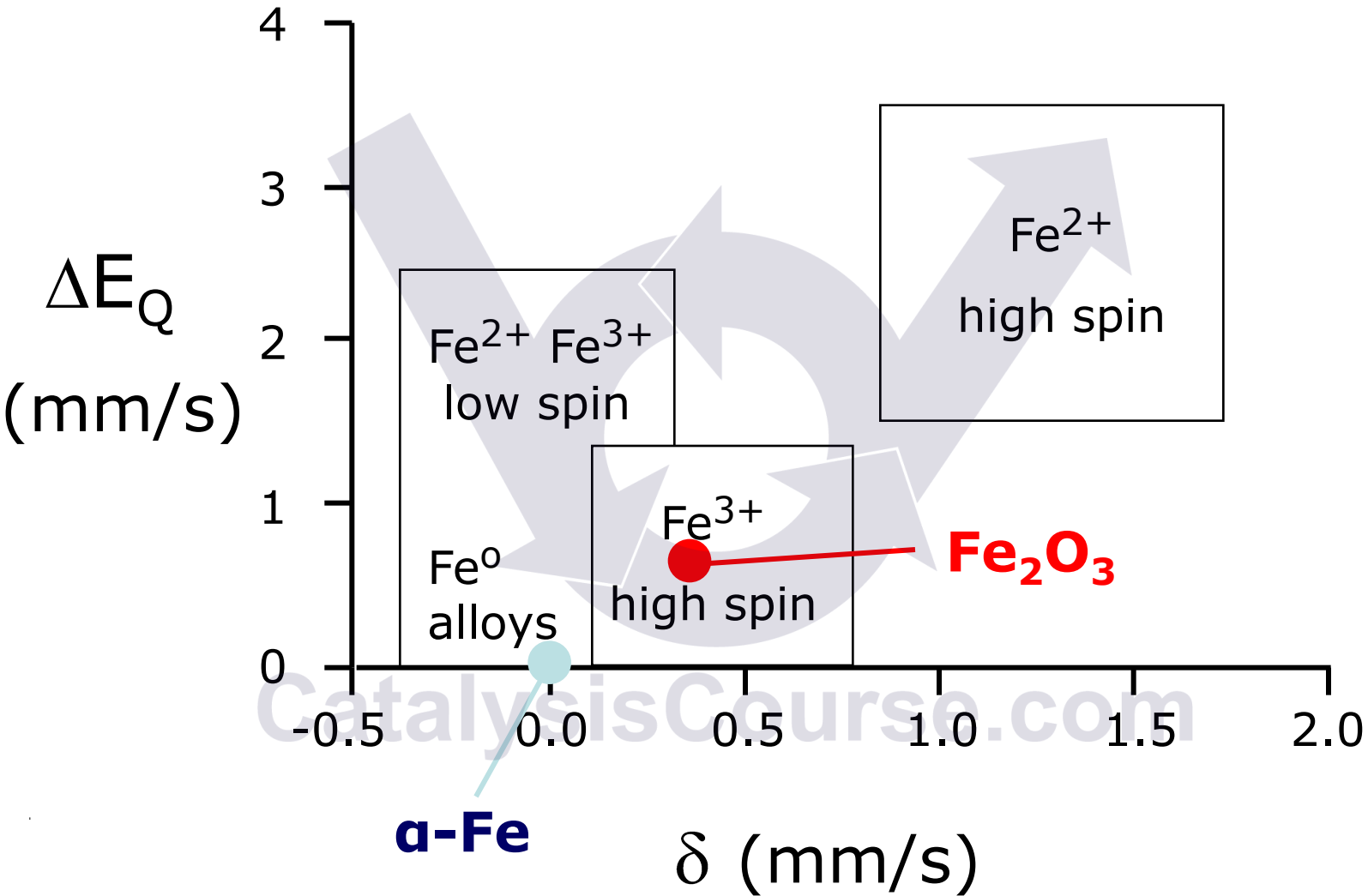
CatalysisCourse.com

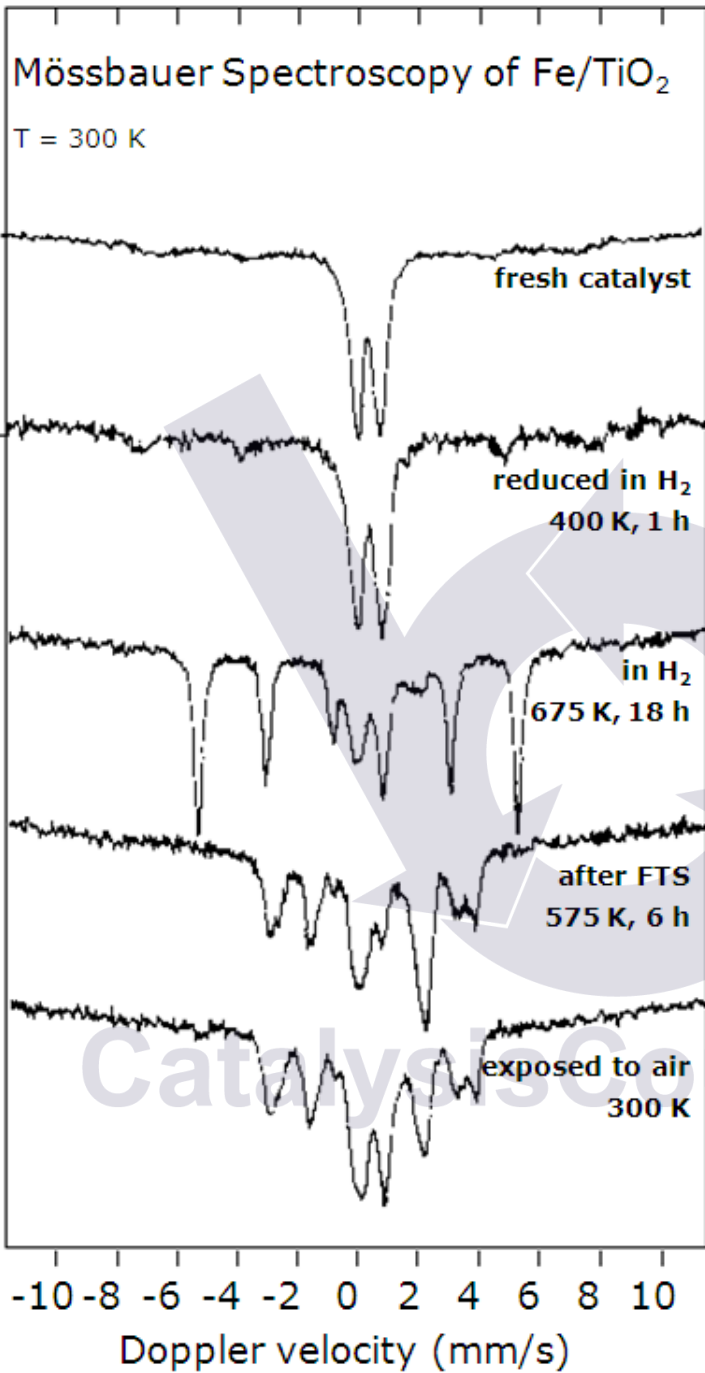
# Isomer Shift depends on Temperature





# Hyperfine Interactions





*dispersed Fe<sup>3+</sup>*

