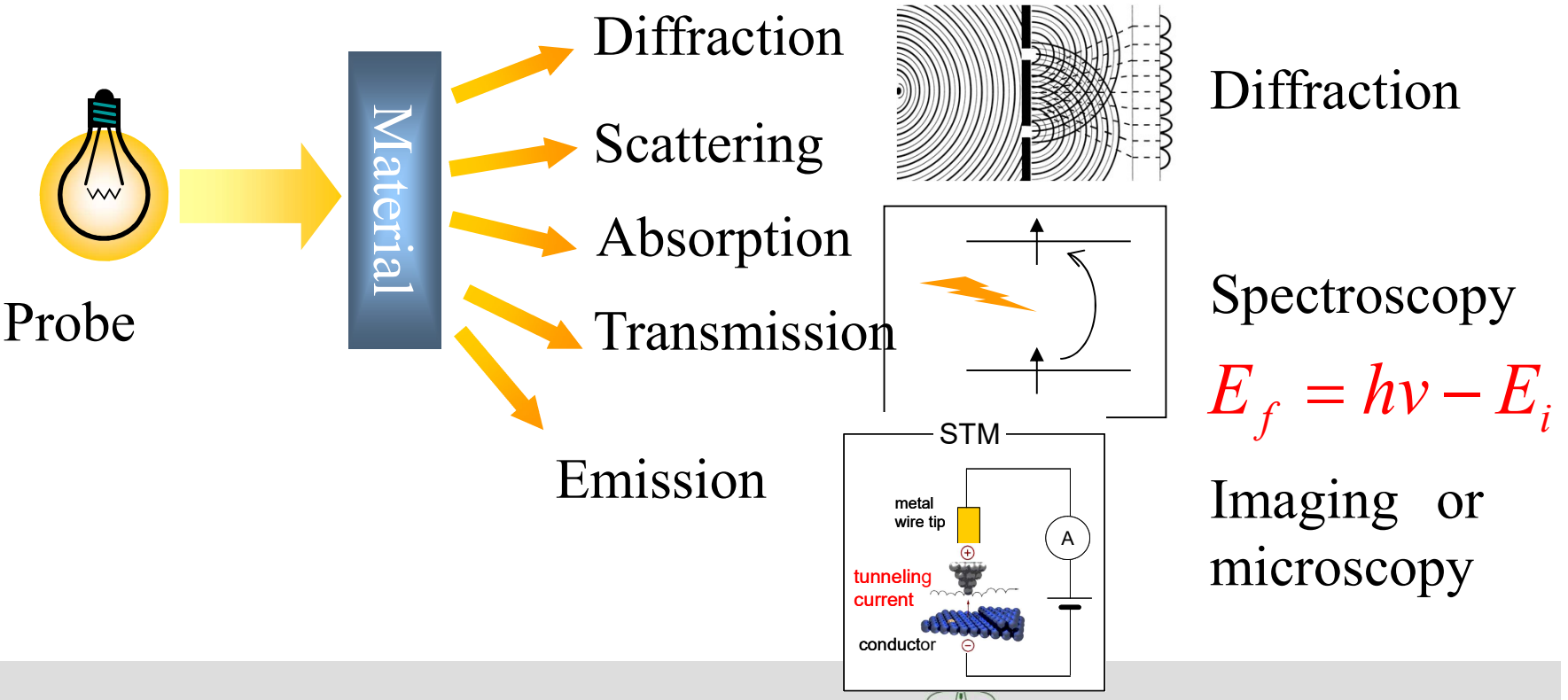
HOKKAIDO UNIVERSITY

Characterization and XAFS

Kiyotataka Asakura (2018.Nov.22)

Three categories

- Materials are illuminated by probe(light, electron, neutron, muon, He, ion and sharp tip)



How to characterize the Catalysts

What we would like to obtain

Quality, Quantity and State and structure Analysis

Method

Imaging, Spectroscopy and Diffraction

Temporal and Static

Operando and in situ

Characterization techniques

NMR	Nuclear Magnetic Resonance	Nuclear spin	Structure
ESR	Electron Magnetic Resonance	Electron spin	Structure
IR	Infrared	Vibration	Adsobate
RAMAN	Raman scattering	Vibration	Structure
UV-VIS	Ultraviolet and visible absorption	Electron absorption	Electronic state
XPS	X-ray photoelectron spectroscopy	Photoelectron mission	Electronic State
XRD	X-ray diffraction	Diffraction	Structure
XSAS	X-ray small angle scattering	Scattering	Long range order
XAFS	X-ray absorption fine structure	X-ray absorption	Local structure
Mössbauer		Gamma-ray absorption	Electronic state
TEM	Transmission electron microscopy	Electron	Morphology
SPM	Scanning probe microscopy	Probe tip	Morphology
EPMA	Electron probe microanalysis	Fluorescent x-ray	Local composition
XRF	X-ray fluorescence	Fluorescent X-ray	Composition
PEEM	Photoemission electron microscopy	Photoemission	WF
ND	Neutron Diffraction	Diffraction	Structure

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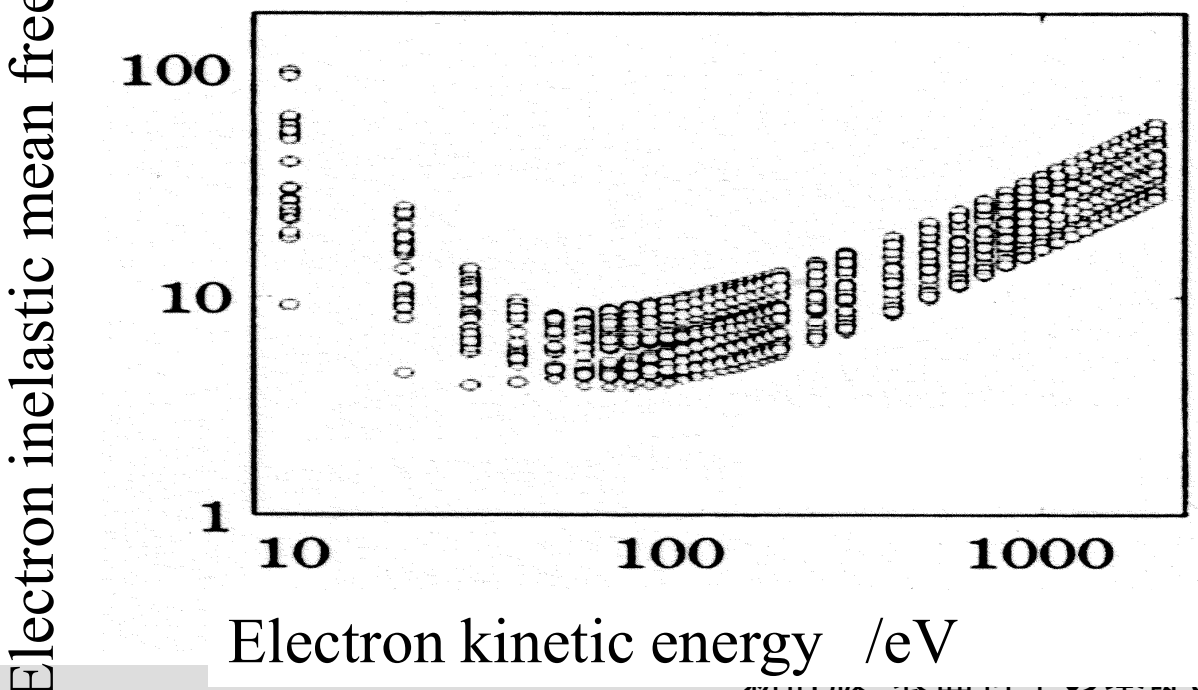
Surface Sensitive

Inelastic Mean Free Path of electron

- The initial kinetic energy of the electron.
- The nature of the solid.



Electron is surface sensitive

X-ray photoelectron spectroscopy（XPS）

- **Elemental analysis, electronic structure**
  - **Non-destructive, Surface sensitive**

UHV is necessary.

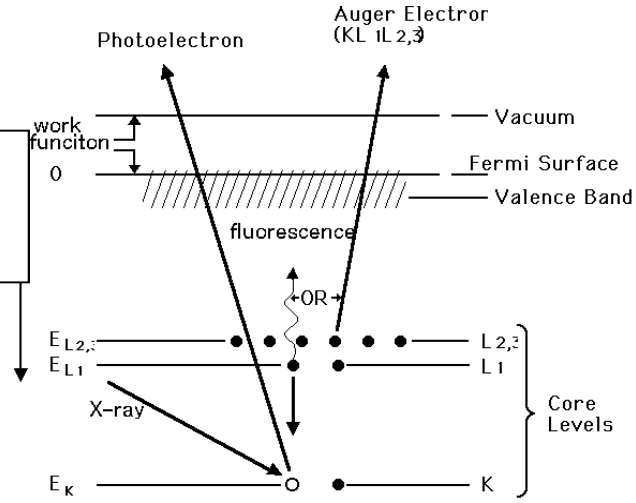
Recently ambient pressure XPS is available

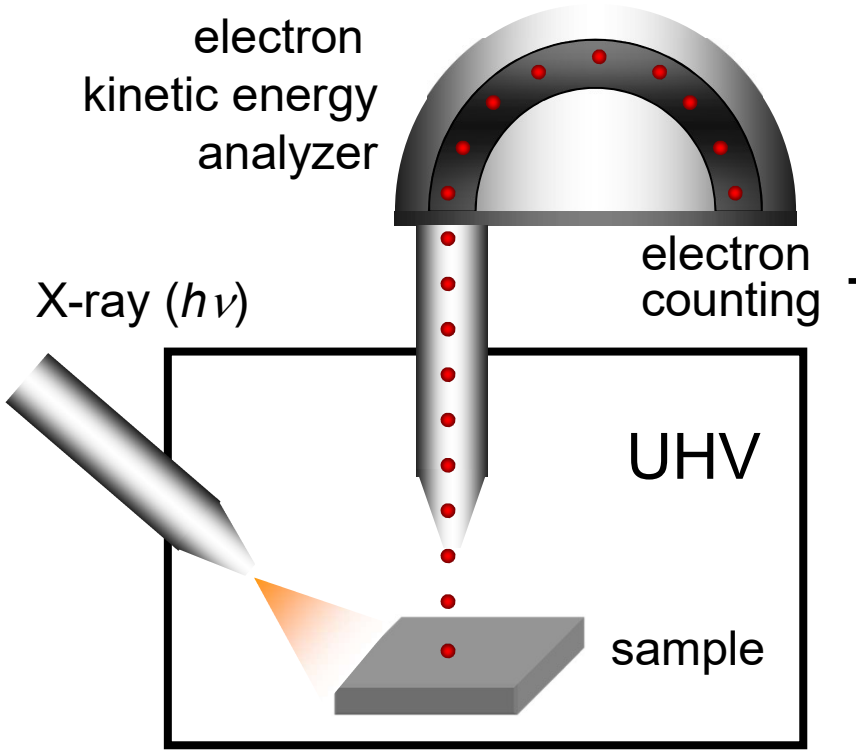
A scheme of XPS

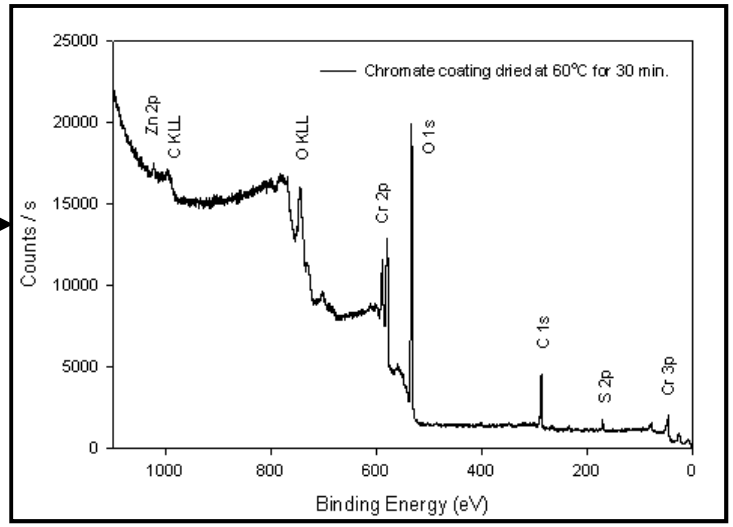
X-ray excite core electron

$$E_k^{vacuum} = h\nu - E_b - \phi$$

at vacuum level







XPS gives

Binding energy

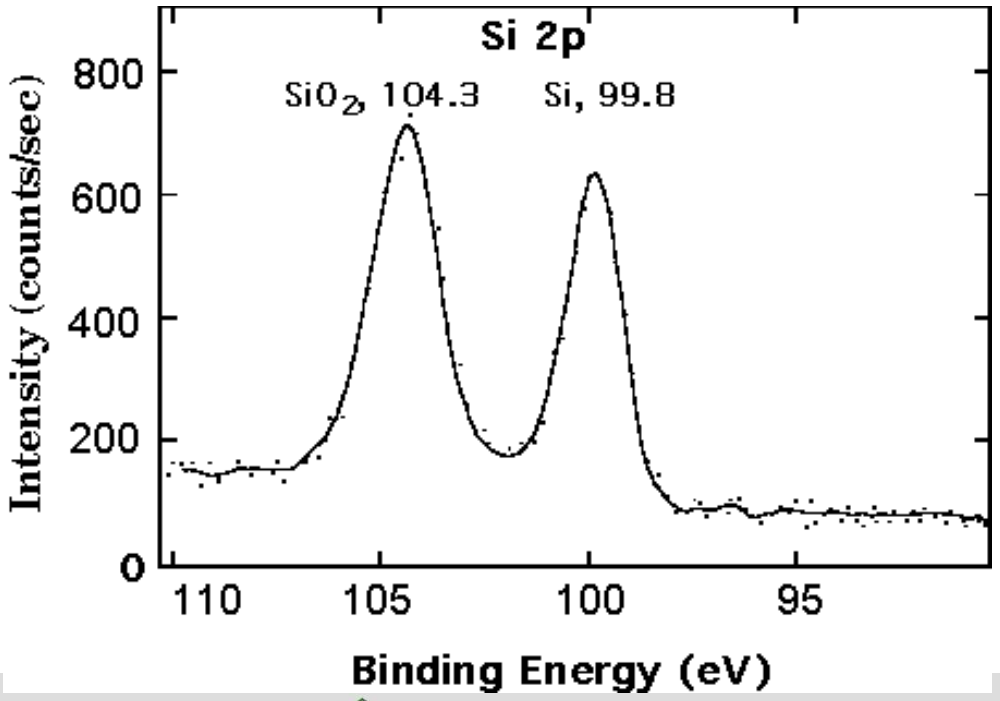
- **Element analysis and chemical state**

Intensity

- **Surface concentration**

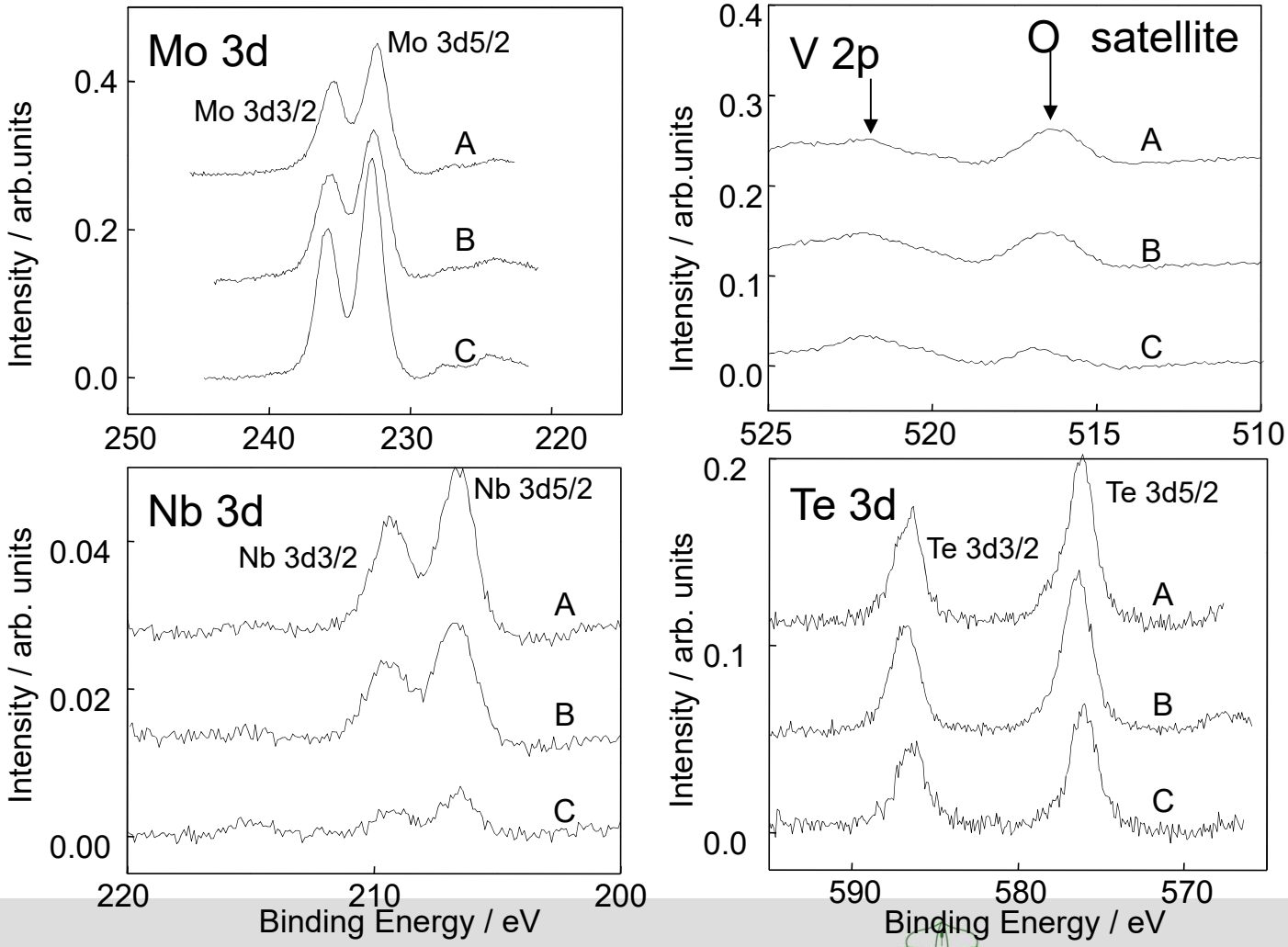
$$E_k^{\text{vacuum}} = h\nu - E_b - \phi$$

at vacuum level

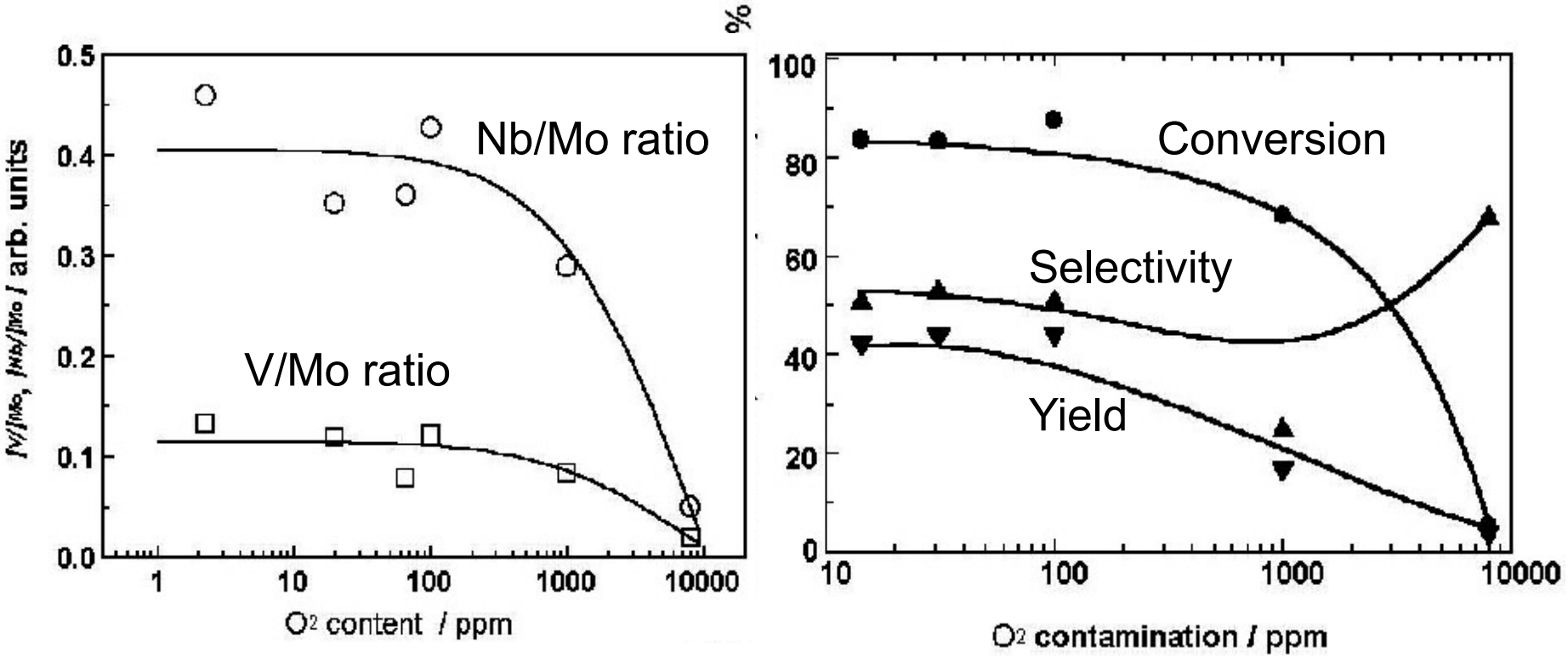


Mo-Te-V-Nb Oxide

Increase the oxygen concentration in order of A,B, and C



XPS results on surface concentration composition and ammoxidation



Oxygen concentration increases and Surface composition changes

Propane oxidation

Peak deconvolutions

The binding energy depends on the valence state.