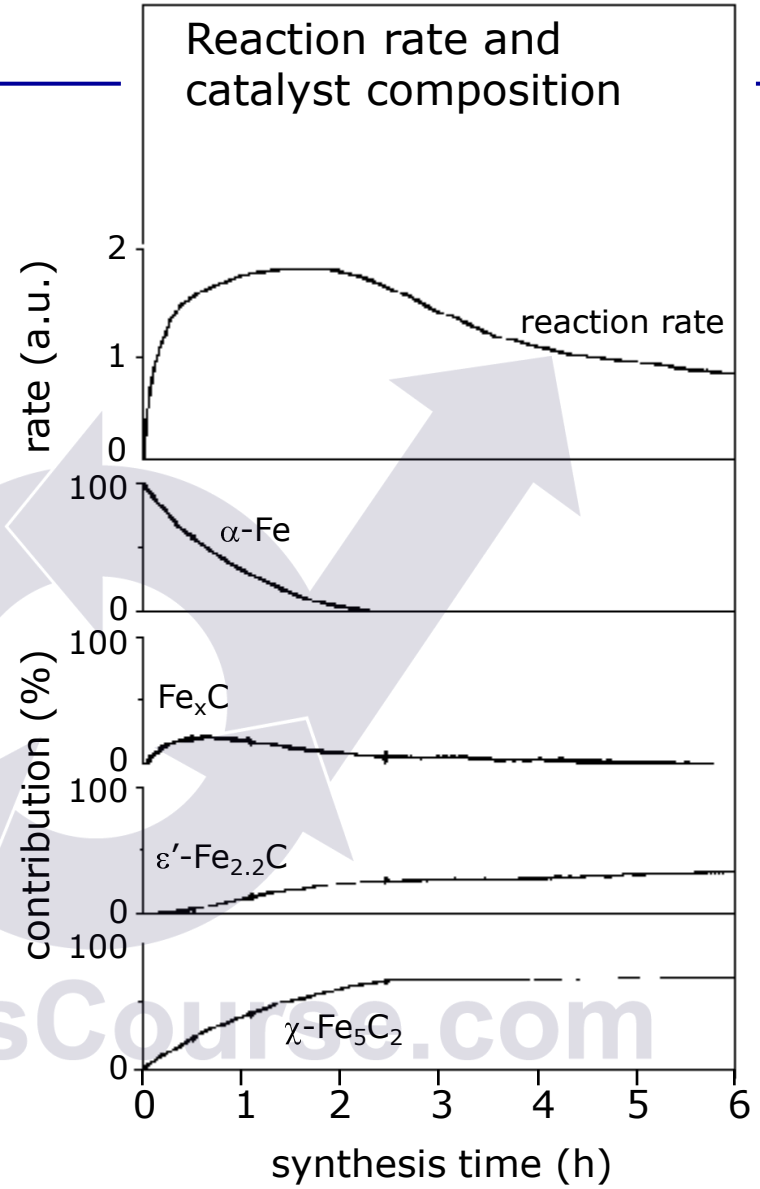
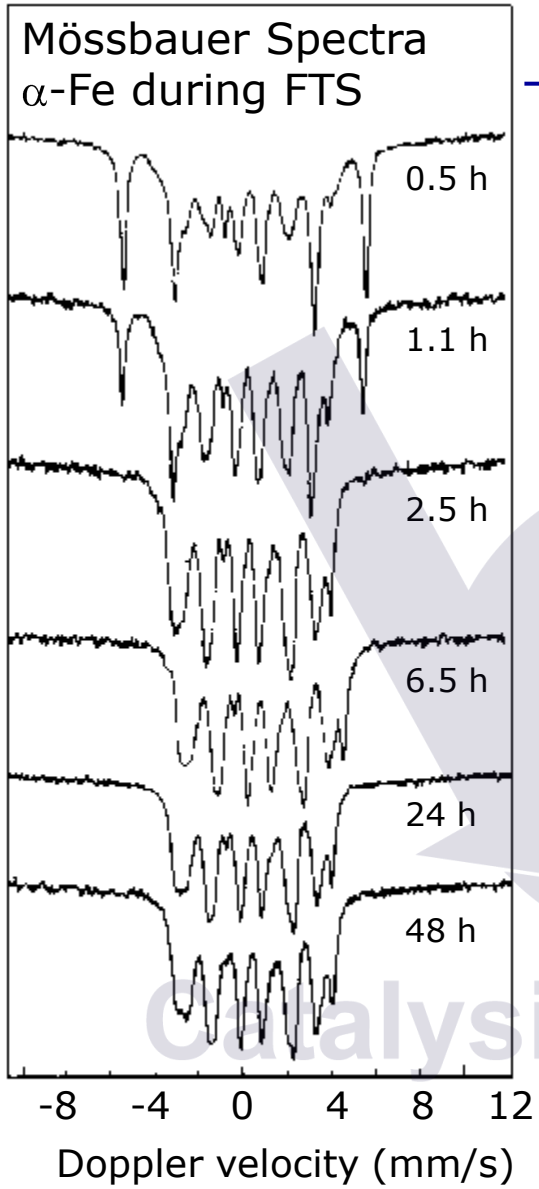
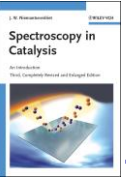
*dispersed Fe<sup>3+</sup>; some larger iron oxide (6-line pattern)*

*mostly reduced iron + unreduced residue Fe<sup>3+</sup> Fe<sup>2+</sup>*

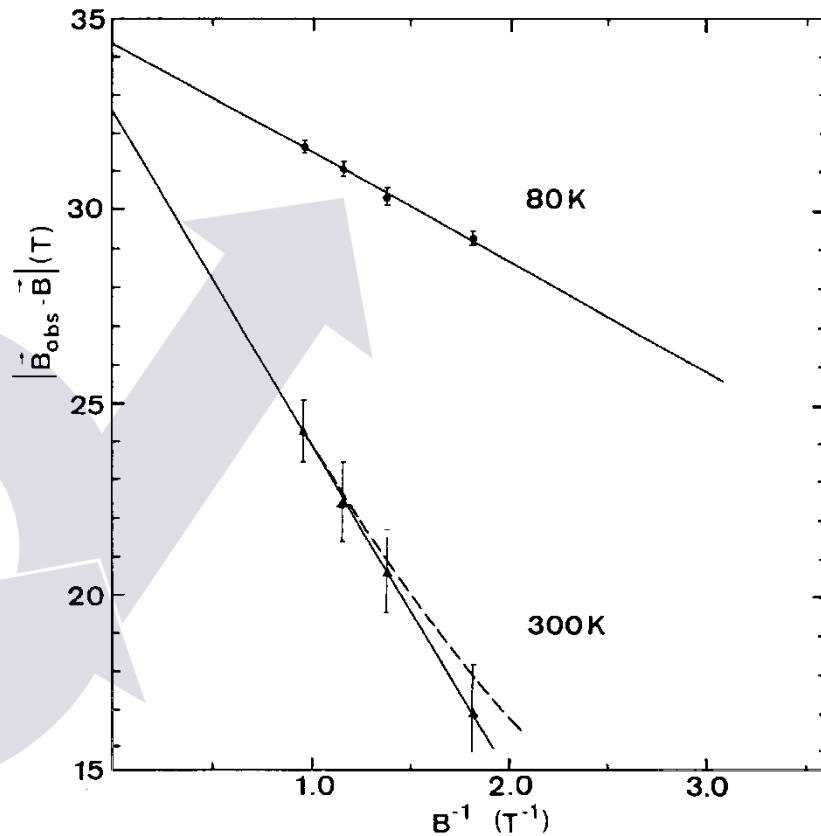
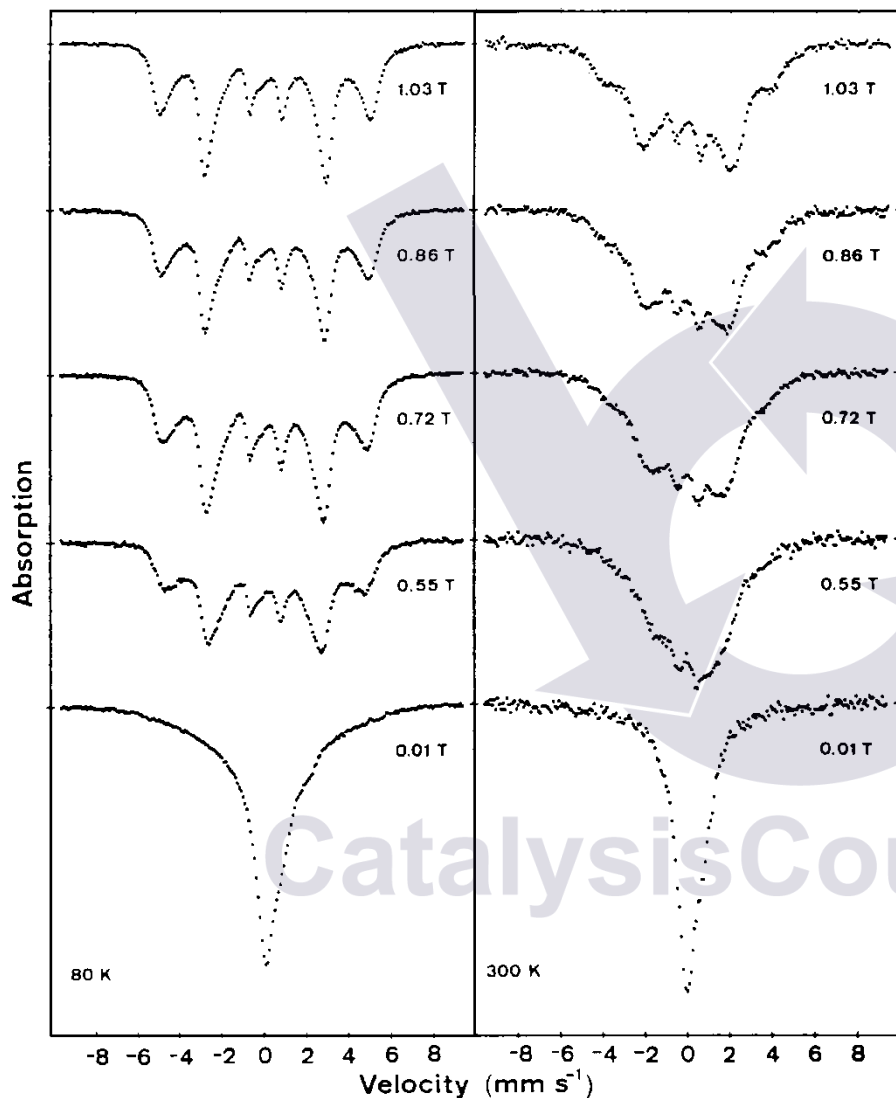
*iron converted to carbide + residual iron oxides*