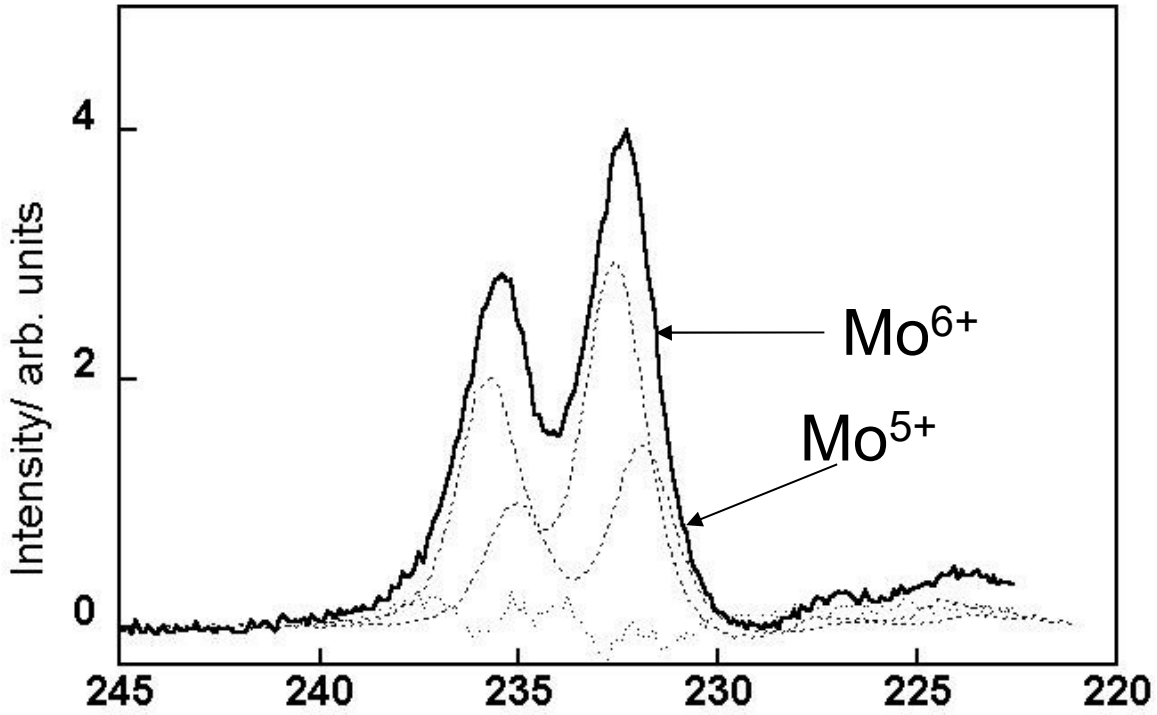


Fig. 7 K.Asakura et al.

High pressure XPS

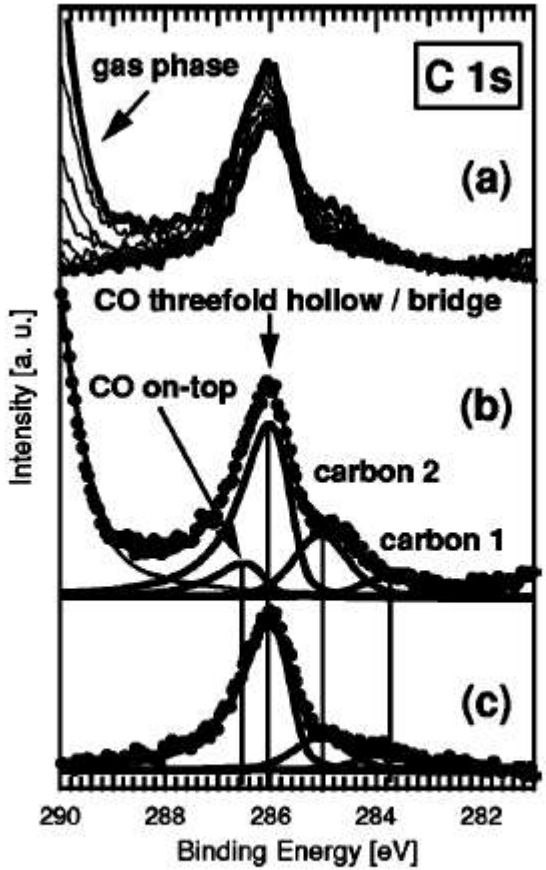


FIG. 11. Fitting results of *in situ* C 1*s* spectra ($h\nu$=1486.6 eV, ϑ=0°) at different CO pressures from 5×10^{-8} mbar to 1 mbar. (a) Data from Fig. 5 after normalization and subtraction of a Shirley background; (b) fit of the data for p=1 mbar; (c) fit of the data for $p=5\times10^{-8}$ mbar (see the text for details).

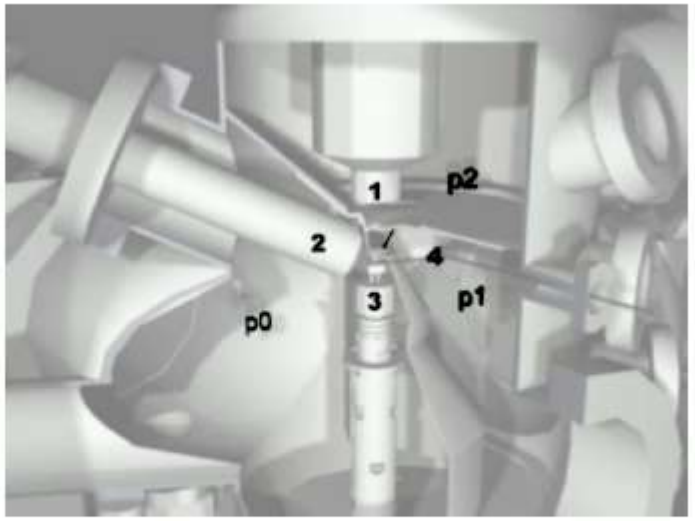
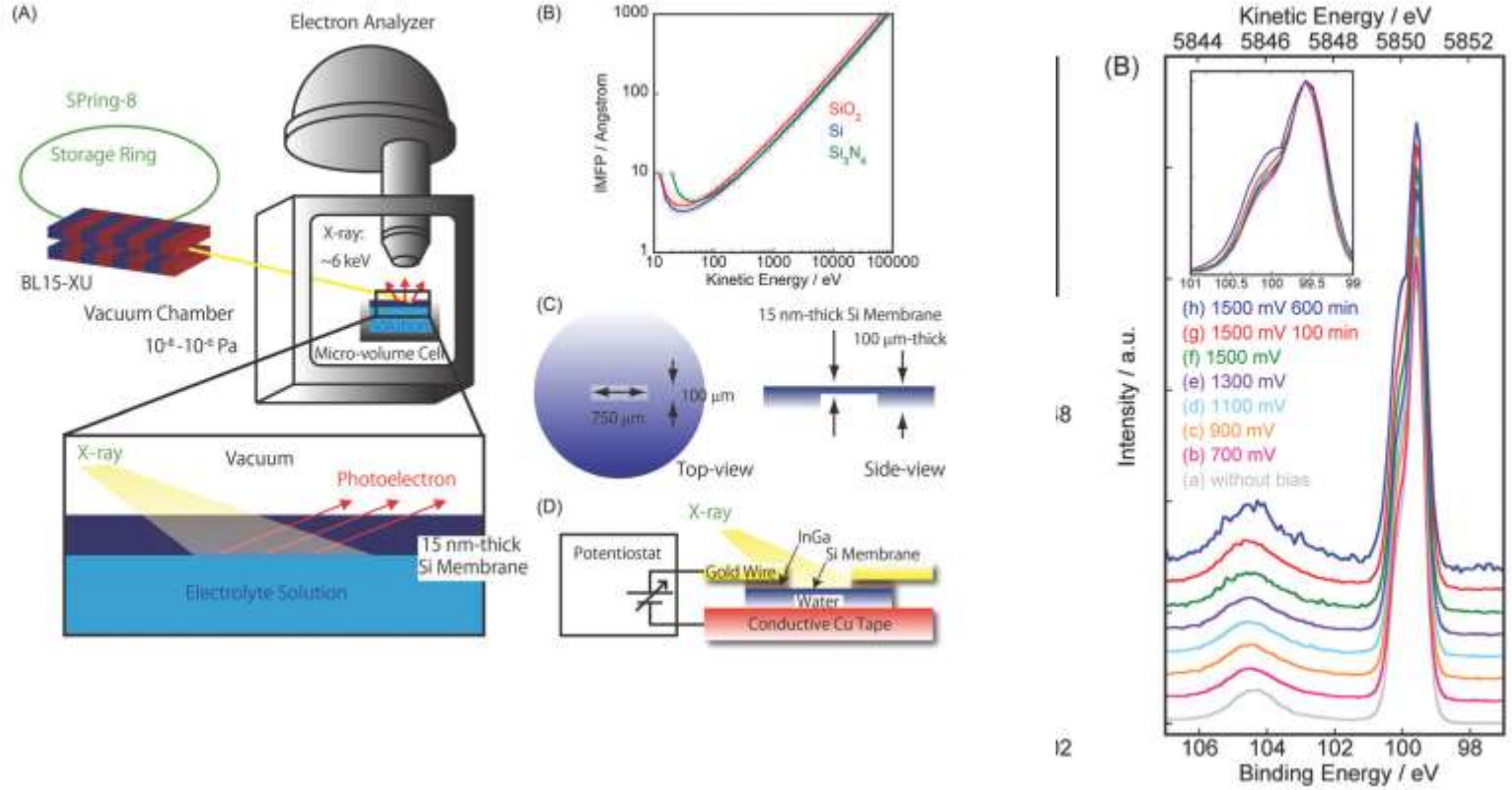


FIG. 2. Schematic cut through the analysis chamber of the XPS apparatus with aperture system. The sample stage and the first two pumping stages are indicated by the pressures p_0, p_1, and p_2. (1) Electron energy analyzer lens, (2) aluminum window of the x-ray source, (3) sample holder, (4) dosing system for beam pressures.

Detector Differential pumping

Pantforder, J. RSI 76 014102 2005

XPS from interface with liquid



T. Masuda, H. Yoshikawa, H. Noguchi, T. Kawasaki, M. Kobata, K. KobayashiandK. Uosaki, *Applied Physics Letters* ***2013, 103, 111605.***

TEM (Transmission Electron Microscopy)

Information

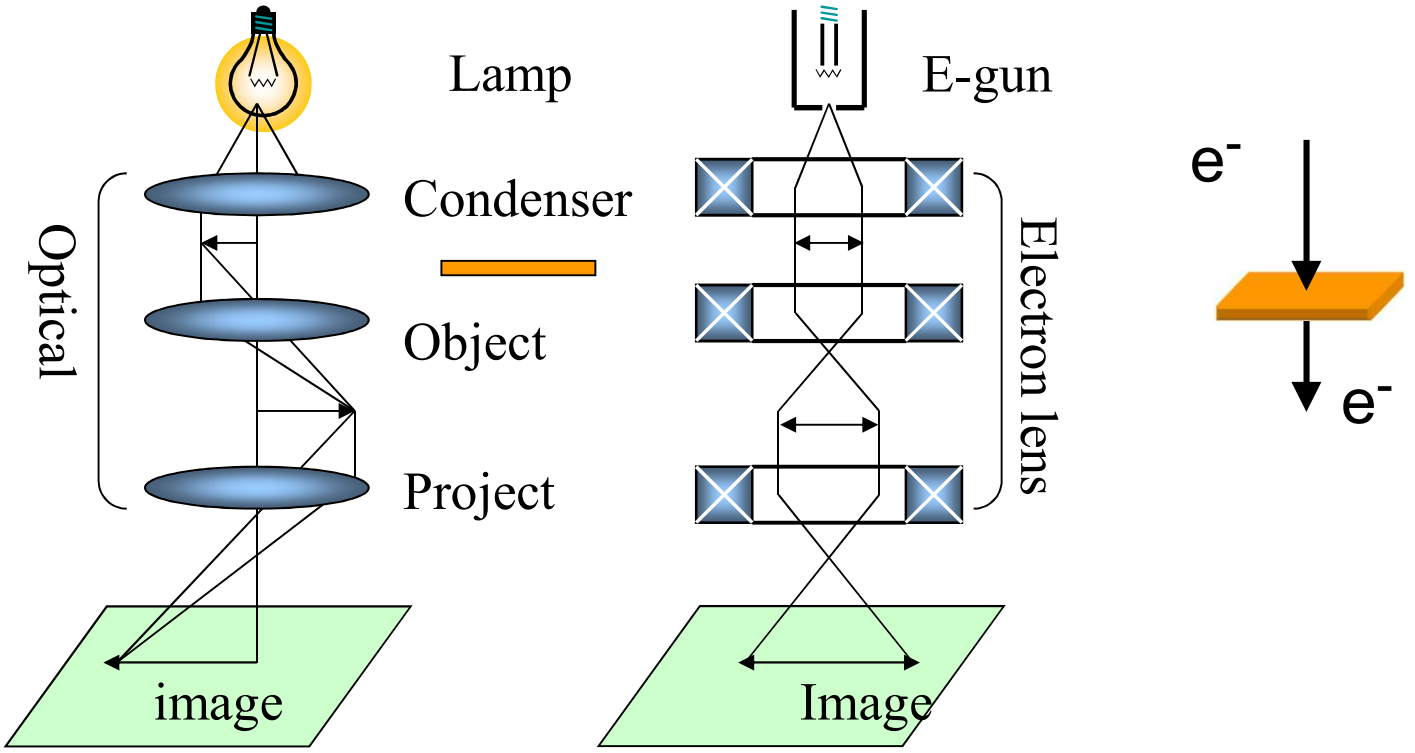
- **Atomic level structure and morphology**
- **Composition analysis by Analysis TEM**

■ Disadvantage

- Sample damage
- Sample size and thickness

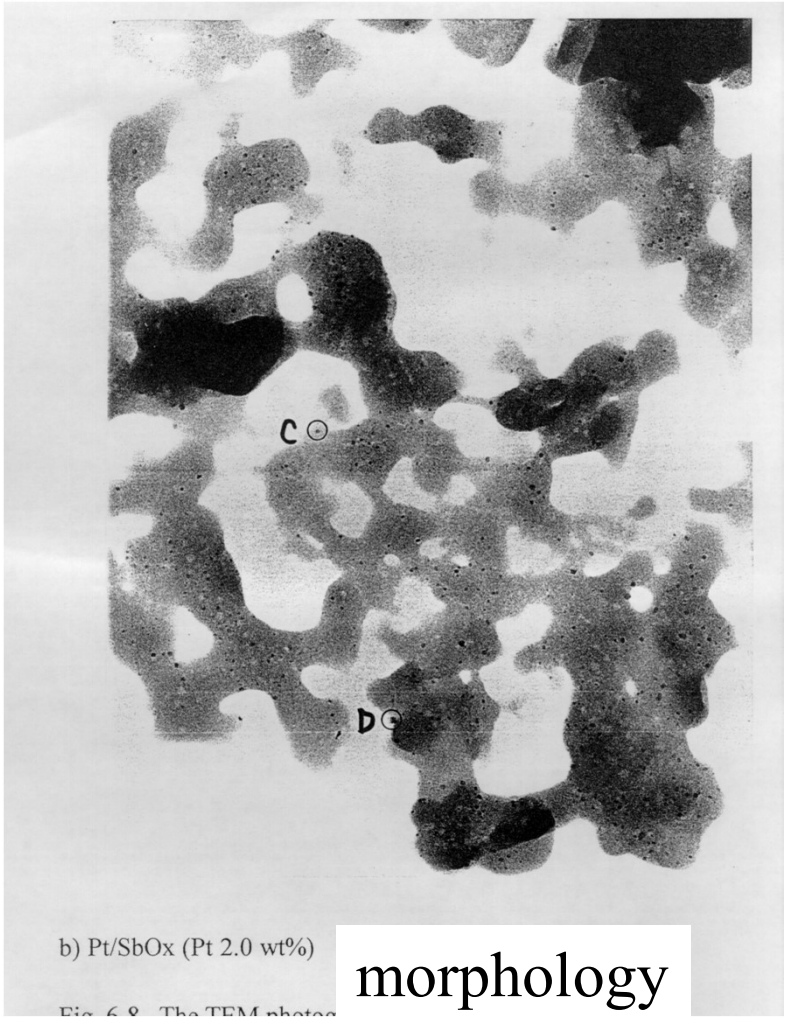
A scheme of Transmission Electron Microscopy

Scattered and diffracted beams are imaged



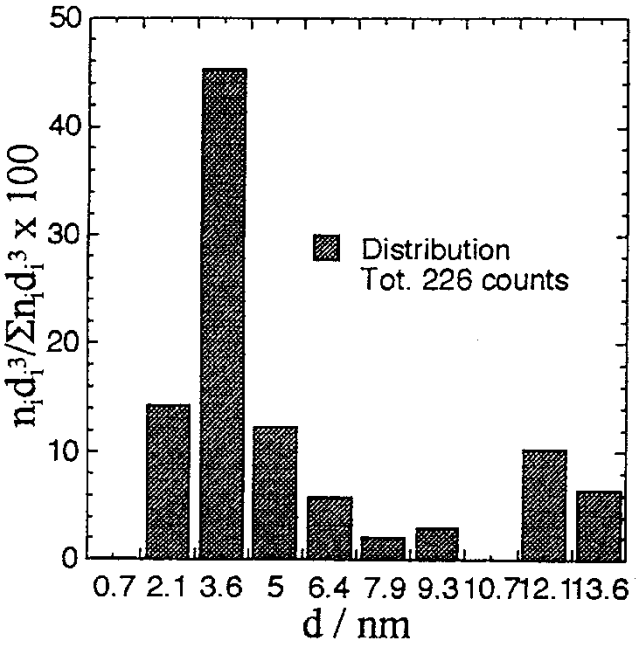
Optical microscopy TEM

Particle size and morphology



b) Pt/SbOx (Pt 2.0 wt%)

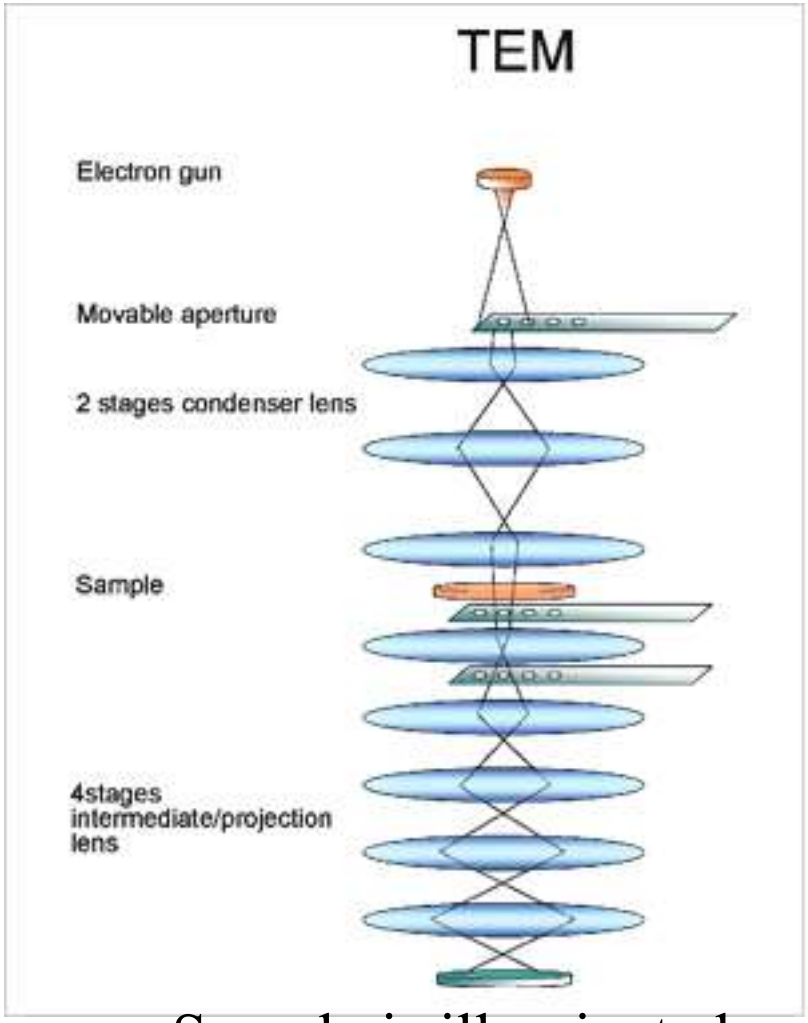
morphology

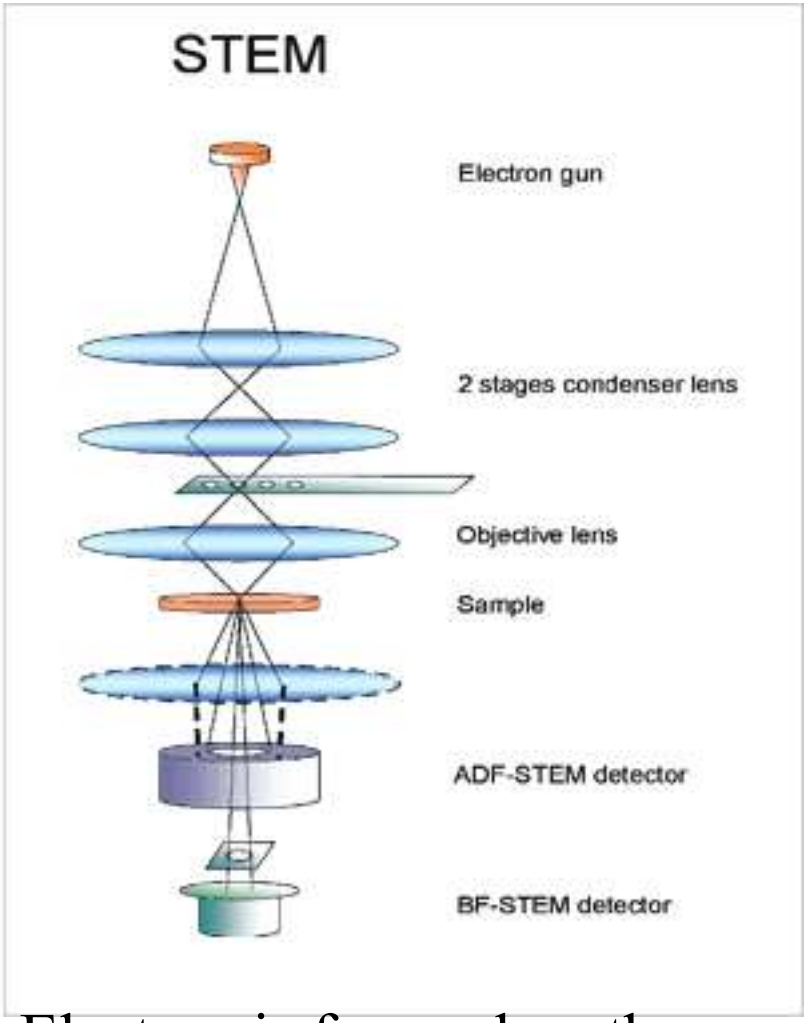


a)Pt/SbOx 0.5 wt%

Particle size distribution

TEM and STEM

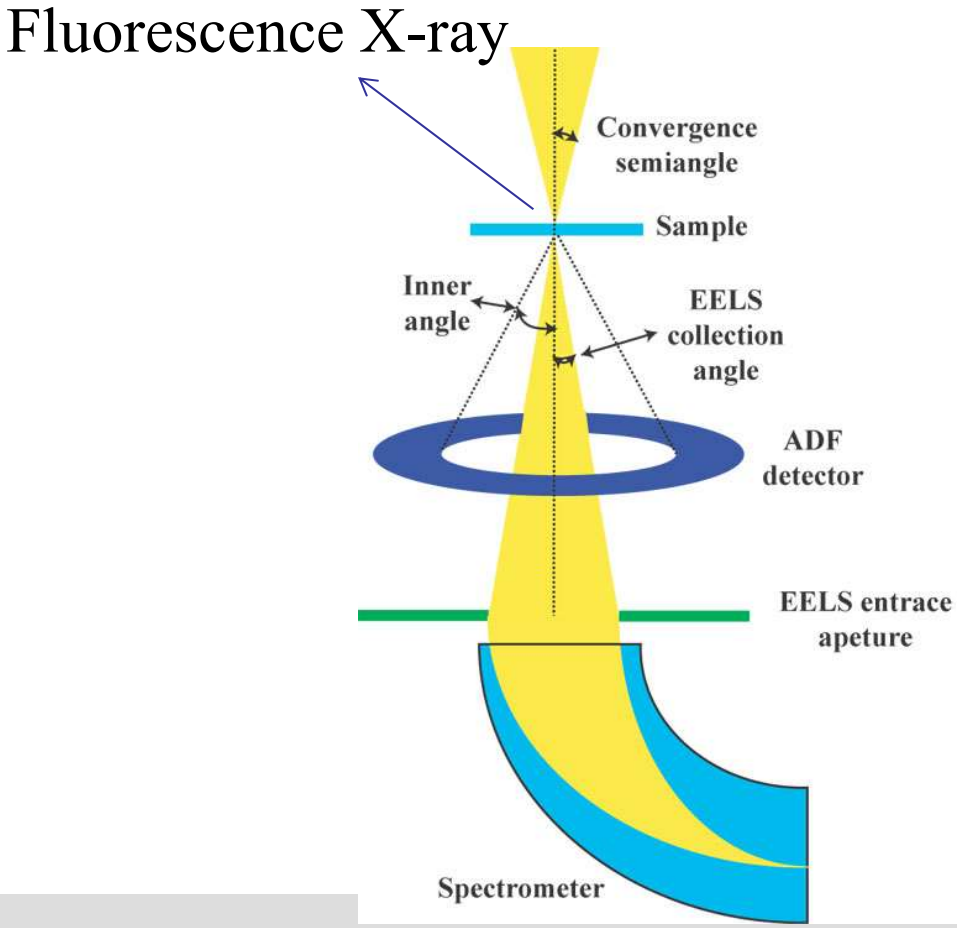




Sample is illuminated

Electron is focused on the sample

Analysis STEM

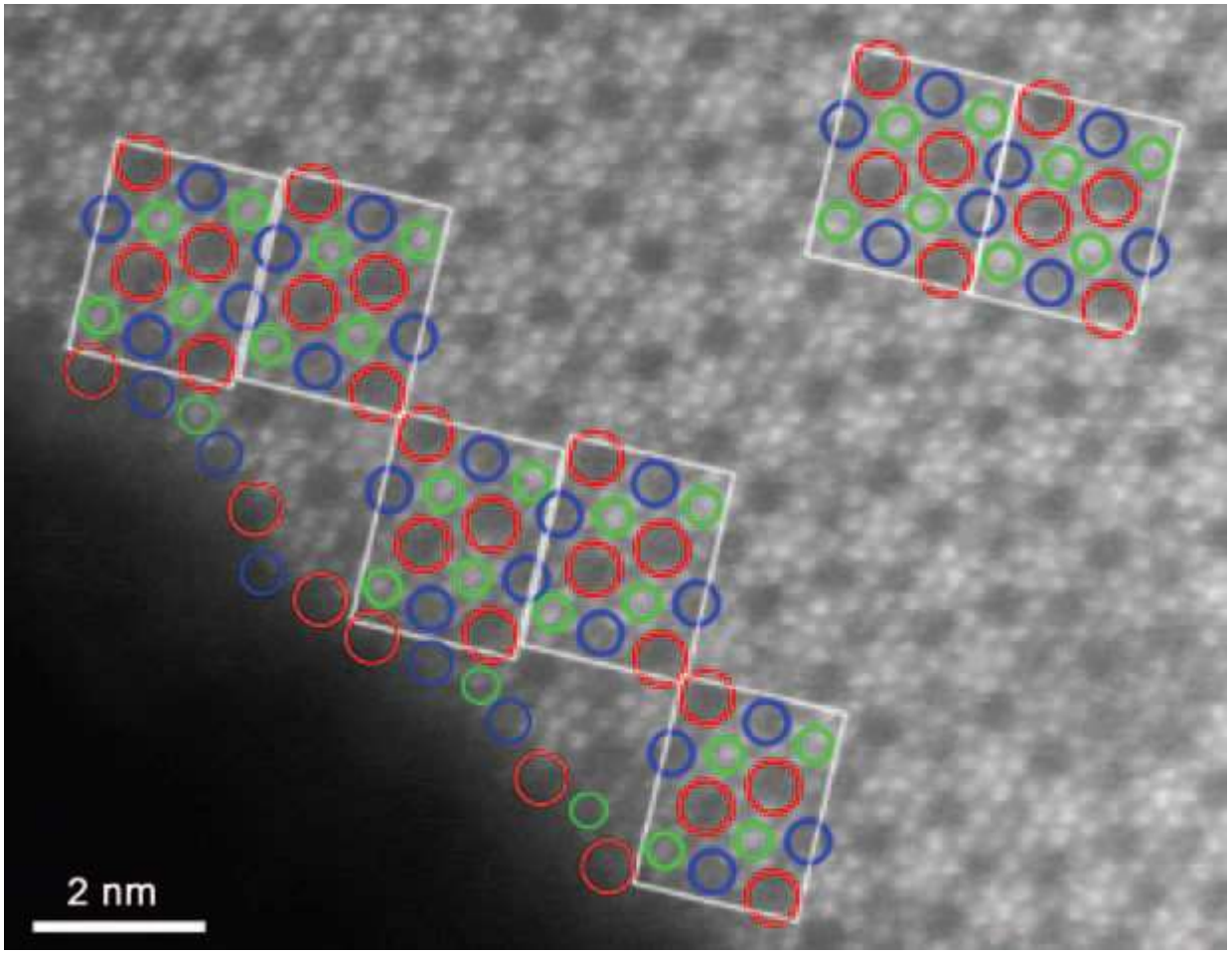


Fluorescence X-ray elemental analysis

HAADF(High angle annular dark field) Large Z scatter the electron to a higher angle. More electron on ADFdetector

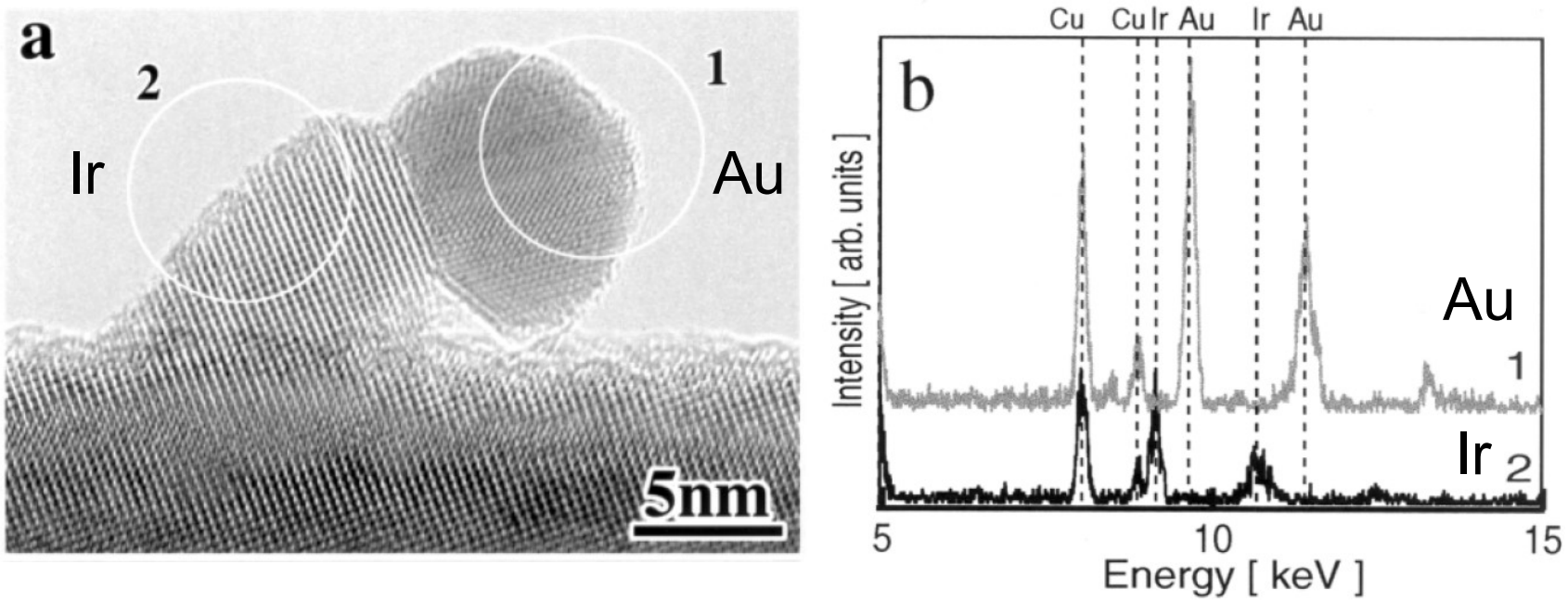
EELS(eletron energy loss spectroscopoy) --elemental and chemical state analysis

HAADF STEM of MoVTeO6



1 Z. Wei, T. Annette, S. RobertandS. Dangsheng,
Angewandte Chemie International Edition ***2010, 49, 6084.***

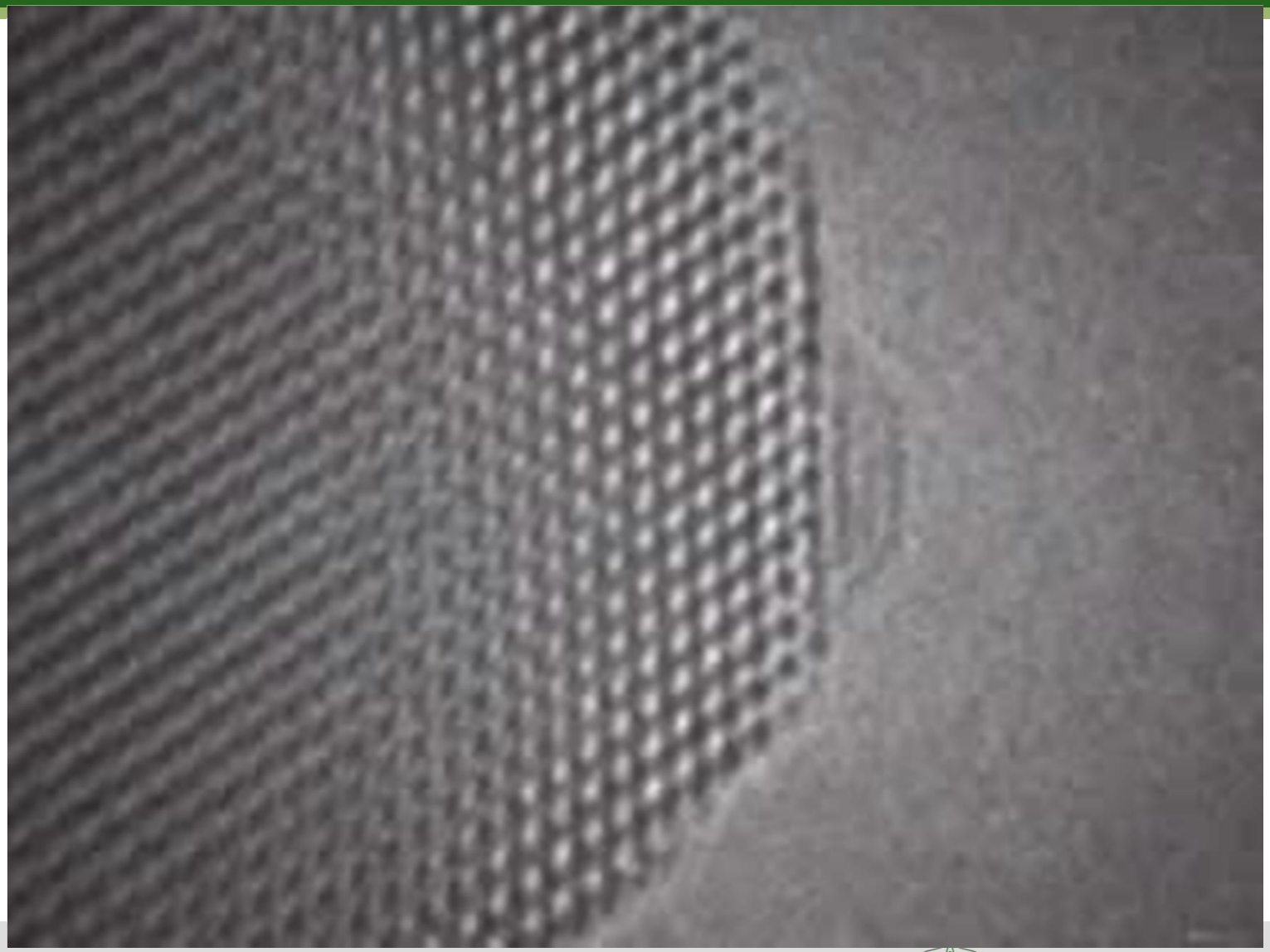
A TEM image of Au-Ir deposited on TiO_2



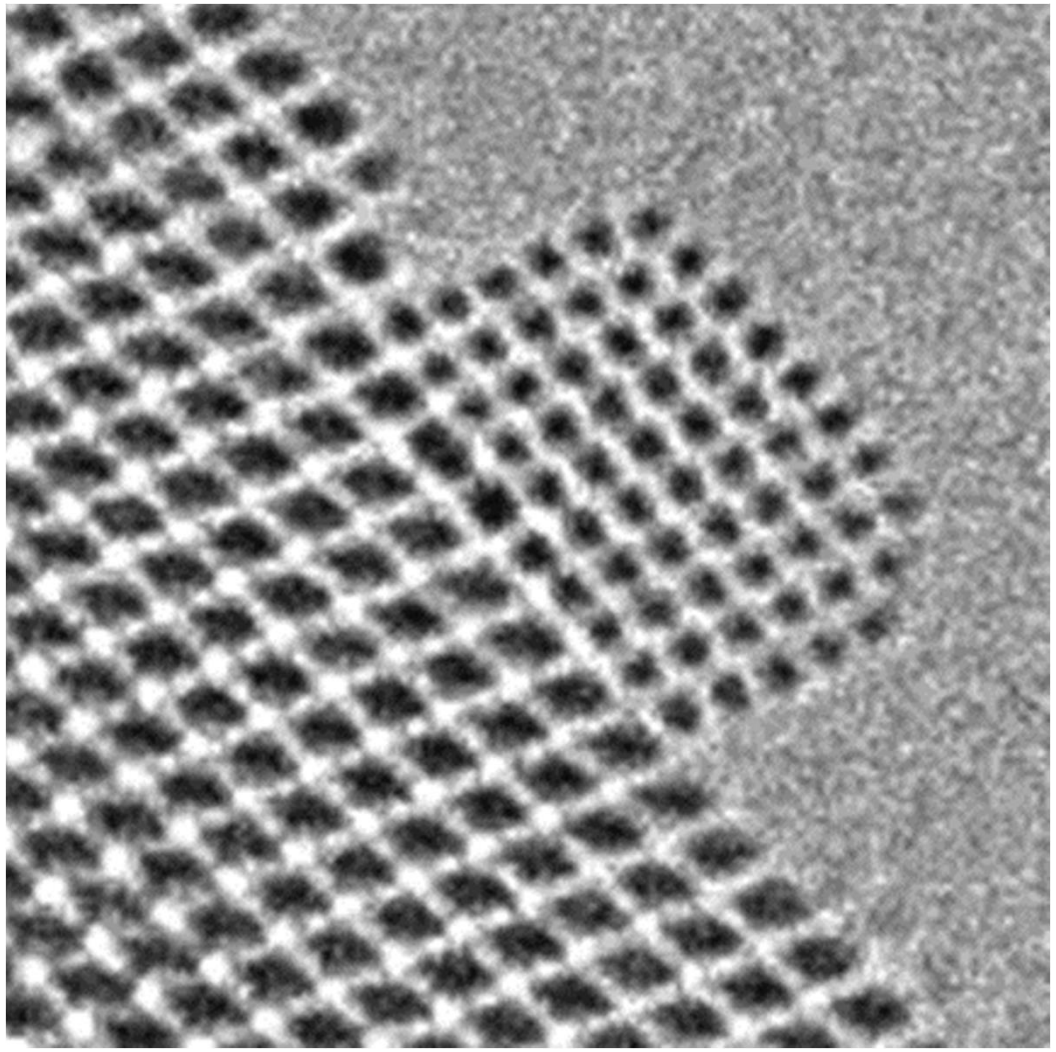
A TEM image of Au-Ir deposited on TiO_2 (a) and corresponding EDS spectra obtained from each area indicated in the TEM image (b).

Tomoki Akita et al., *Journal of Electron Microscopy* 52(2): 119–124 (2003)

Au/CeO2 during electron irradiation.