*part of carbide oxidized to dispersed iron oxide*



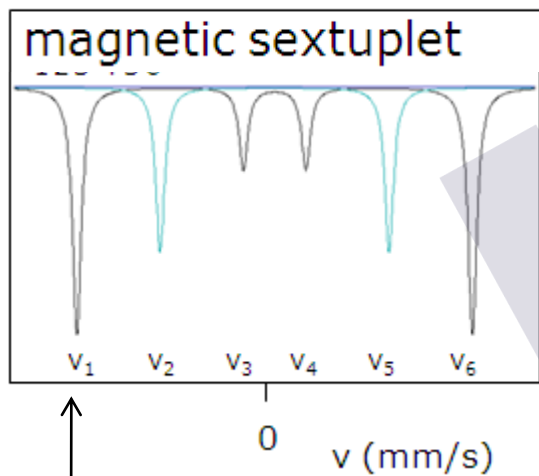
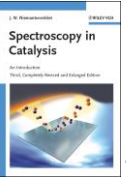


# Superparamagnetic Fe on a carbon support

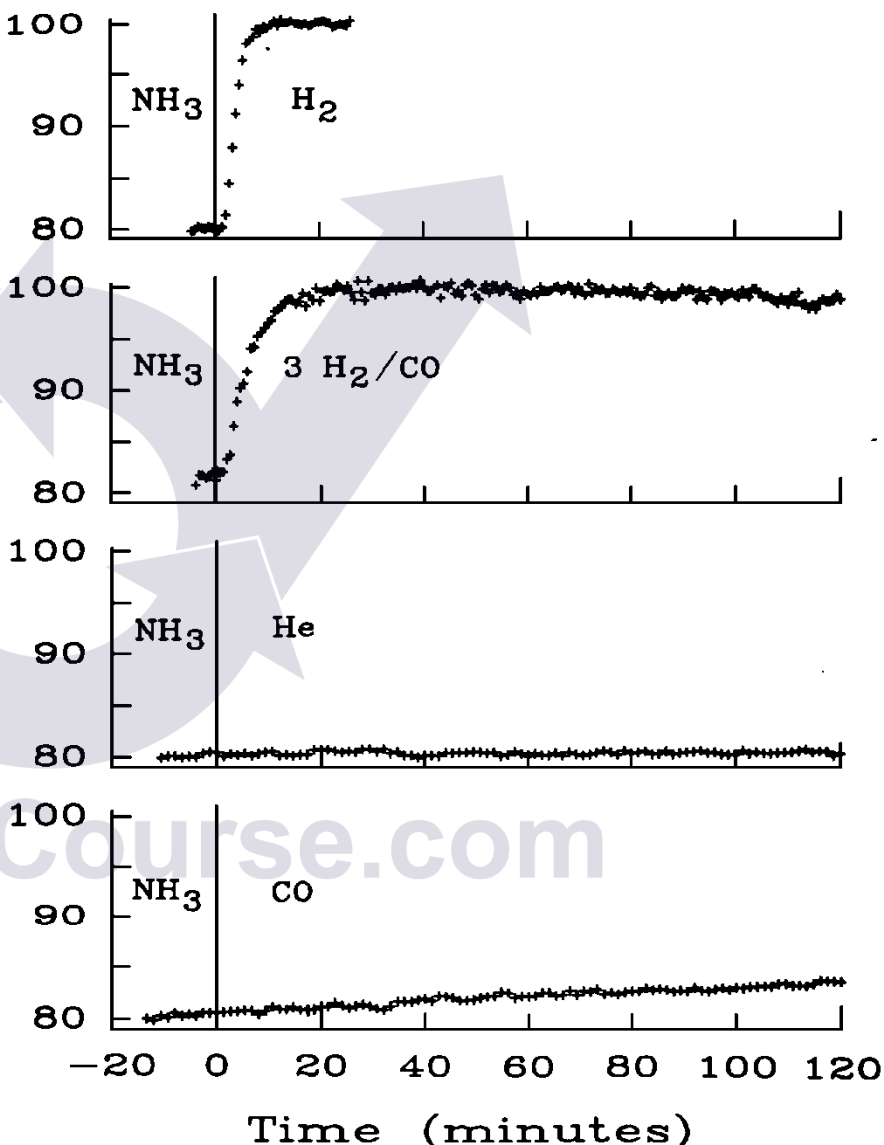


Langevin equation:  
 2.5 nm Fe particles

# Kinetics of solid state reactions



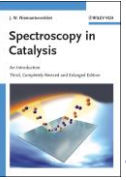
**Fe<sub>2</sub>N converts to metallic iron:**



'single velocity' experiment:  
follow intensity during reaction

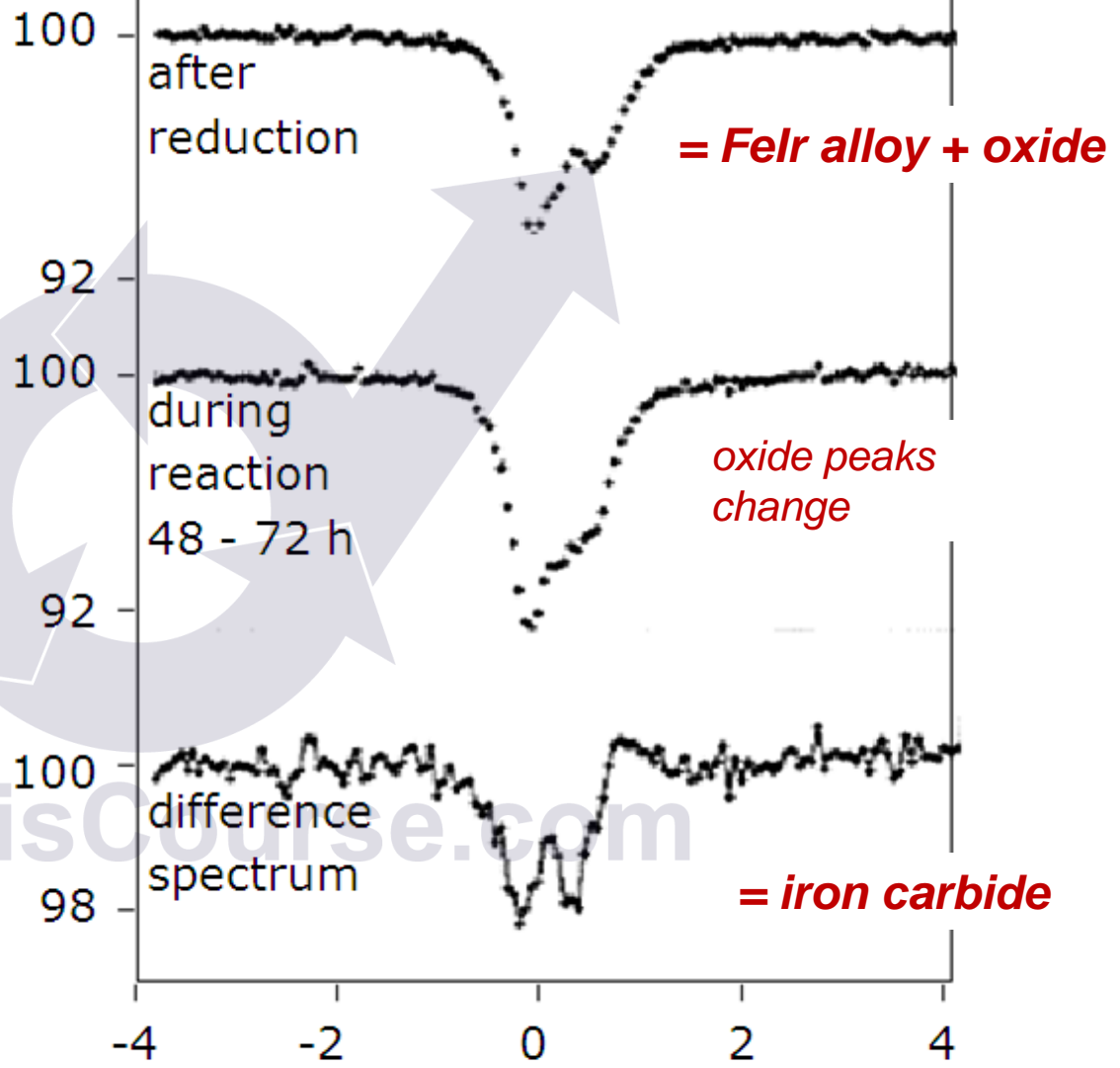
A.A. Hummel, A.P. Wilson  
and W.N. Delgass,  
J. Catal. 113 (1988) 236

CatalysisCourse.com



# Mössbauer spectroscopy during CO + H<sub>2</sub> reaction

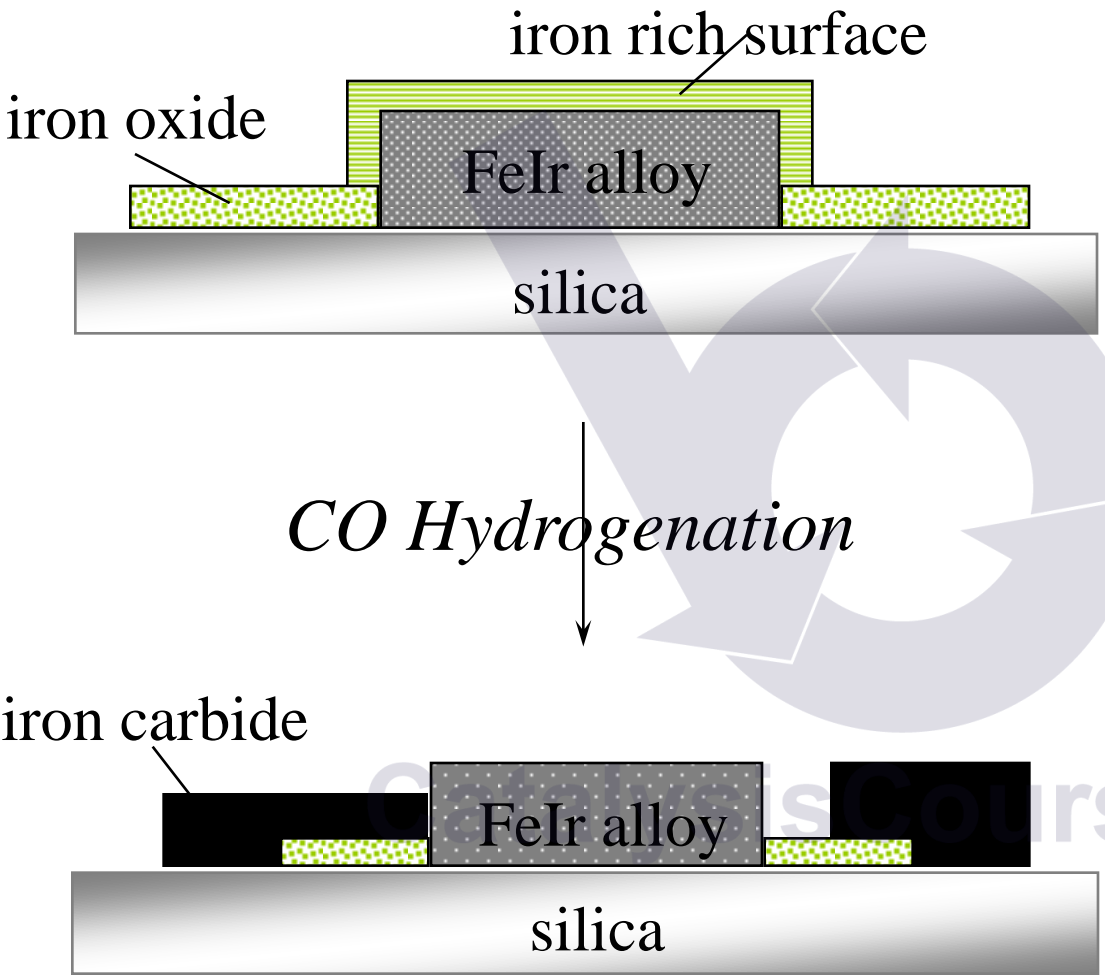
*in situ* Mössbauer Spectroscopy  
1:1 FeIr/SiO<sub>2</sub> at 523 K