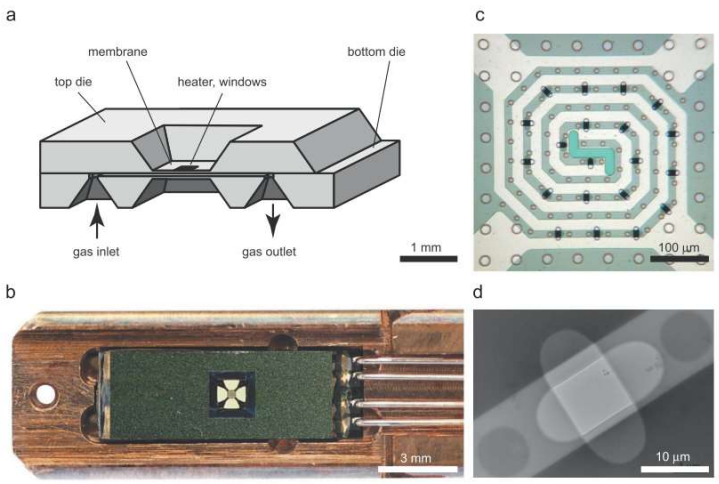
1



Ambient TEM

A few mbar

J. F. Creemer, S. Helveg, G. H. Hoveling, S. Ullmann, A. M. Molenbroek, P. M. SarroandH. W. Zandbergen, *Ultramicroscopy* ***2008, 108, 993.***



H2 **H2＋H2O** **H2+CO**

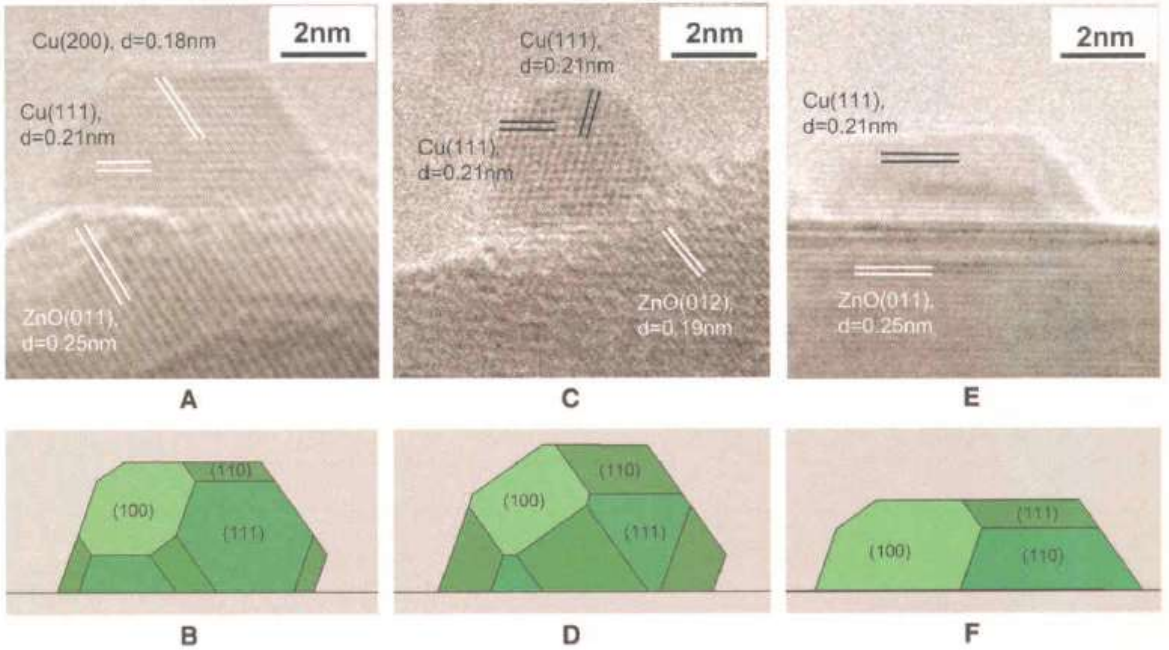


Fig. 1. In situ TEM images (**A**, **C**, and **E**) of a Cu/ZnO catalyst in various gas environments together with the corresponding Wulff constructions of the Cu nanocrystals (**B**, **D**, and **F**). (A) The image was recorded at a pressure of 1.5 mbar of H_2 at 220°C. The electron beam is parallel to the [011] zone axis of copper. (C) Obtained in a gas mixture of H_2 and H_2O, H_2: H_2O = 3:1 at a total pressure of 1.5 mbar at 220°C. (E) Obtained in a gas mixture of H_2 (95%) and CO (5%) at a total pressure of 5 mbar at 220°C.

Contents

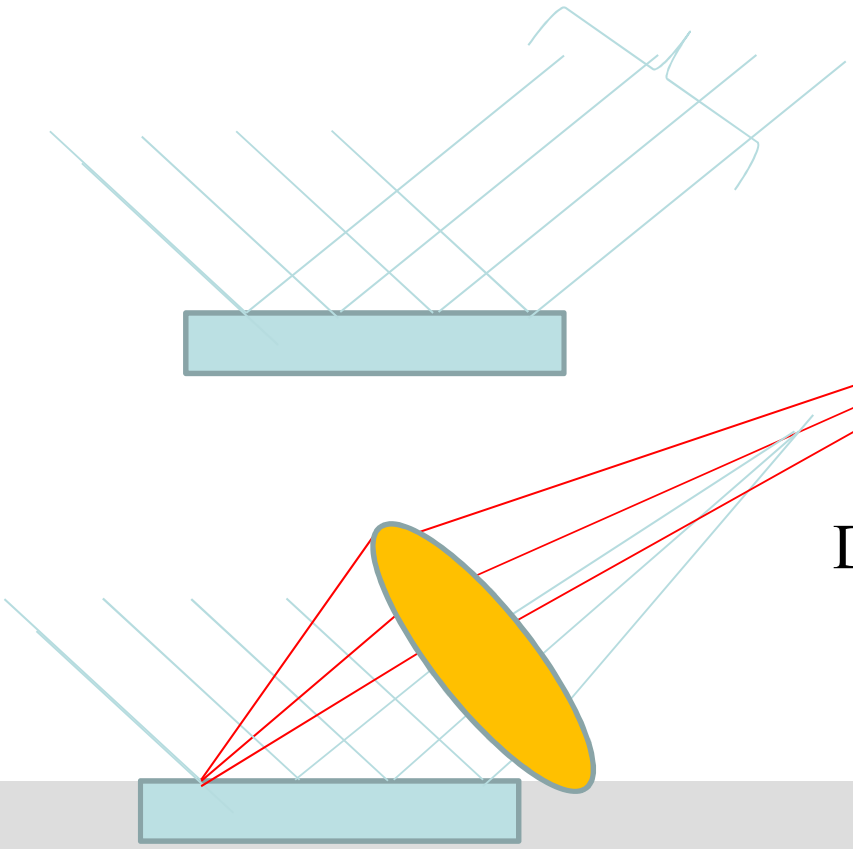
Spectroscopy:
Solid State NMR, IR, RAMAN,XPS.

imaging
Principle of SEM, Analysis SEM and TEM STM and PEEM.

Diffraction
XRD,TED and LEED
Diffraction is a backside of Imaging.

Diffraction

Diffraction is a interference of waves in the same direction



Infinity all beams meet and interfere

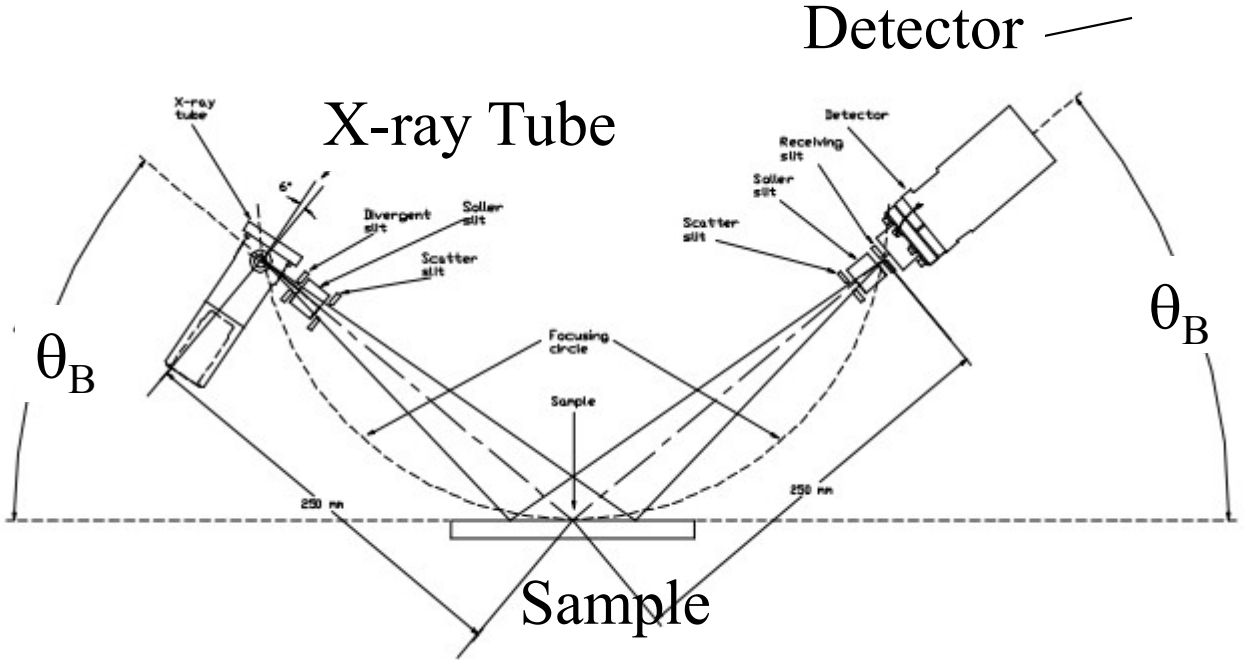
$2d\sin\theta = n\lambda$

Image

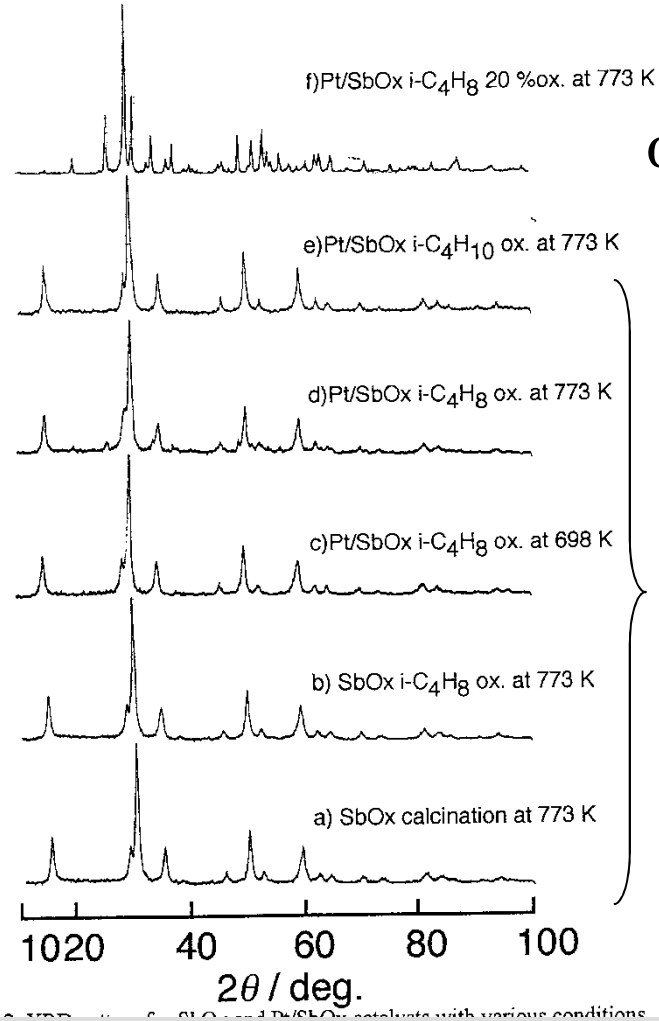
Diffraction plane

XRD=X-ray diffraction

crystalline



XRD gives crystalline forms



α-Sb2O4

Sb6O13

Methacrolein selectivity decreases

Inoue, *J.Catal.* **1997**, *171*, 457-466.

Particle size

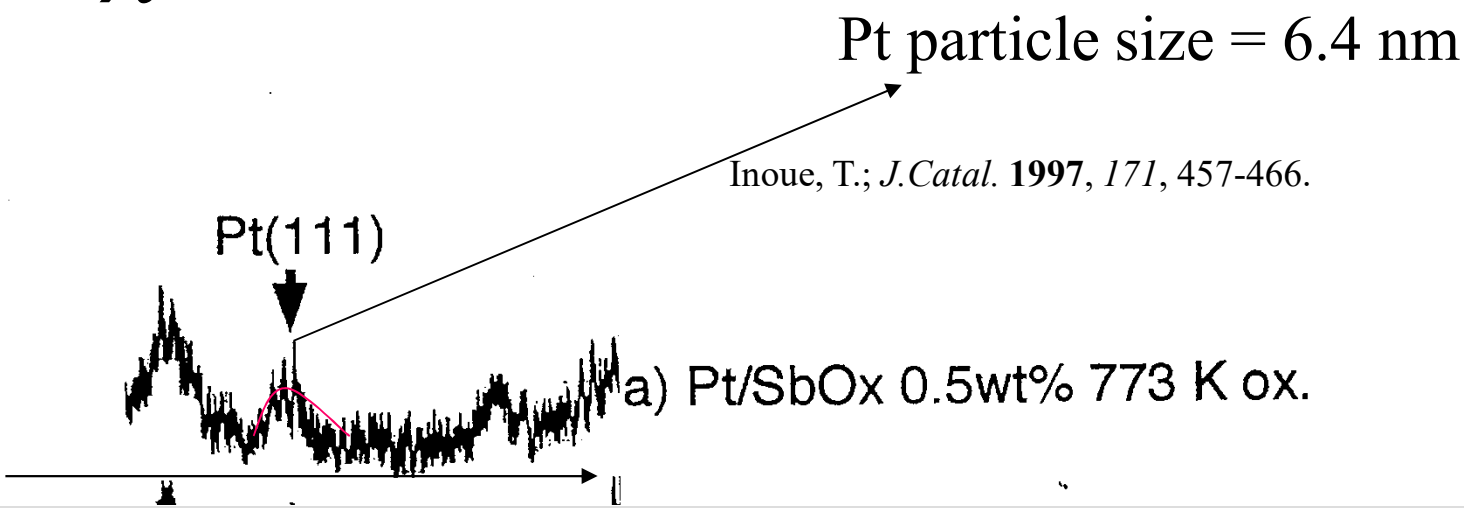
$$L = K\lambda / \Delta(2\theta)\cos\theta_B$$

Scherrerの式 L:crystaline size,

K=0.89-1.39

$\Delta(2\theta)$ **half width**

λ 波長



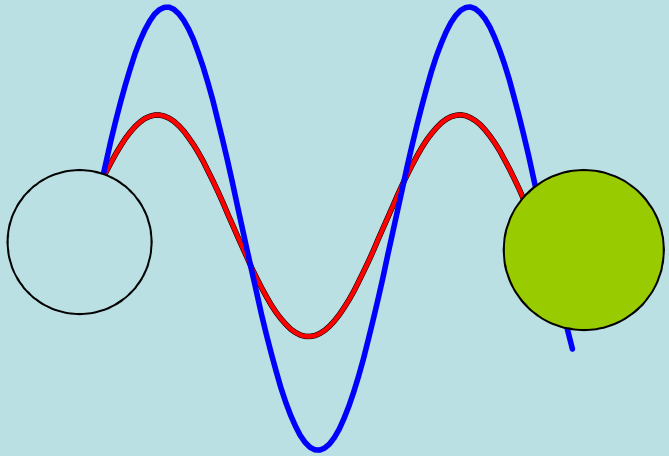
Scattering of electron and interference

$$\frac{\hbar^2 k^2}{2m} = E - E_0$$

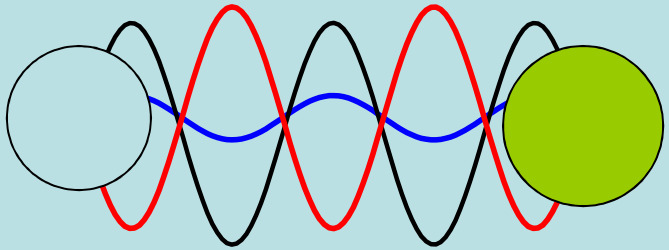
K: wave vector、

$\hbar$: Plank Const

E：Photon energy E0:threshold

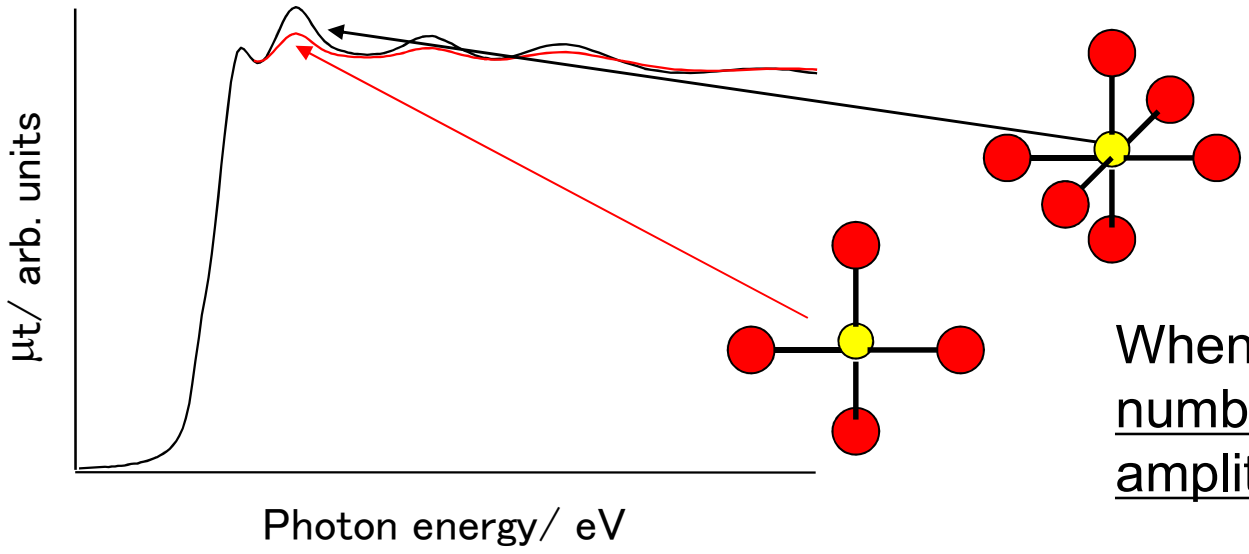


Enhancement

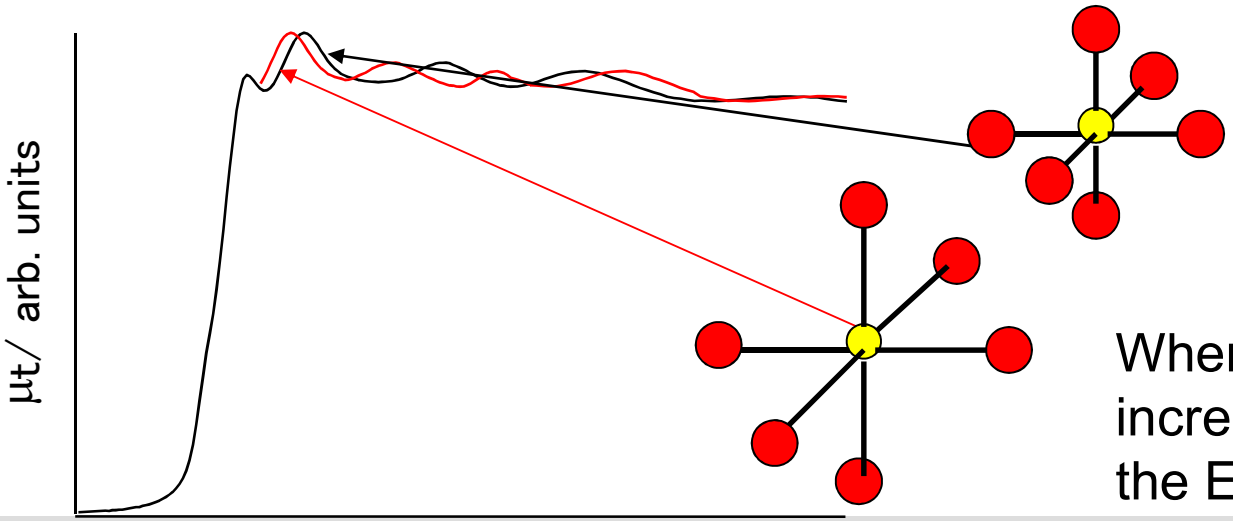


suppression

XAFS gives you bond distance and coordination number



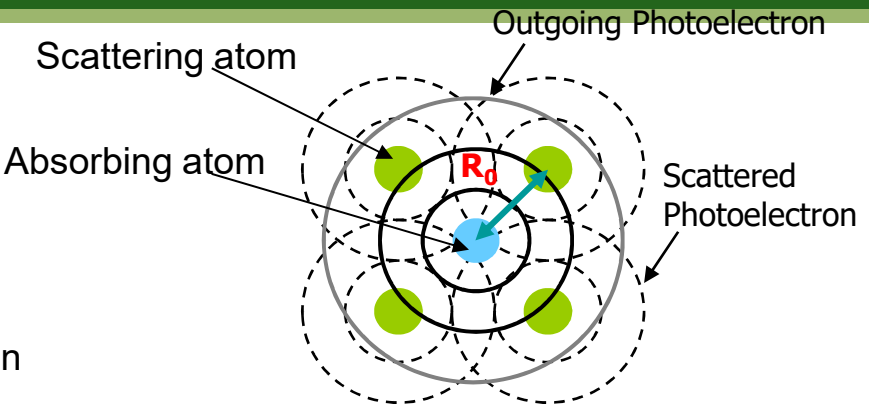
When the coordination number increases, the amplitude also increases



When the bond length increases, the frequency of the EXAFS oscillation will higher

The EXAFS equation

1. leaving the absorbing atom
2. scattering from the neighbor atom
3. returning to the absorbing atom



XAFS oscillation Absorbance Smooth backgroun

$$\chi(k) = \frac{\mu(E) - \mu_s(E)}{\mu_0(E)} = S_0^2 \sum_i \frac{N_i F_i(k_i)}{k_i r_i^2} e^{-2k_i^2 \sigma_i^2} \sin(2k_i r_i + \phi_i(k_i))$$