J.W. Niemantsverdriet  
and W.N. Delgass,  
Topics Catal. 8 (1999) 133

# CO Hydrogenation on FeIr/SiO<sub>2</sub>

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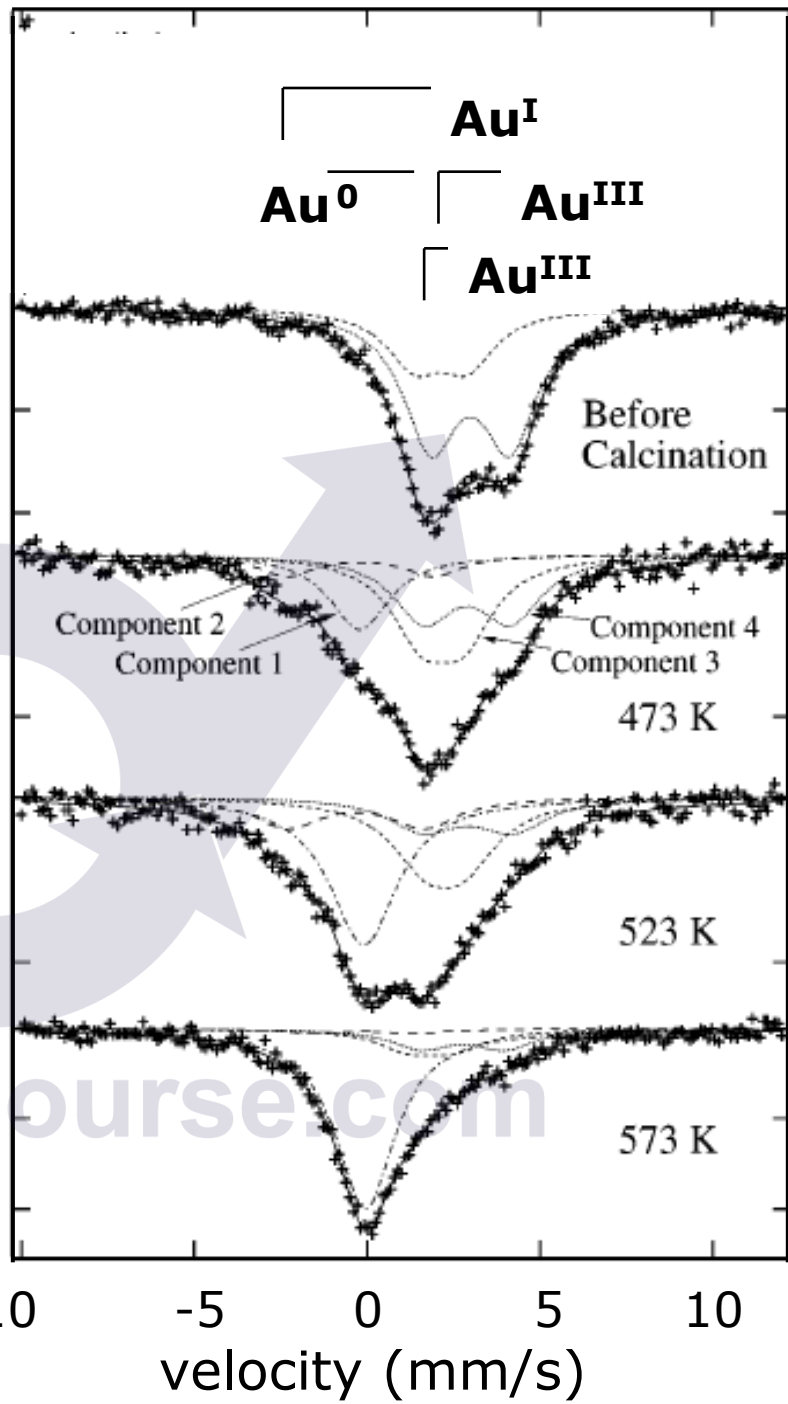
Slow Activation:  
• restructuring !!

Active State for  
MeOH Production

- weak CO adsorption
- more hydrogenation

# Mössbauer spectroscopy of Au catalysts

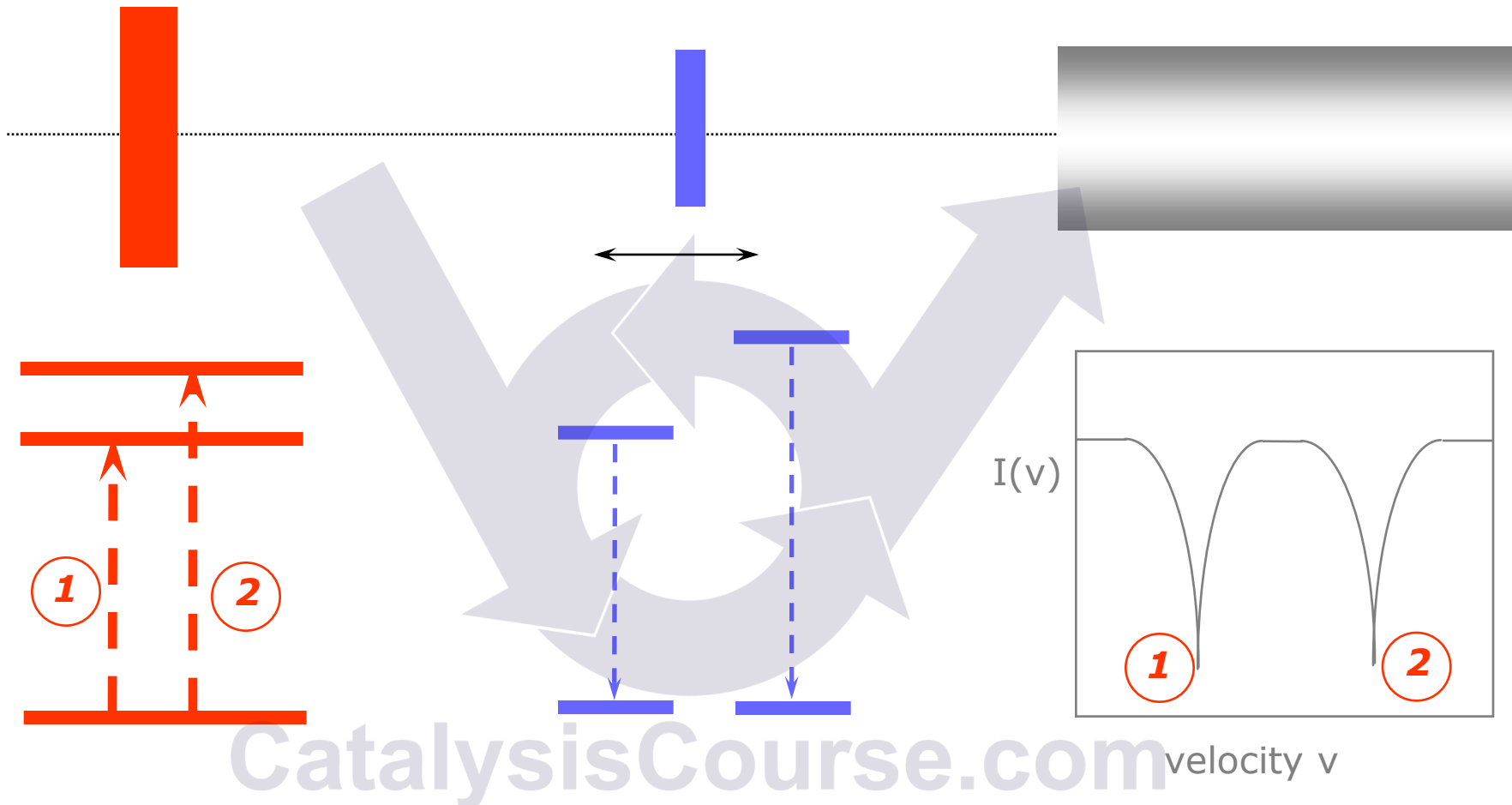
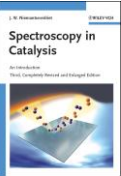
Y. Kobayashi,  
S. Nasu,  
S. Tsubota  
and M. Haruta,  
Hyperfine Interactions  
126 (2000) 95



transmission

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# Mossbauer Emission Spectroscopy



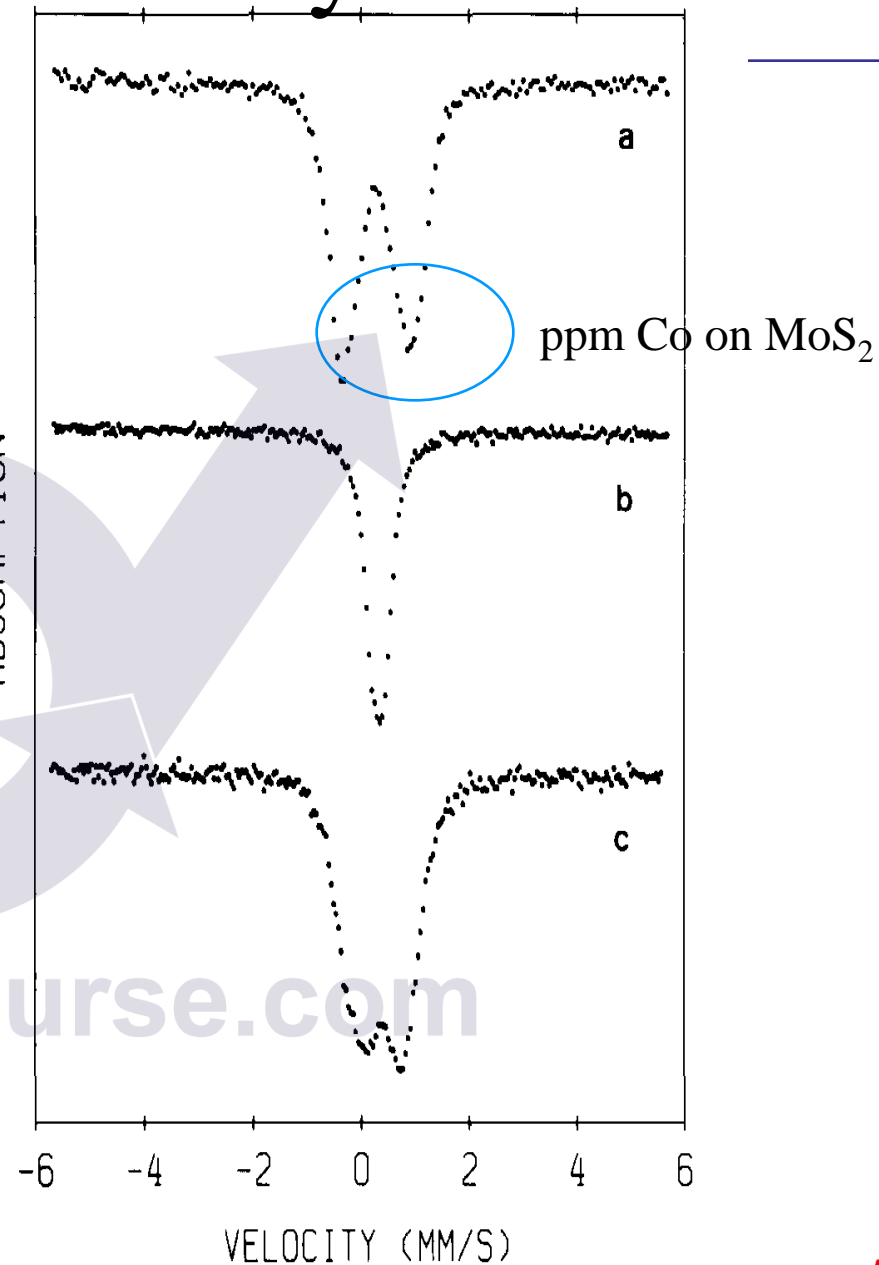
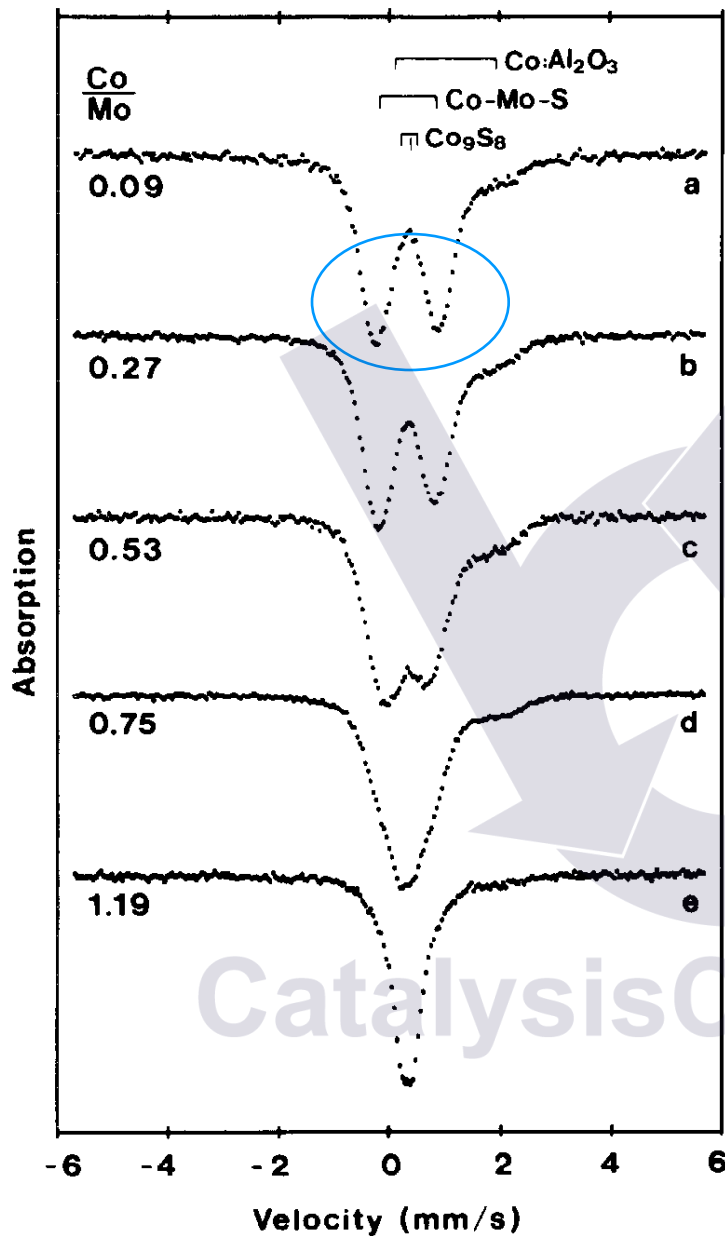
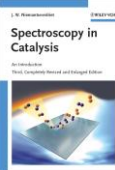
- emitter with  $^{57}\text{Co}$