Edge-jump

$$k = \sqrt{2m_e(E - E_0)/\hbar}$$

Theorptically or empirically derived Parameters

F_i : Backscattering amblitude

$* e^{-2r_i/\lambda(k_i)}$

ϕ_i : Phase shift

Curve-Fitting Parameters

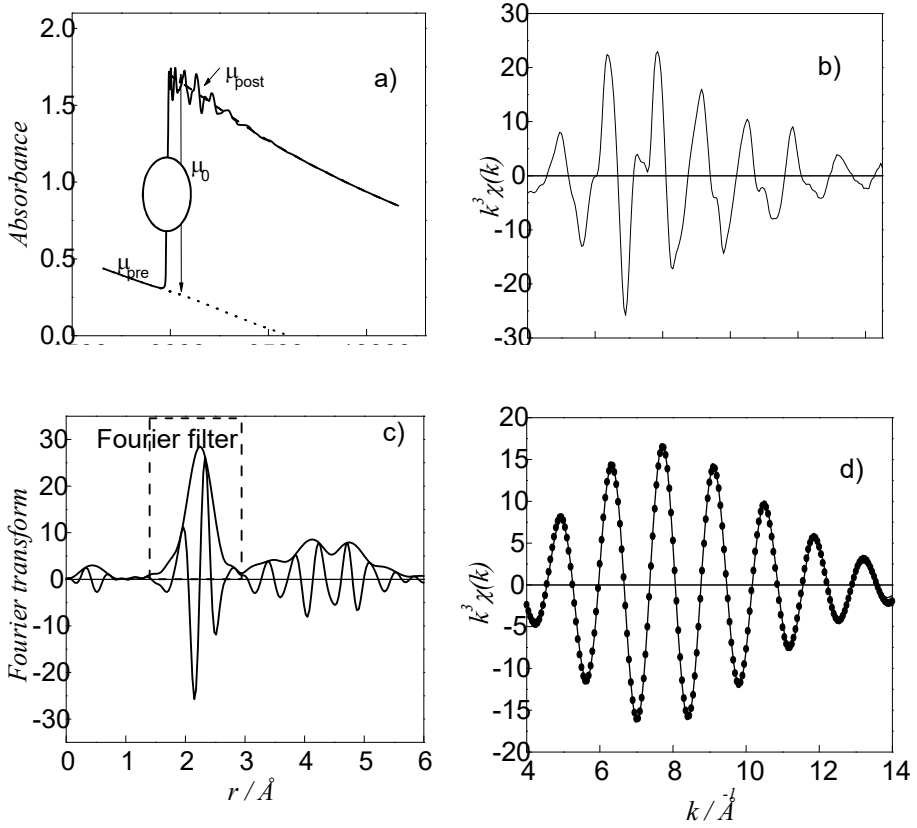
N_i Coordination number

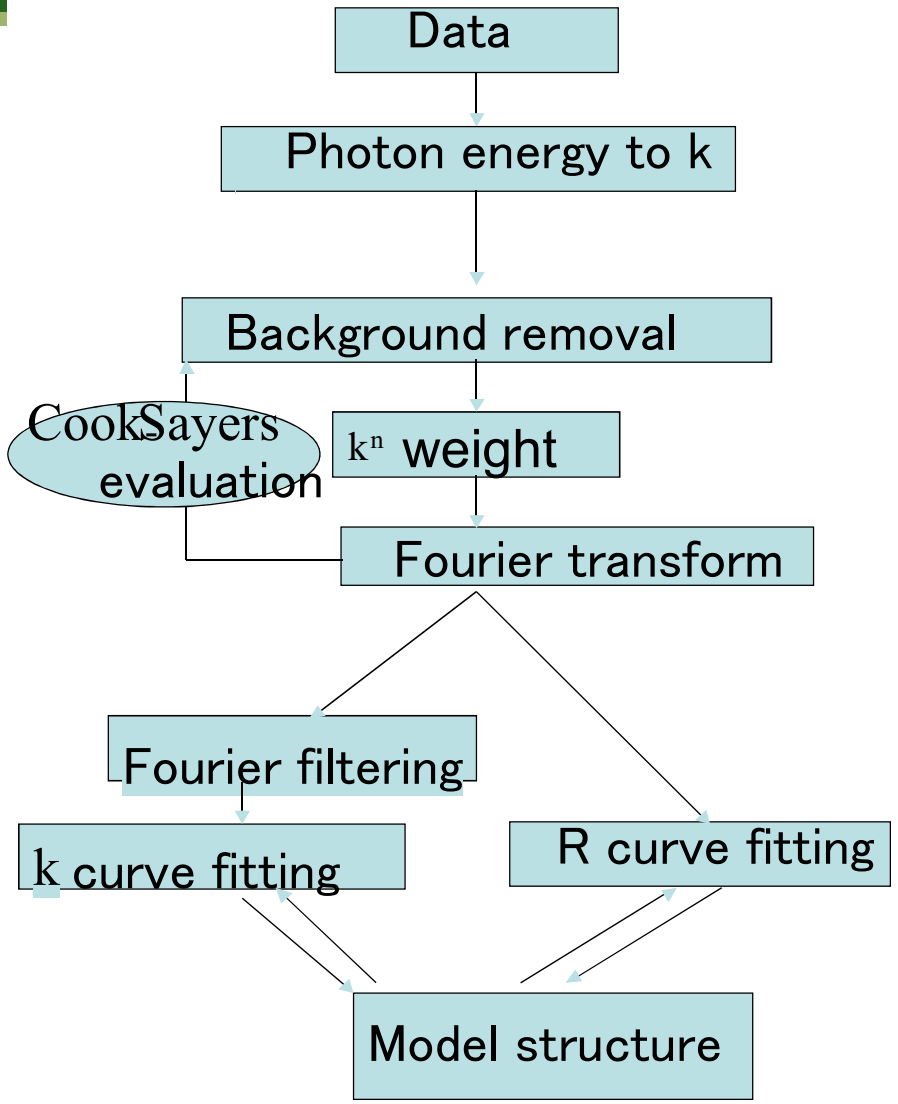
σ_i^2 DWfactor

E_0 energy shift

r distance

Sketch of XAFS analysis





Feature of XAFS

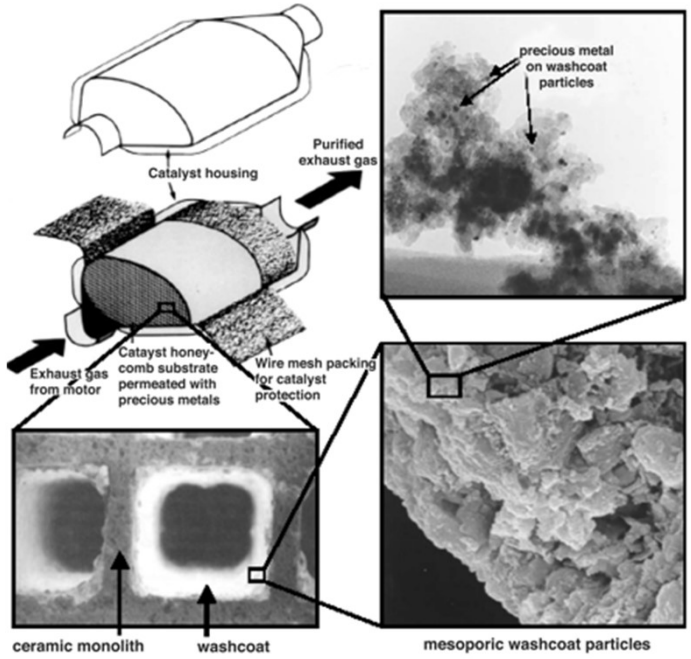
Sample is not necessarily in a crystalline form.

Solution, Surface, amorphous, and so on.

In the presence of gas phase, we can measure XAFS.

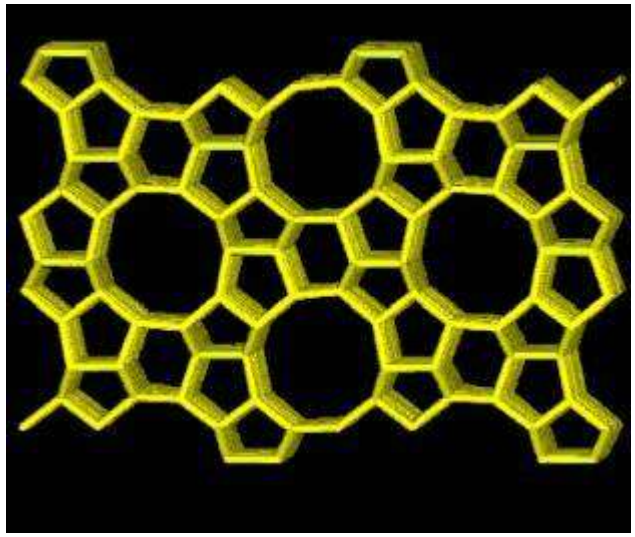
Automobile catalysts

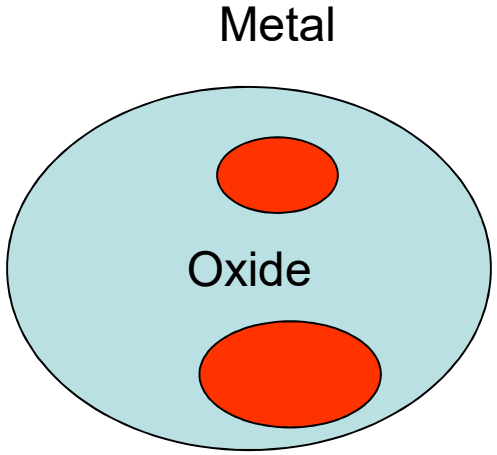
Automobile catalyst
To remove NOx
From exhausted gas

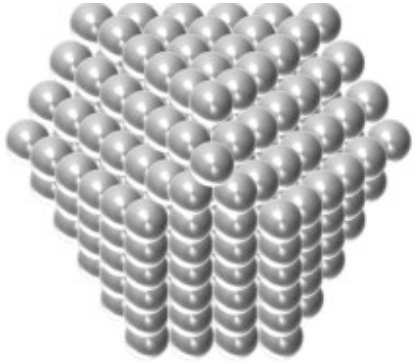


Supported metal catalysts
Industrial practical catalysts

Metal nanoparticles are dispersed on the metal oxide surfaces in order to obtain high surface area.







Metal morphology, structure and electronic states are moified by the interaction from oxie supports

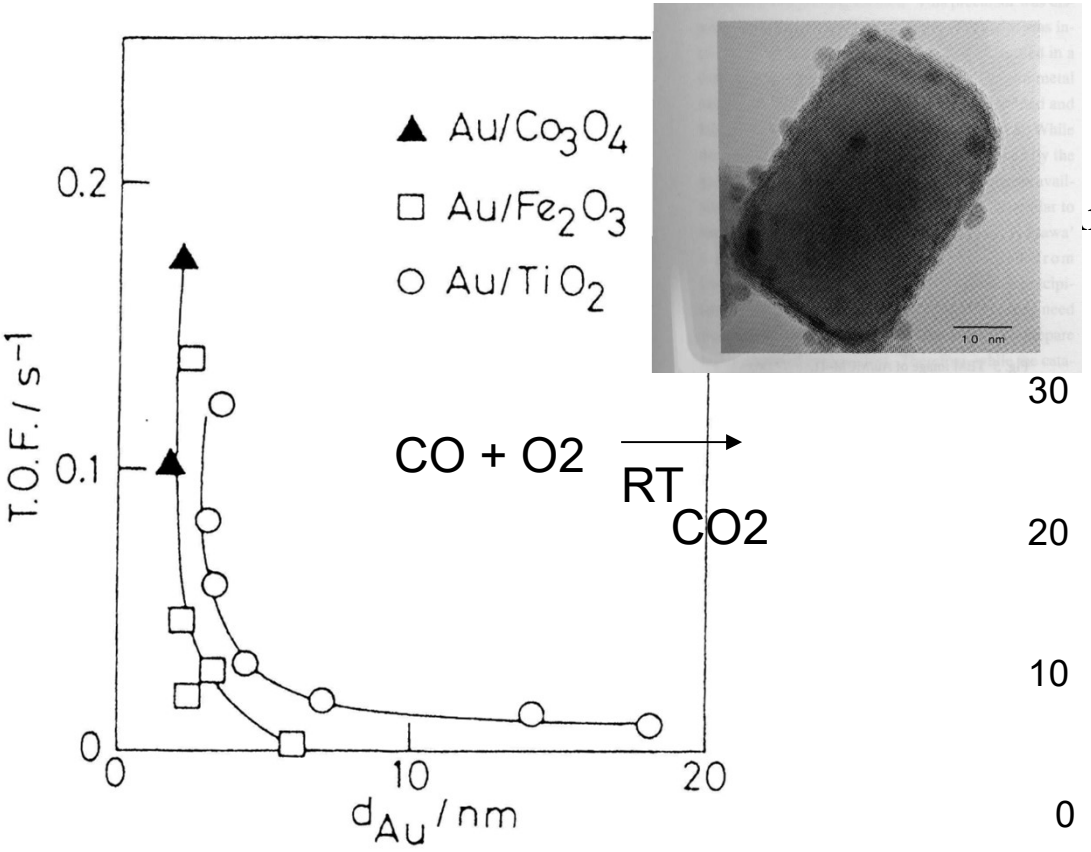
Diffraction techniques are not unavailable

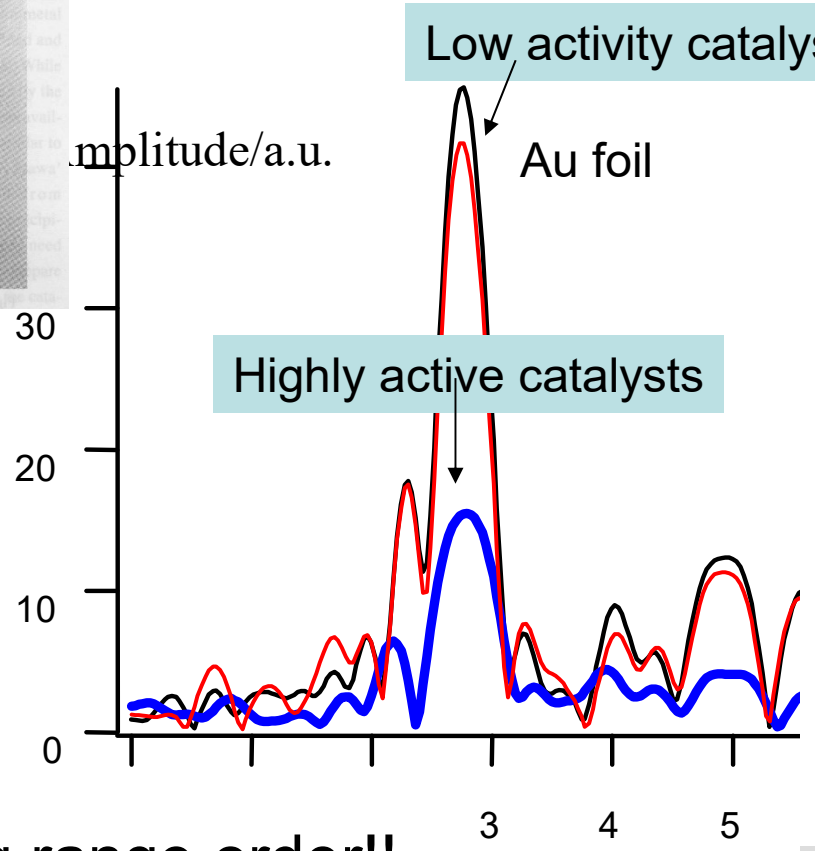
Because no crystalline structure is present on the surface, diffraction techniques become difficult to be applied.

How to obtain the supported metal catalysts.

Supported nano Gold catalsyts

High activity for CO oxidation at room temperature when it is in nanosize





EXAFS does not require long range order!!
Amorphous, liquid, Enzyme, powder

Question?

What is the real structure of catalyst species?

What is the structure during the reaction？

Is it the same as that in its initial state?

Answer is no!!

- **Catalysts are always changing.**

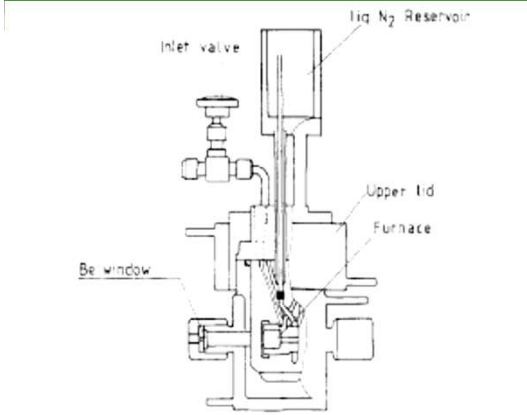
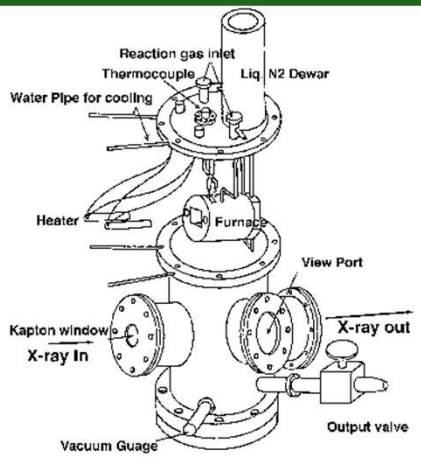
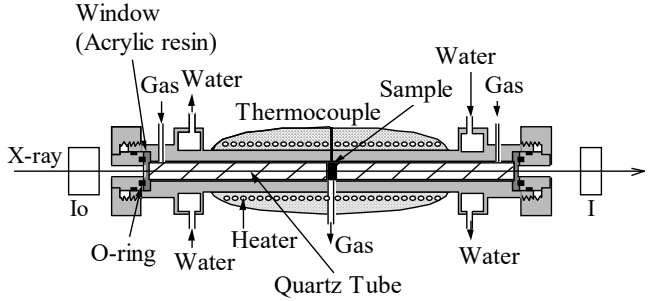


Figure 2. Chamber for the EXAFS measurements under vacuum and at high pressures.

High pressure cell J.Phys. Chem.93,4213(1989)

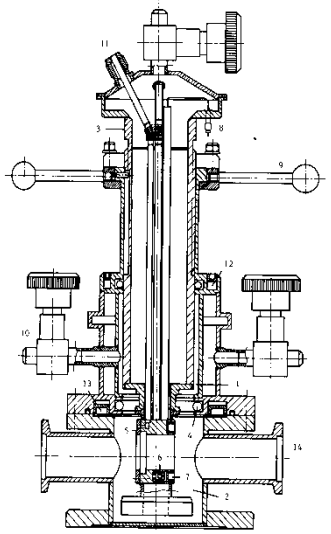


Z.Phys.Chem.,144,105(1985).



J.Synchro.Rad.8, 581(2001).

X-ray absorption, Principles, applications, techniques of EXAFS, SEXAFS, and XANES, New York, John Wiley & Sons, 1988.



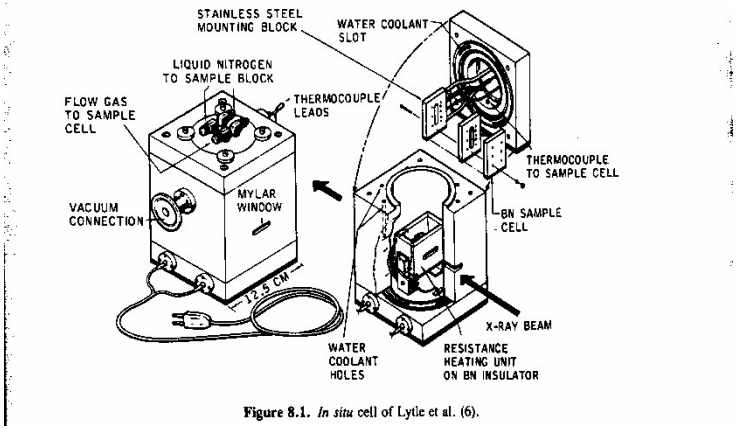
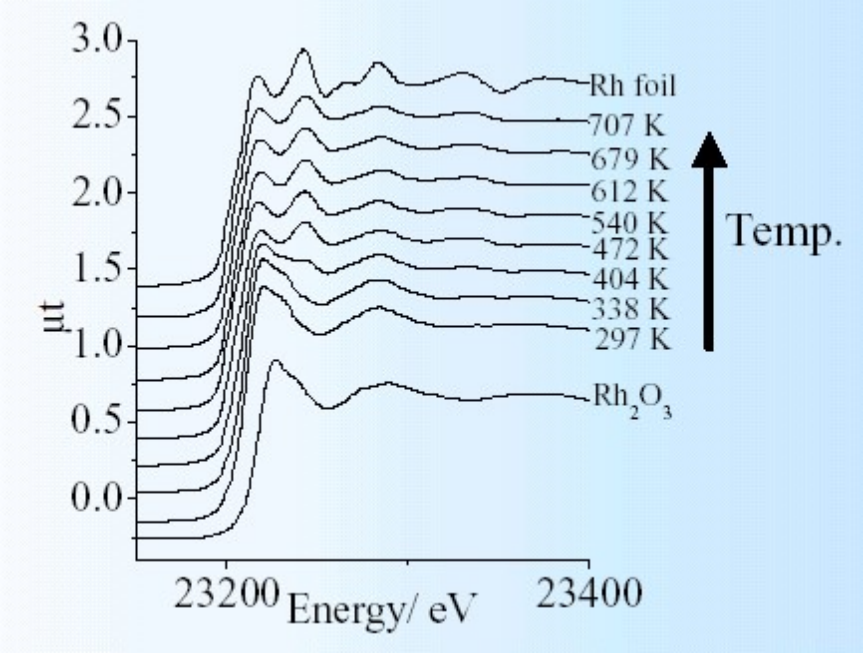


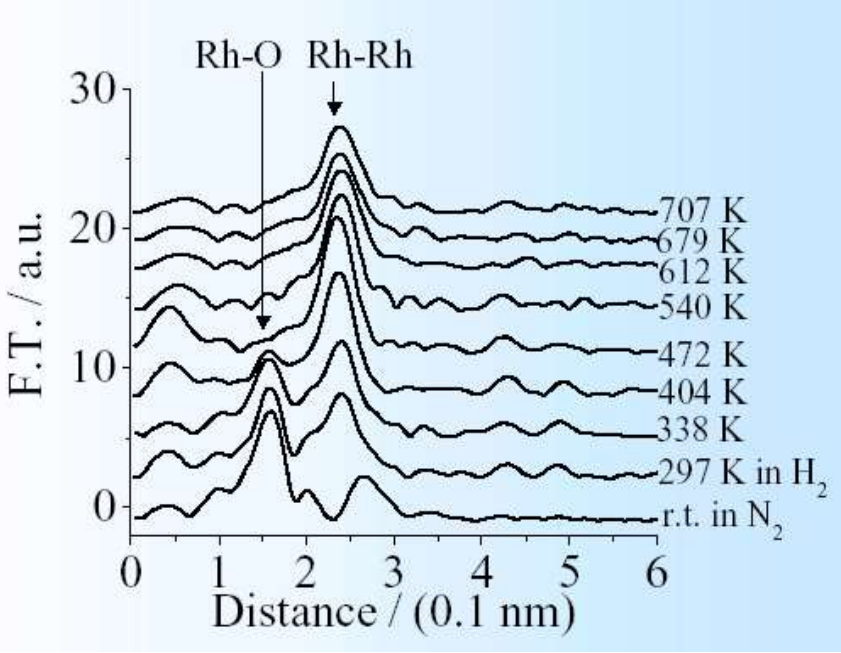
Figure 8.1. *In situ* cell of Lytle et al. (6).

J.Chem.Phys. 70 (1979) 4849.

In-situ work

Structure change during the reduction processes





Flow rate :20 % H_2/Ar 100ml/min
Temperature rate: 7K/min

XANES : Oxidized Rh species → Rh metal
EXAFS : Rh-O → Rh-Rh

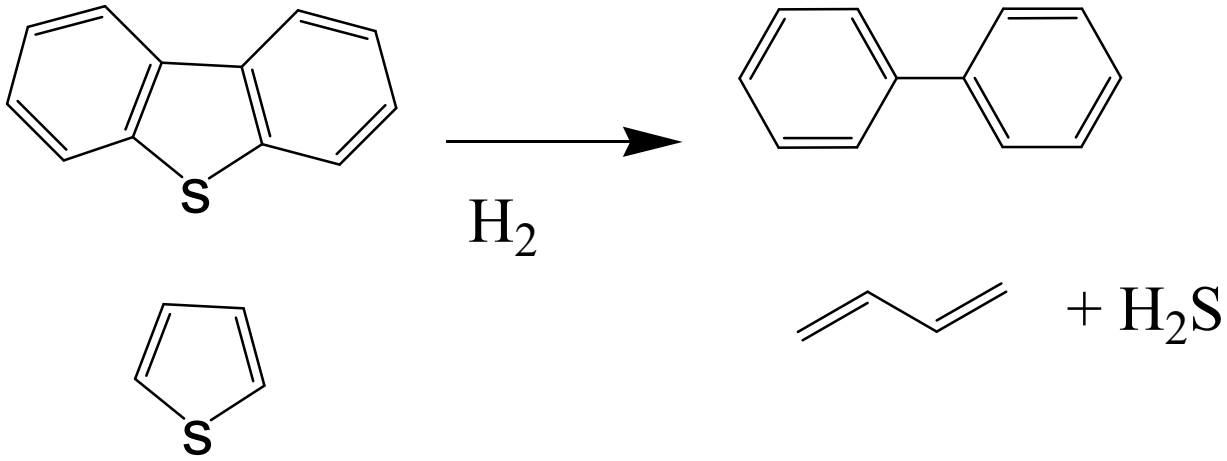
***K. Bando et al.* in-situ high temperature XAFS**

HOKKAIDO UNIVERSITY

Hydrodesulfurization(HDS) catalyst

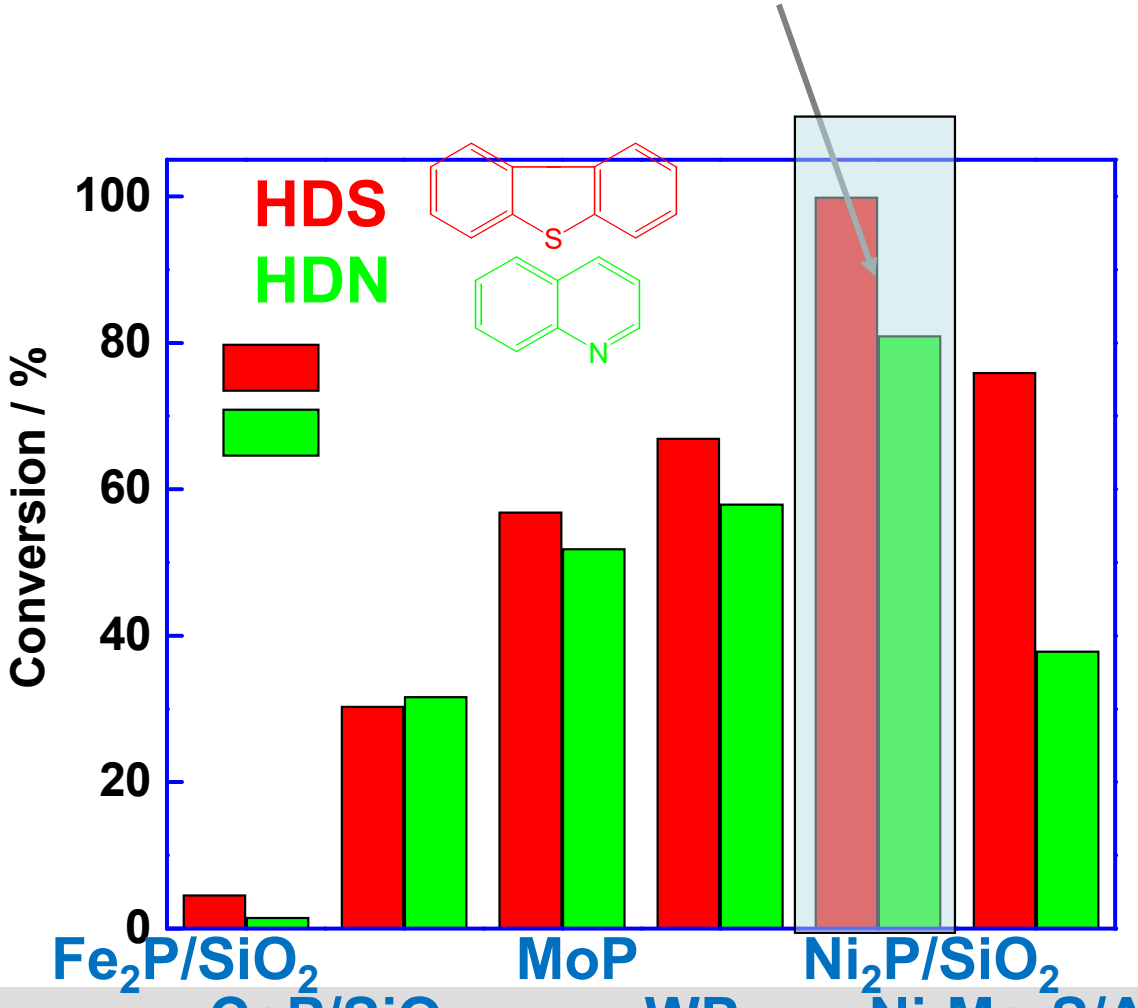
It removes sulfur compounds from fossil fuel.

Reactions are conducted under high pressure condition in the presenc of oil.



Metal phosphides

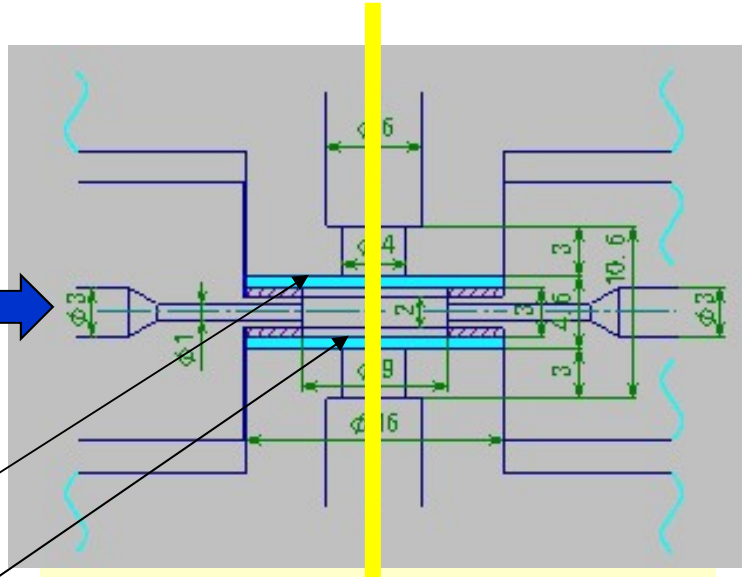
More active than commercially avaialbe NiMoS



X-ray is strongly absorbed by oil

Sample and X-ray windows should be located closeby.

•oil and gas



•Windows

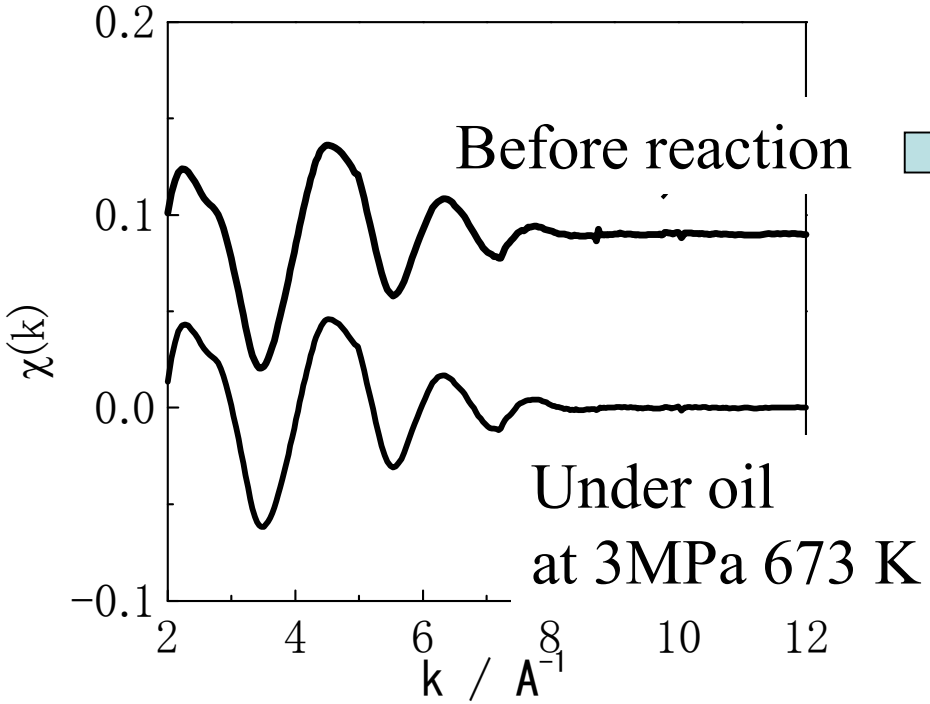
- •**Ceramic type(c-BN)**
  - •Cheap, non-toxic

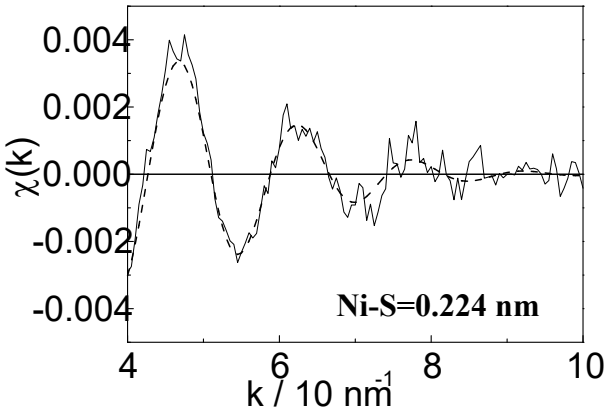
<u>Specification</u>:
Up to 733K and 15MPa
(depends on a window)

•sample

- ***J. Cat.* 2006, *241*, 20-24.**
- **Rev. Sci. Instrum. 2008, 79,014101**

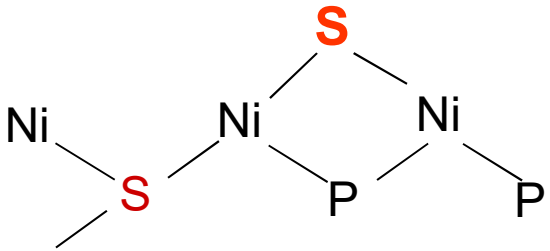
EXAFS of Ni_2P in the presence of Oil





***J. Cat.* 2006, *241*, 20-24.**

Rev. Sci. Instrum. 2008, 79,014101



Active site structure

Diagram of conventional XAFS technique

XANES

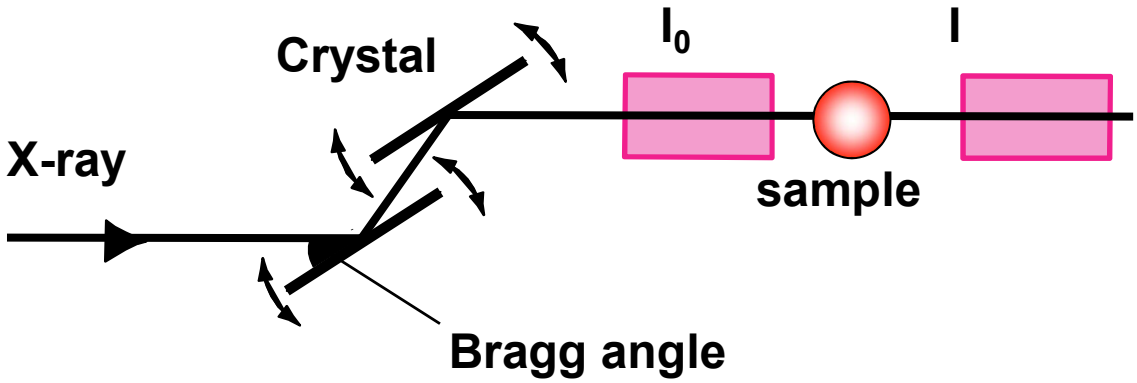
(1) Oxidation state

(2) Symmetry, etc.

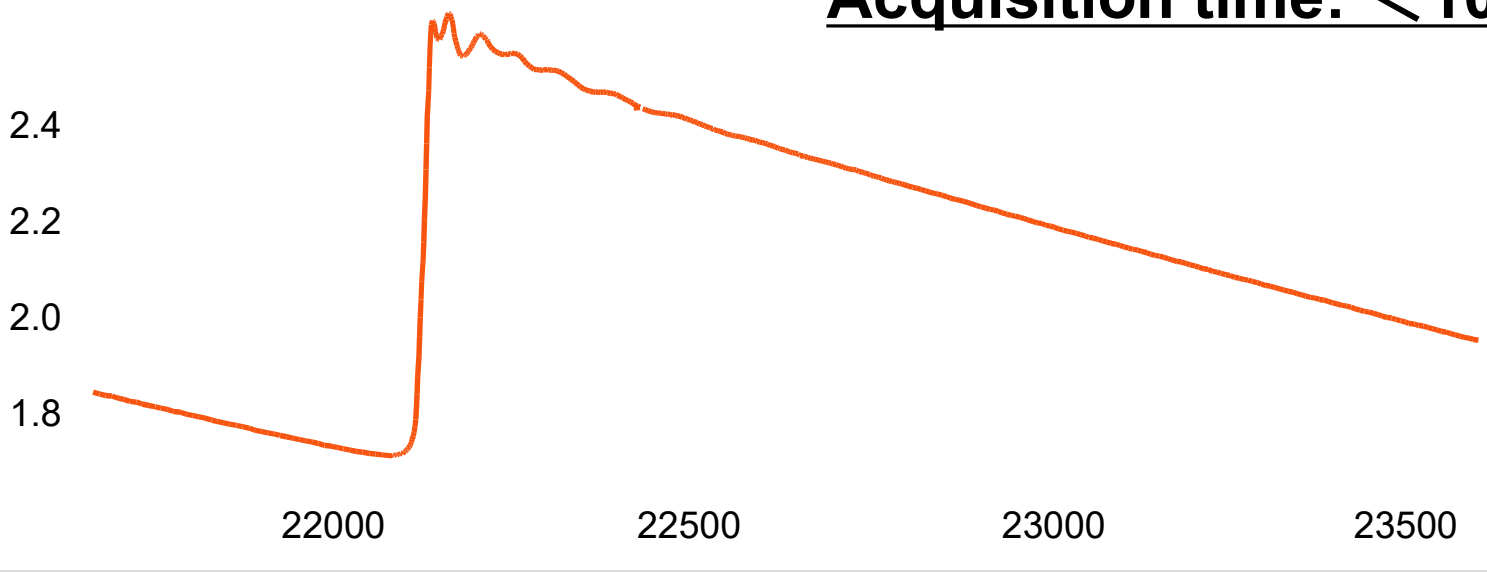
EXAFS

(1) Interatomic distance

(2) Coordination number



Acquisition time: ＜10 s

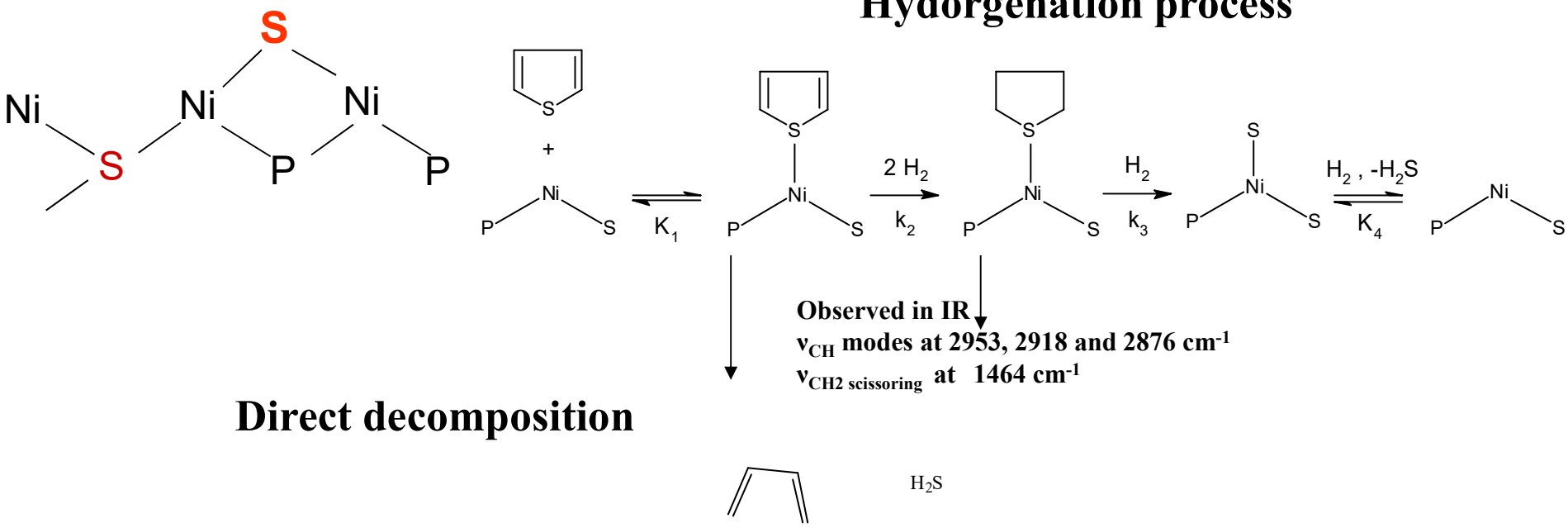


Questions and how?

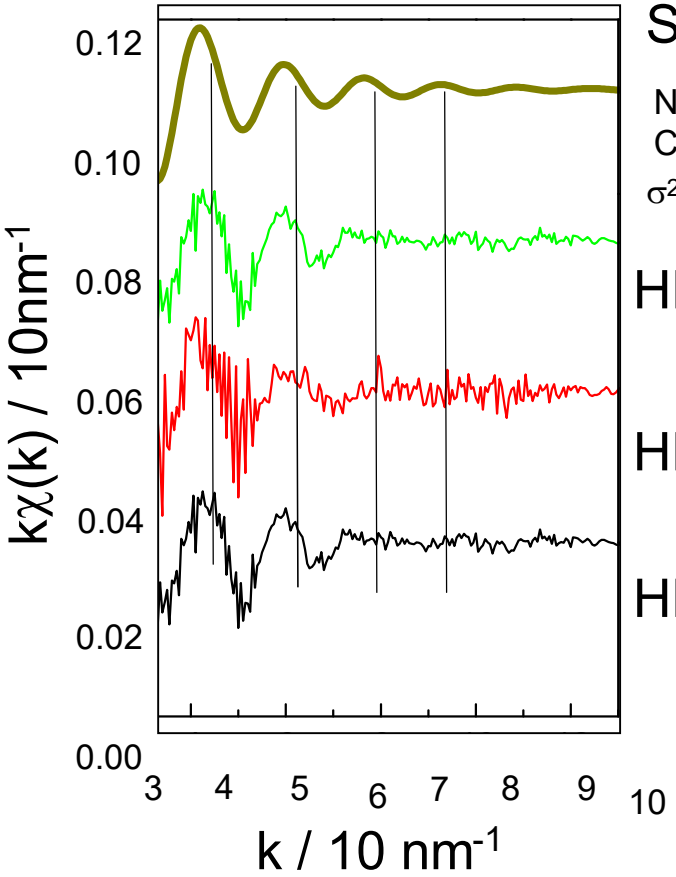
Is NiPS really active site?