- single line absorber
- Doppler effect:  
 $E(v) = E_0 (1+v/c)$

- gamma ray detector,
- transmitted intensity versus velocity

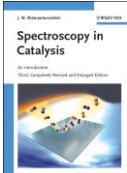
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# Sulfided CoMo Catalysts:



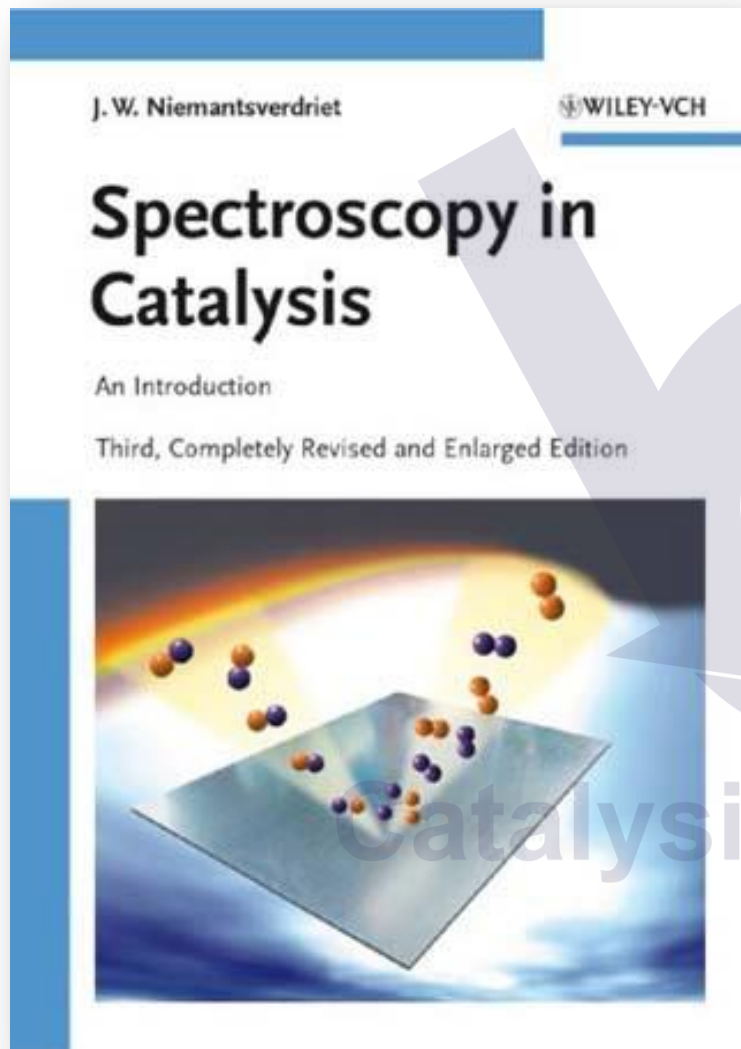


# Mossbauer Spectroscopy in Catalysis



- Limited to characterization of catalysts (Materials Science of Catalysts)
- Great advantage: ***in situ*** application
- Highly relevant information on a small number of important catalysts

Download the handout for this lecture from  
[www.catalysiscourse.com](http://www.catalysiscourse.com)



Read more about Mössbauer spectroscopy

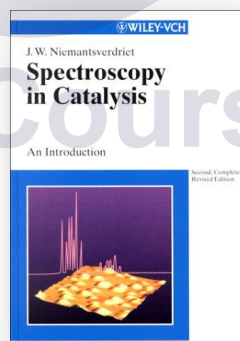
in Chapter 5 of

**Spectroscopy in Catalysis: An Introduction, Third Edition**

**J. W. Niemantsverdriet**

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ISBN: 978-3-527-31651-9



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gives many examples and references to the literature

**TU/e** Technische Universiteit  
Eindhoven  
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