What is the reaction path?

Combination of IR, product analysis and QXAFS



Difference spectra in HDS – before reaction



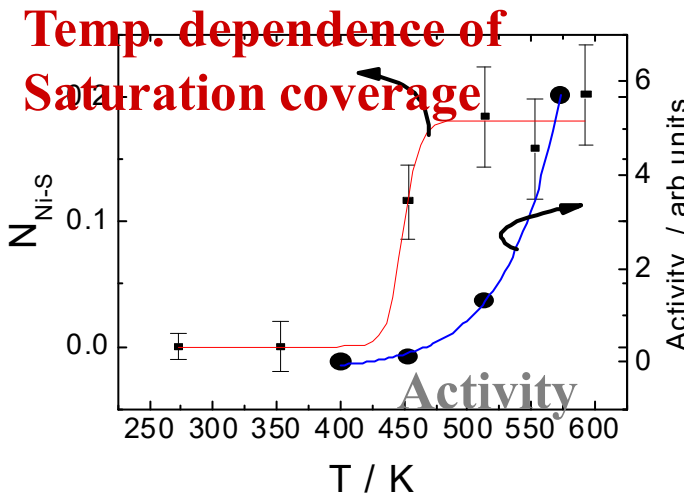
Simulated XAFS based on Ni-S bond

Ni – S (FEFF)
CN = 0.2, R = 0.227 nm,
σ^2 = 0.0064 Å^2

HDS at 593 K

HDS at 553 K

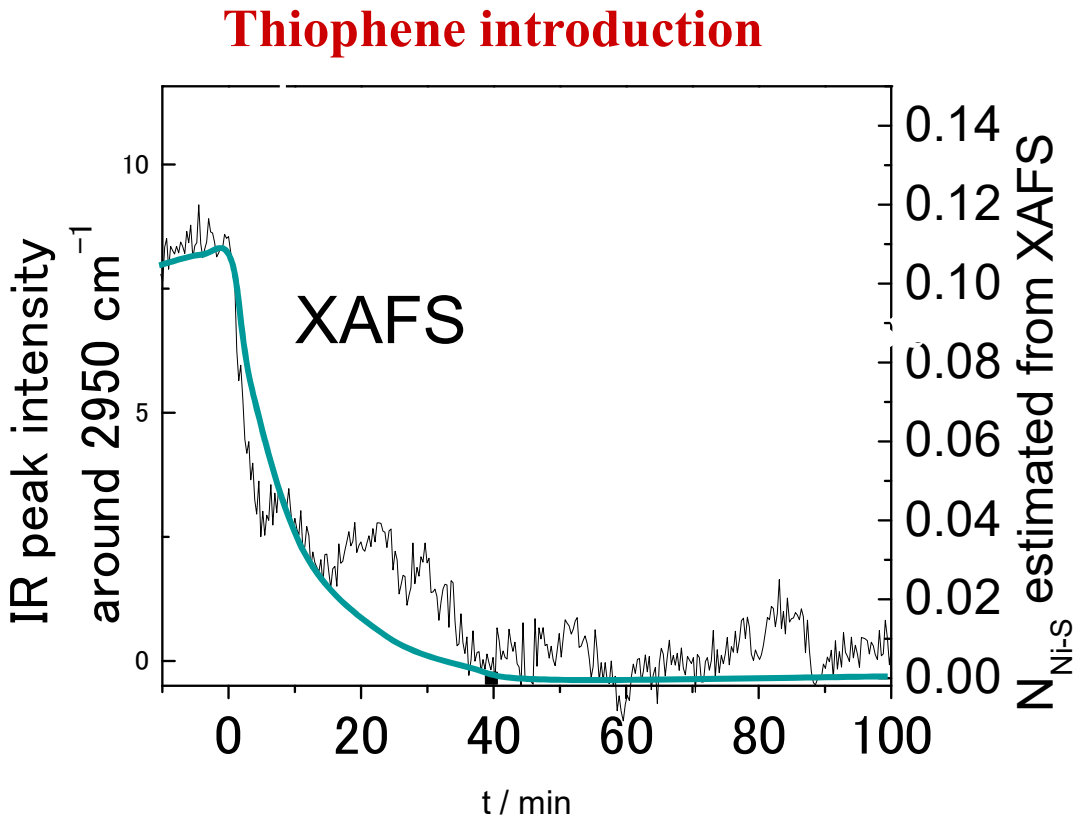
HDS at 513 K



- **CF results of Ni-S**
  R=0.227 nm; CN=0.2.
- **Judging from the ratio of surface Ni to the bulk ~0.2**
  S/Ni_s=1.0±0.2
- **Little reaction temperature dependence**

XANES change during 513 K

XANES peak change corresponding to the formation of Ni-S

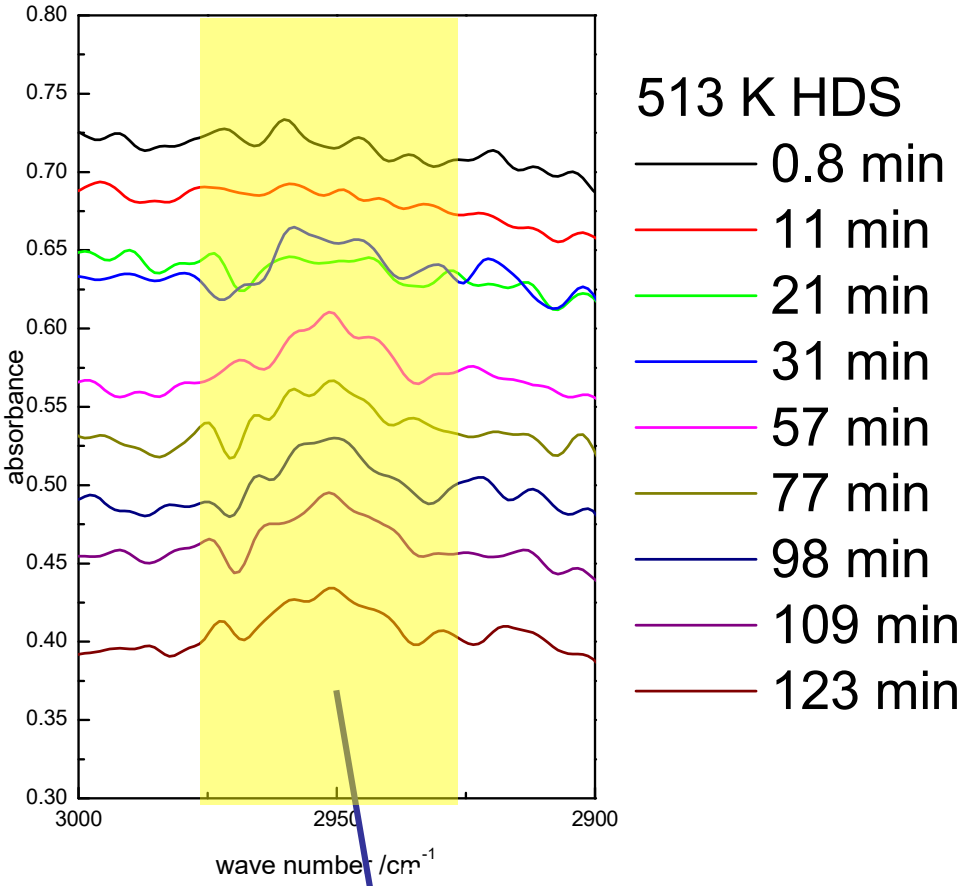


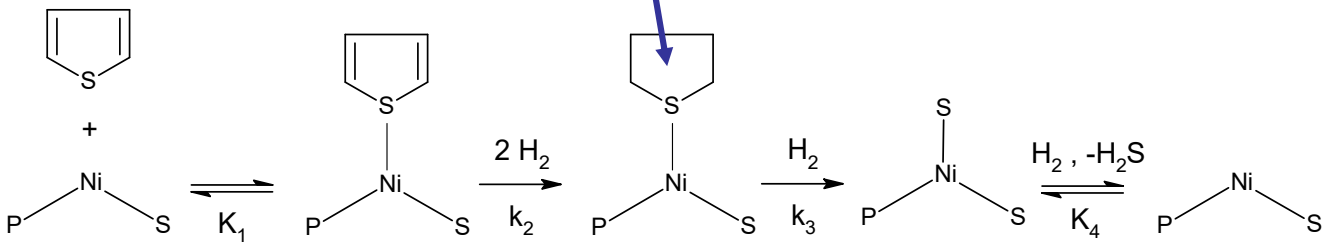
FT-IR of the adsorbed species

No

tetrahydrothiophene adsorption is detected soon after the HDS reaction starts.

A few ten min after the reaction it starts to grow and is saturated.

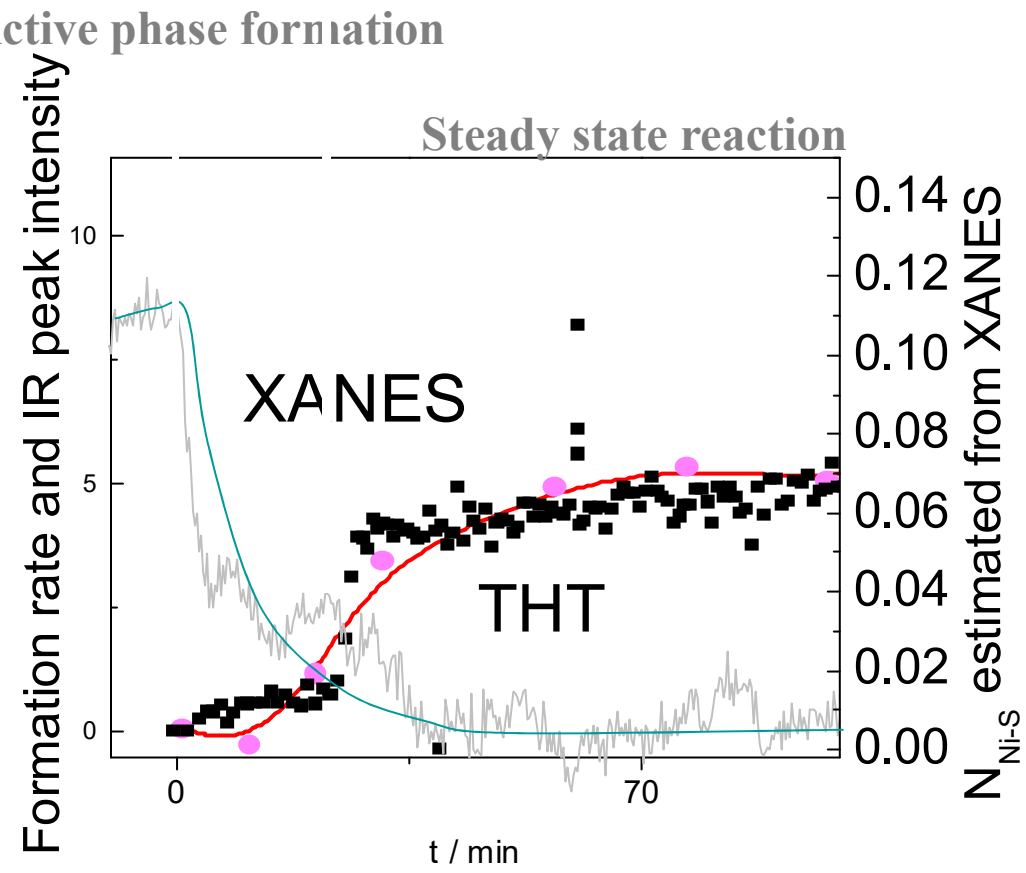




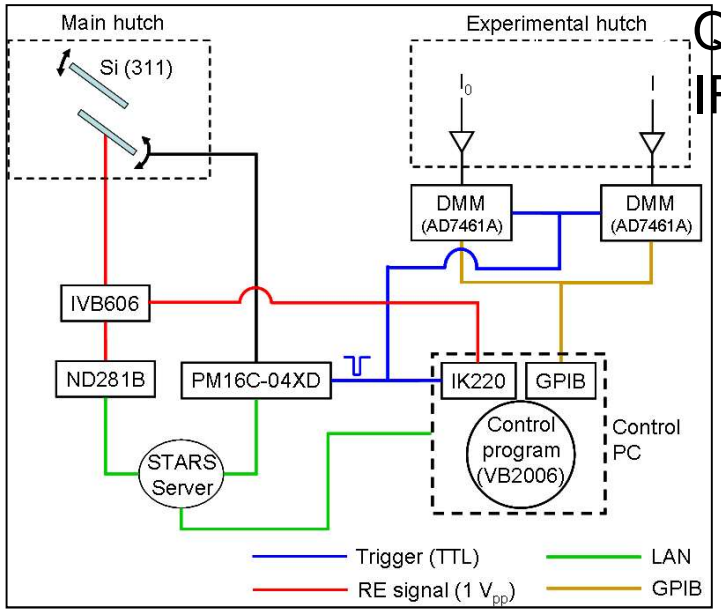
FT-IR and XANES

Ni-S bond forms then THT is formed.

Soon after the formation of THT is decomposed to H_2S and



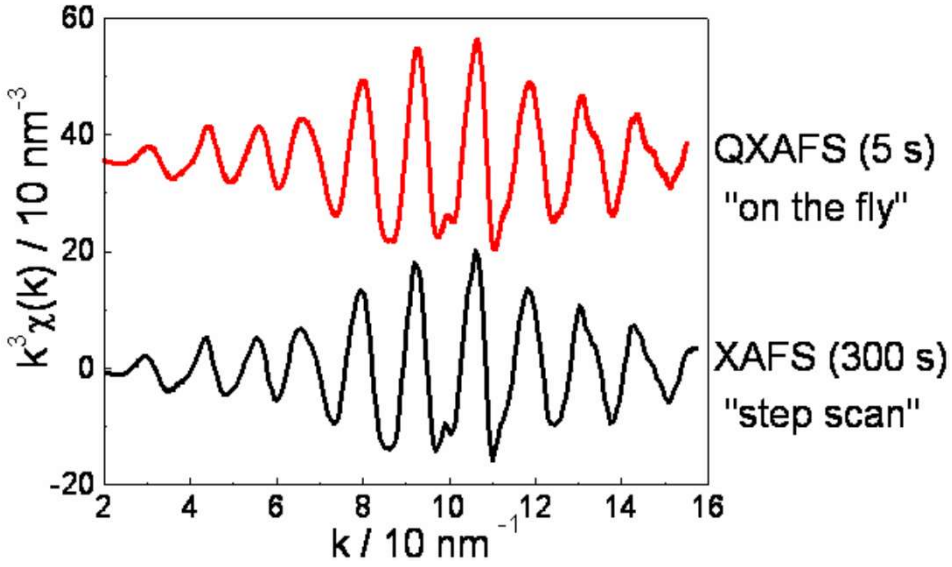
Time resolved --- in-situ QXAFS in BL9C



QMS

IR

Pd foil



Monochromator is rotated quickly

PF 9C QXAFS beam line ->order of 10 s per spectrum.

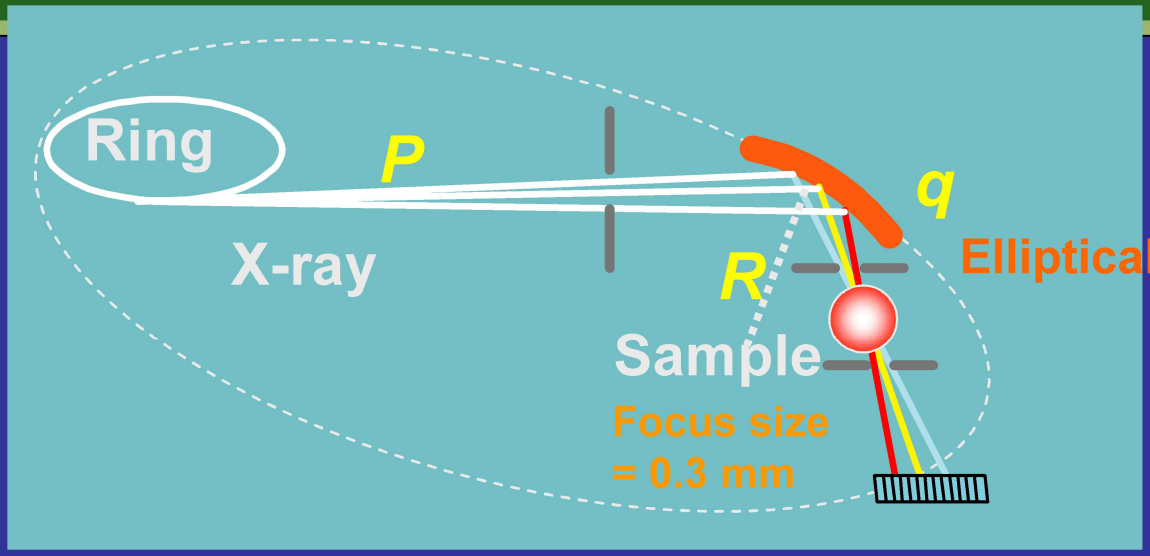
[1] M. Nomura, K. Asakura et al., *AIP Conference Proceedings* 2007, *882*, 896.

Supported by Grand-in-Aid for Scientific Research S(16106010) from JSPS.

Time-resolved EXAFS

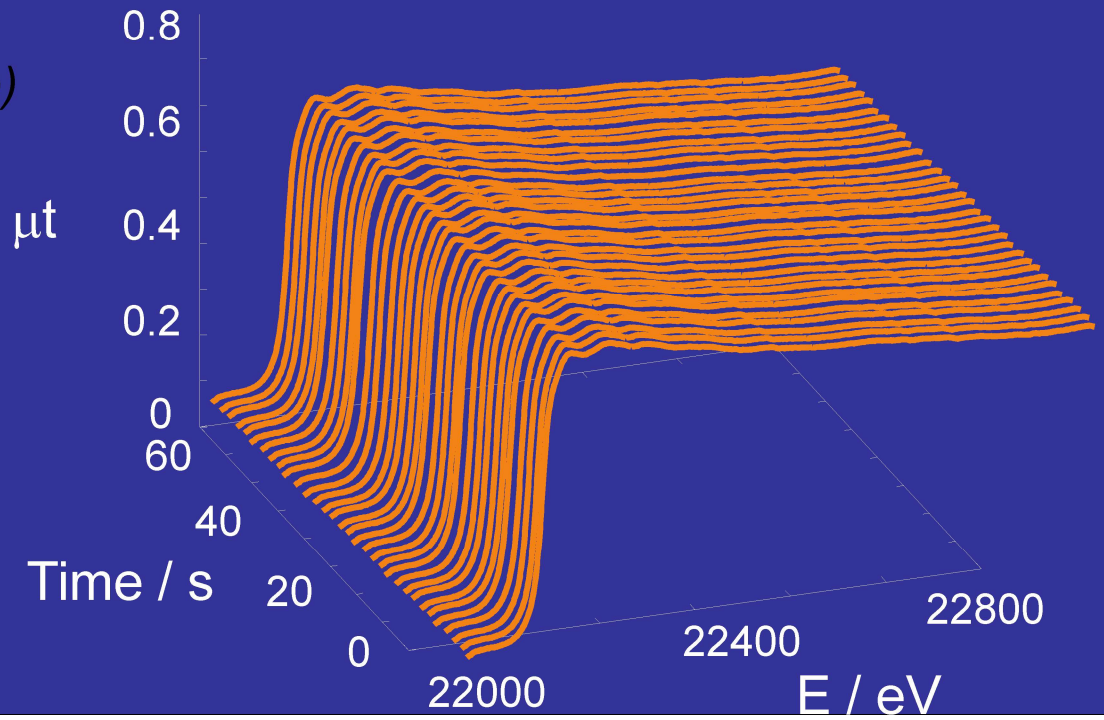
1. **$[Ru_6C]/MgO$ catalysts during CO insertion reactions**
   - **A. Suzuki, et al., *J. Phys. Chem. B* 2004, *108*, 5609.**
2. **Rh/Al_2O_3 CO induced Rh cluster destruction**
   - **A. Suzuki,et al., Angev.Chem. 2003, *42*, 4795.**

Diagram of energy dispersive XAFS(DXAFS) technique (Bragg type)

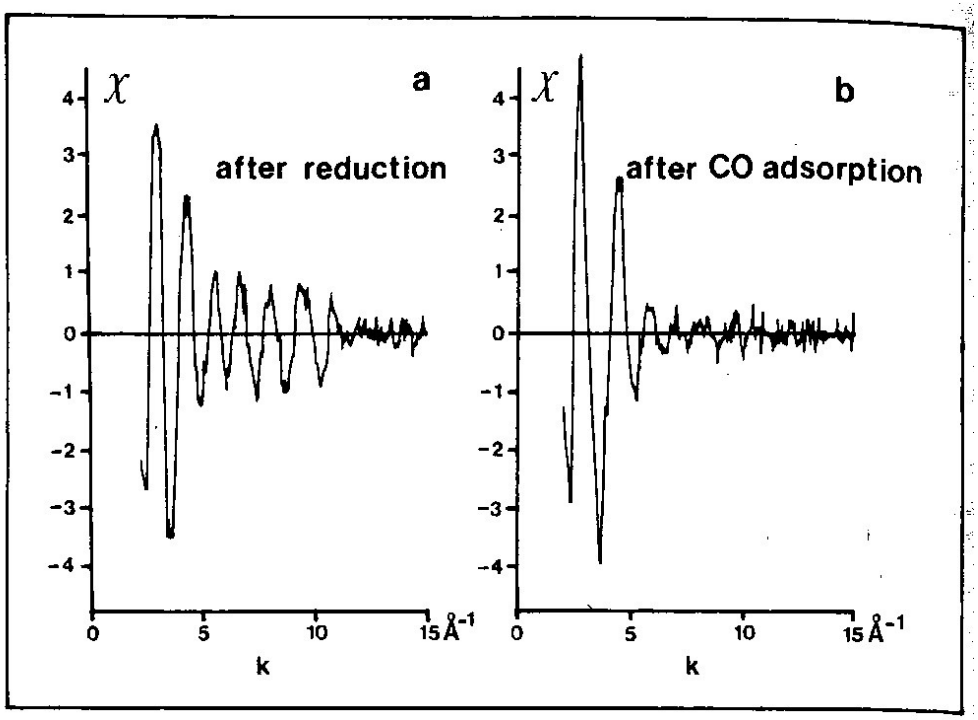


Elliptically bent crystal

θ= 9.4 degree (Rh K-edge)
p = 30 m
q = 0.35 m
R = 1.2 m
1/p + 1/q = 2/(R sinθ)
ΔE/E= L sinθ cotθ /p

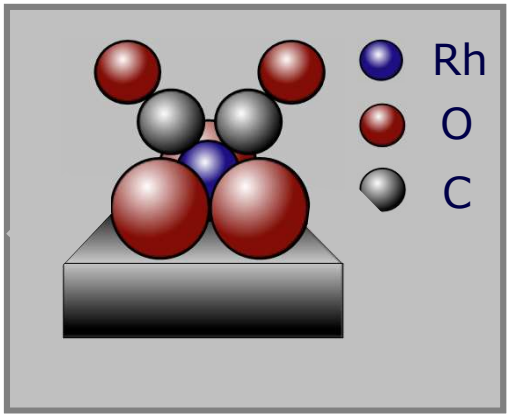


Disruption of Rh clusters on Al_2O_3 surface by CO at RT



Rh_x cluster

CO

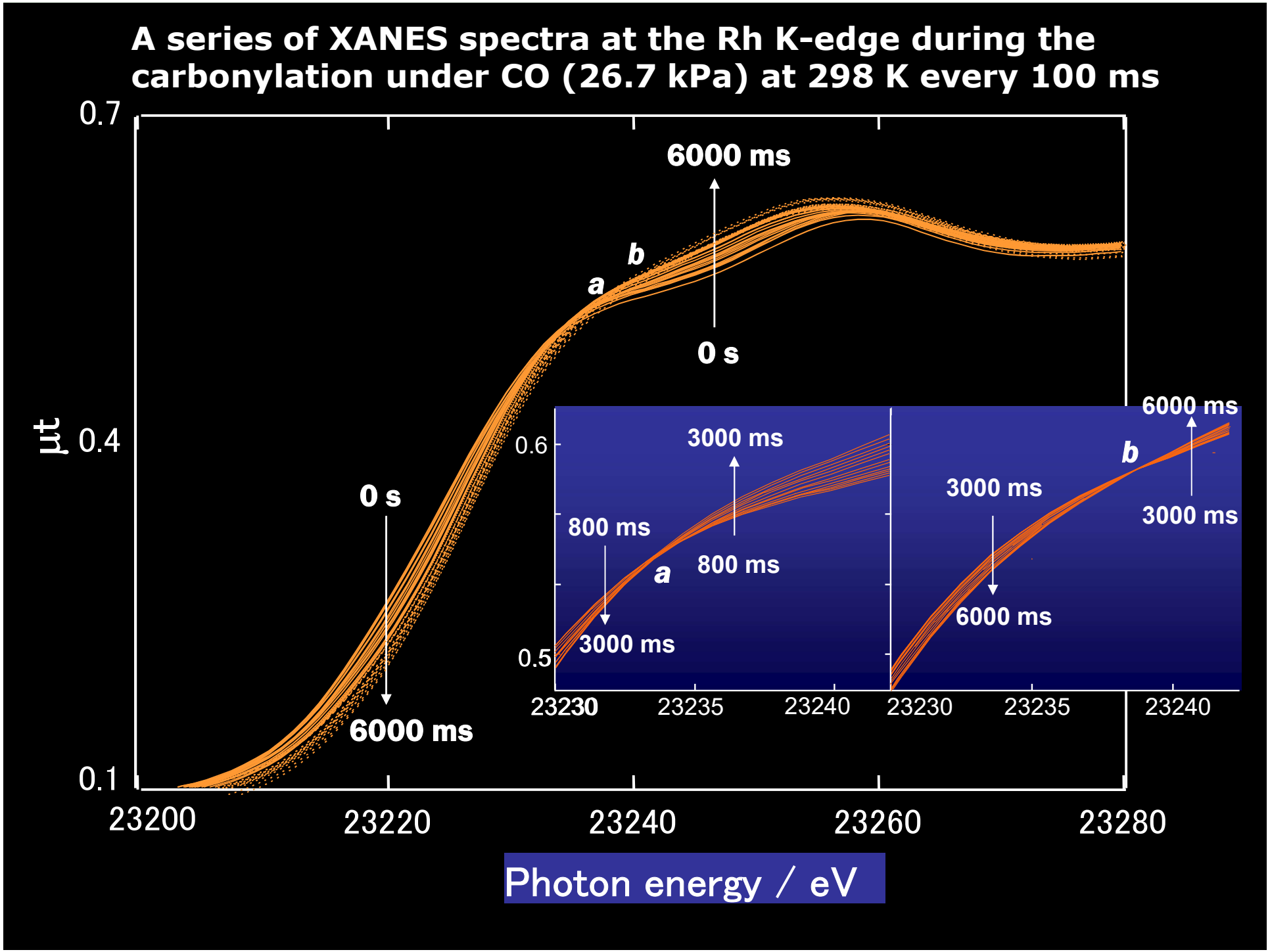


EXAFS Parameter Values for the 0.57 wt % $Rh/\gamma\text{-}Al_2O_3$ Catalyst after Reduction and CO Admission[a]

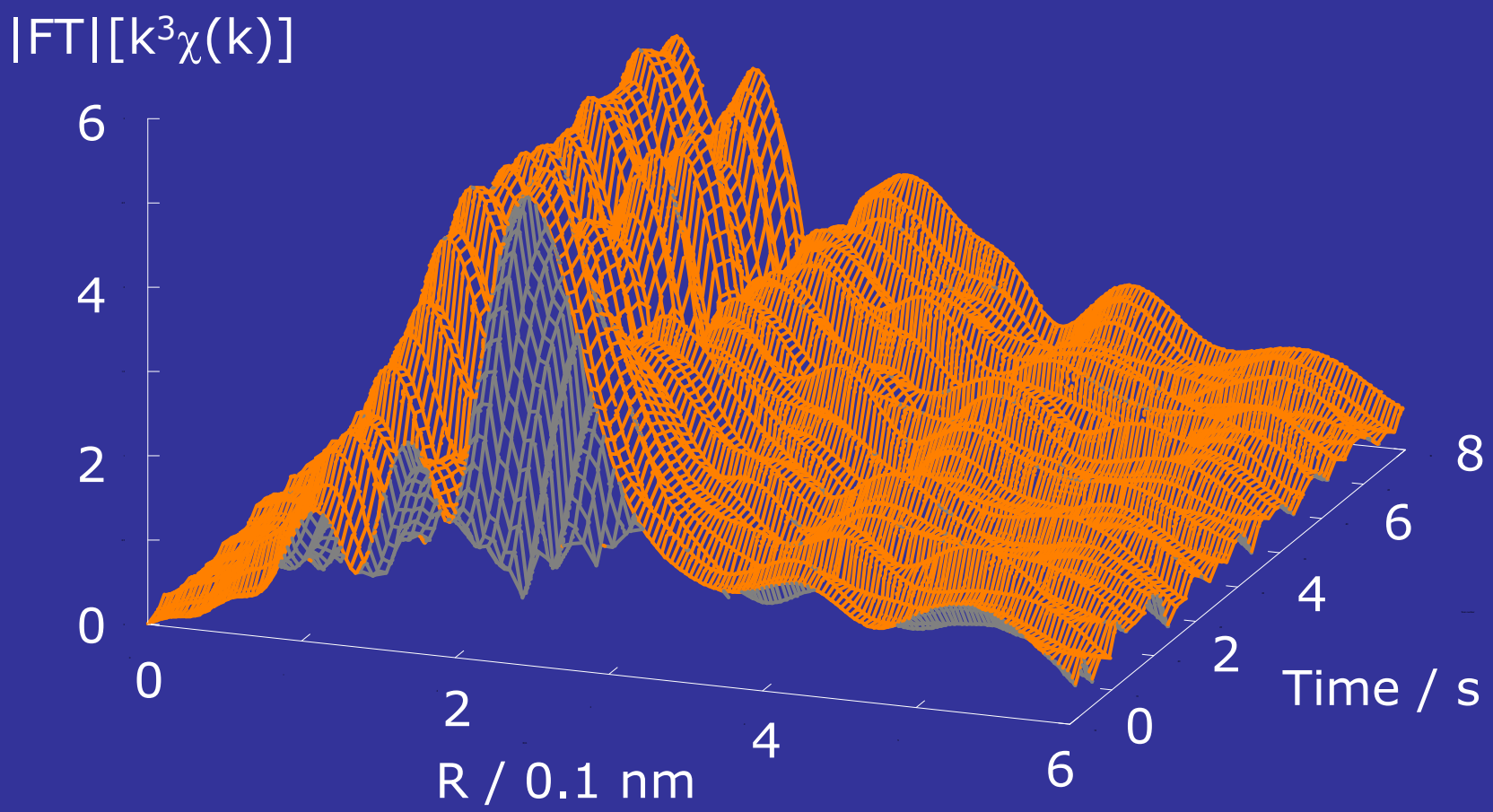
	coordination								
	Rh–Rh			Rh–O			Rh–CO		
treatment	N	R (Å)	$\Delta\sigma^2 \times 10^2$ (Å^2)	N	R (Å)	$\Delta\sigma^2 \times 10^2$ (Å^2)	N	R (Å)	$\Delta\sigma^2 \times 10^2$ (Å^2)
reduction at 593 K	3.7	2.68	0.5	1.9	2.74	0.0			
reduction at 593 K, evacuation at 593 K, CO admission at 298 K				3.1	2.12	0.3	1.8		0.7

[a] Accuracies: N, ±15%; R, ±1%; $\Delta\sigma^2$, ±15%.

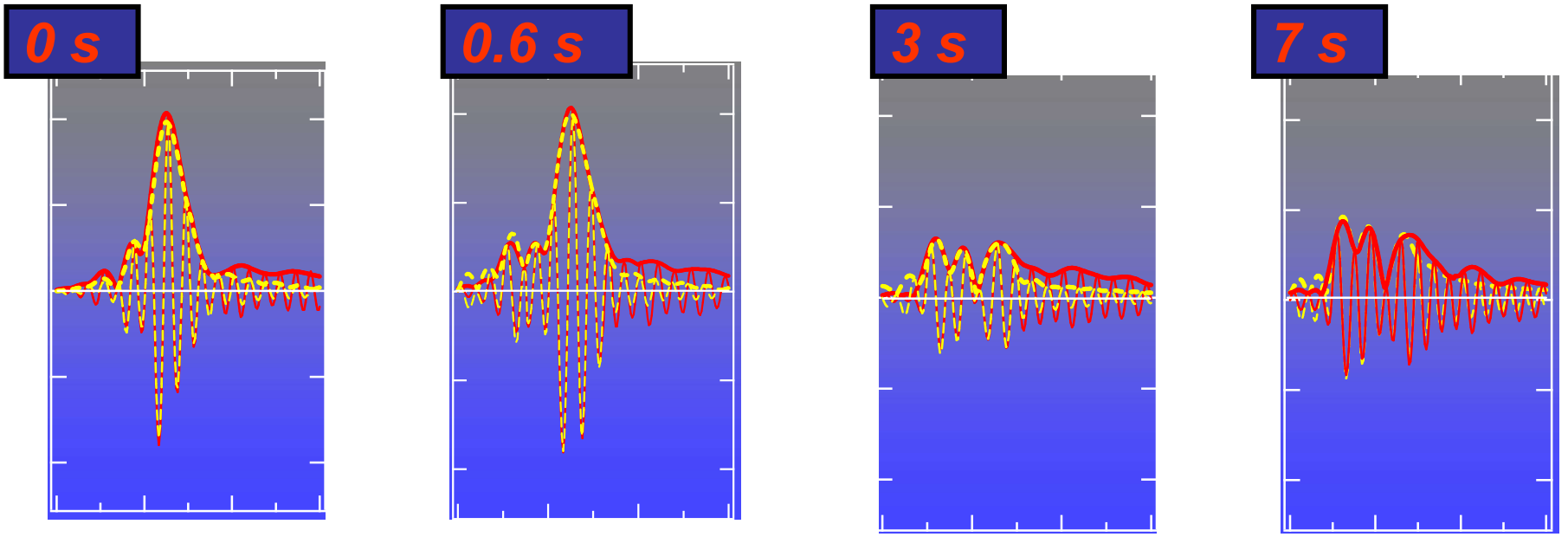
H.F.J.van't Bilk, J.B.A.D.van Zon, T.Huizinga, J.C.Vis, D.C.Koningsberger, and R.Prins, J.Am.Chem.Soc., 107 (1985) 3139.

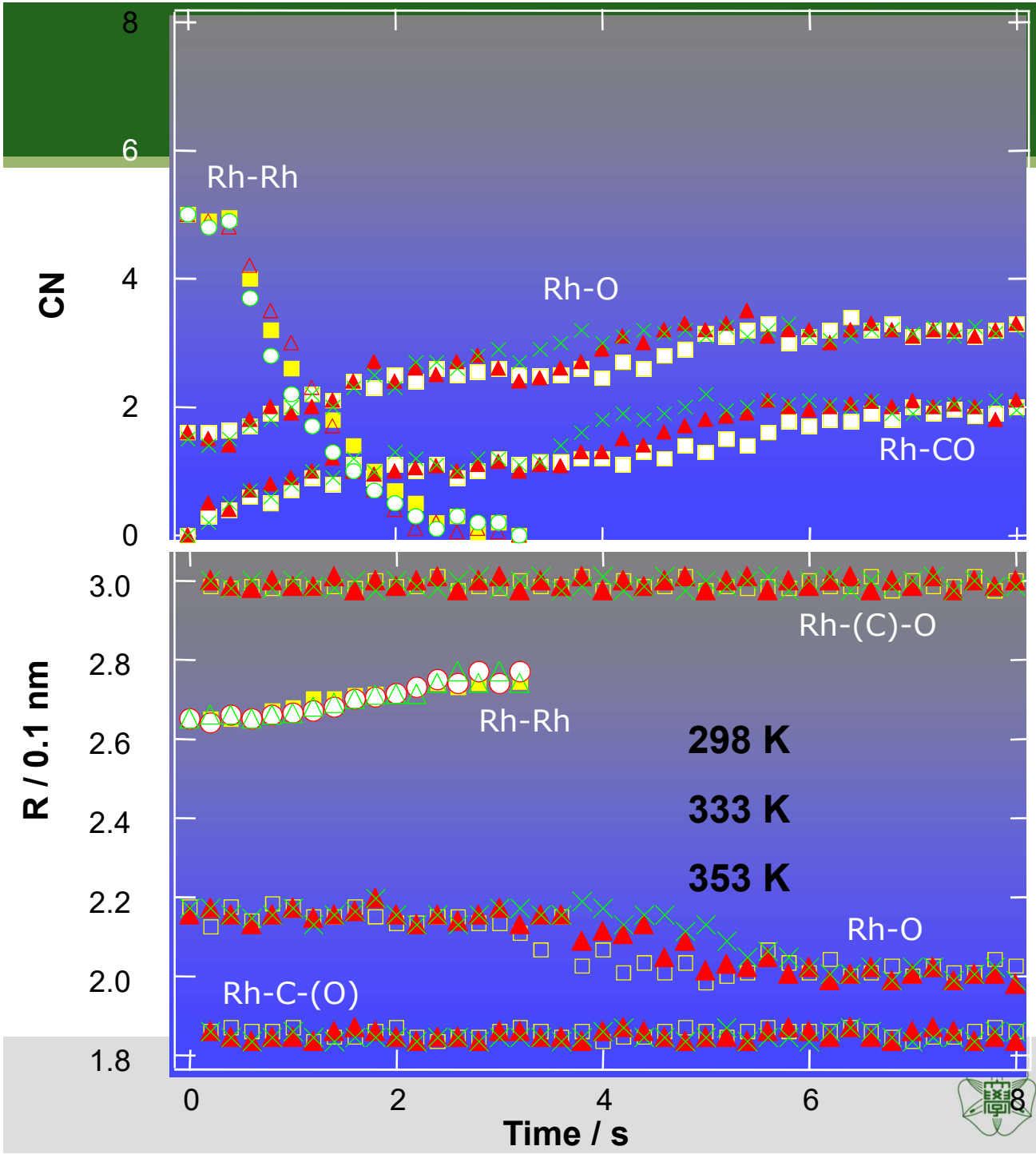

A series of XANES spectra at the Rh K-edge during the carbonylation under CO (26.7 kPa) at 298 K every 100 ms
0.7
0.4
0.1
μt
6000 ms
0 s
b
a
0 s
6000 ms
0.6
0.5
3000 ms
800 ms
a
800 ms
3000 ms
6000 ms
b
3000 ms
3000 ms
6000 ms
23230
23235
23240
23230
23235
23240
23200
23220
23240
23260
23280
Photon energy / eV

A series of k^3-weighted EXAFS Fourier transformed functions at the Rh K-edge during the disintegration of Rh clusters on Al_2O_3 under CO(26.7 kPa)



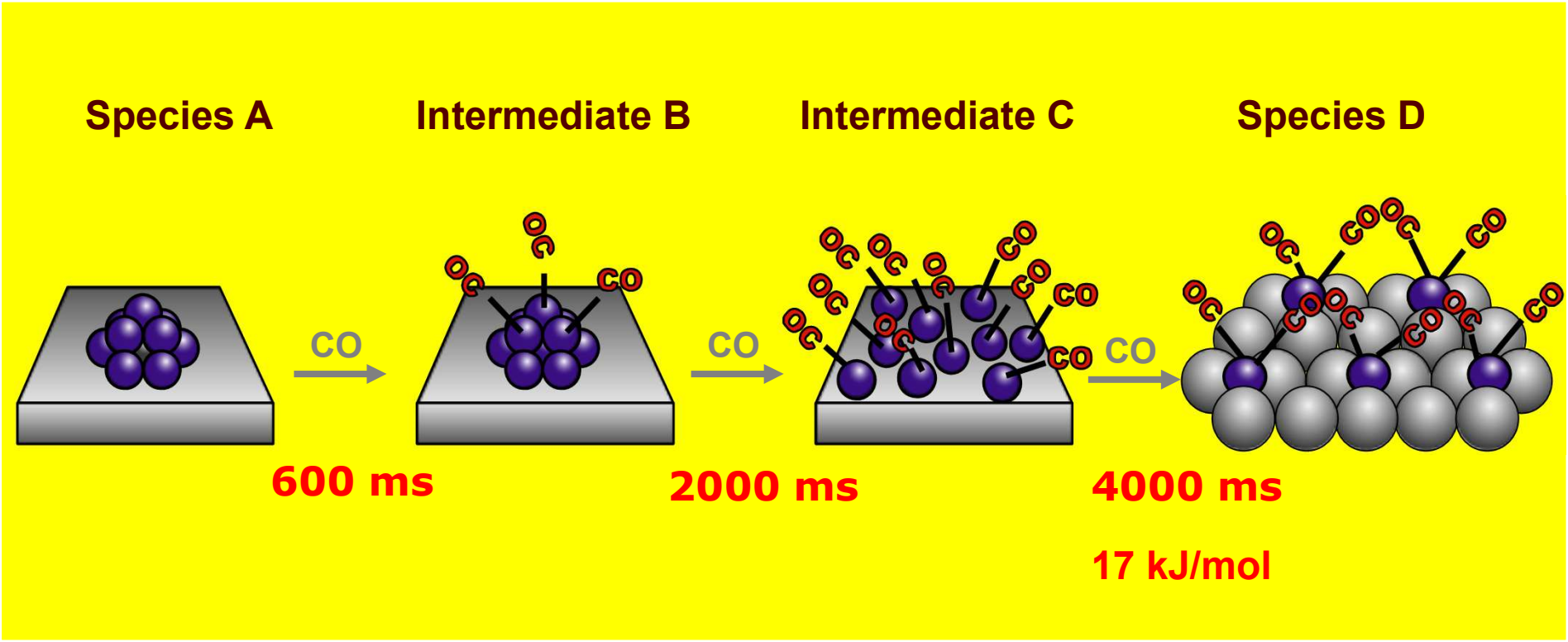
The k^3-weighted EXAFS Fourier transformed functions for Rh/Al_2O_3 under CO (26.7 kPa) at 298 K measured by DXAFS together with the curve fittings of the observed FT data and their imaginary parts





The values of coordination number (CN) and bond distance (R) determined by the curve fitting as a function of CO exposure time

Illustrative mechanism and time scale at 298 K for the disintegration of Rh clusters on Al_2O_3 during CO adsorption by time-resolved DXAFS



Metal – support interaction

Support - maintaining a highly dispersed state

It might show catalytic activitivty forming a bifunctional catalysis.

It affects the metal activity through metal support interaction.

Metal support interaction plays important roles in the catalyst.

- It stabilizes the small particle size.
- It modifies the electronic state.
- It modifies shape and geometry of metal particles.

But there is no clear identification of the metal-support interaction.

In the conventional catalyst, EXAFS from metal-support interaction is hidden by strong framework EXAFS.