Ultrafast analysis of catalyst surface

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What are catalysts?

They accelerate chemical reaction without changing themselves and important in many fields.

- Polymers and plastics are generate using Catalysts (Ziegler Natter or Kaminsky catalysts)
- Automobile catalysts (Pt-Pd-Rh/Al2O3, Pt/CeO2)
- Photocatalysts(TiO_2)
- Enzyme
- Fuel cell electrode

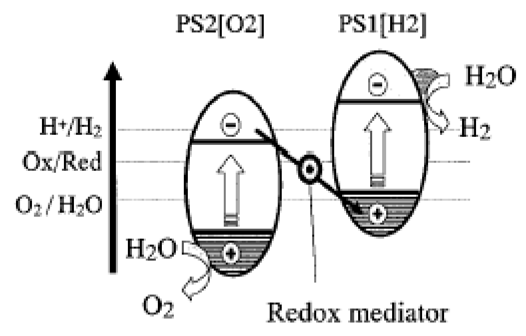
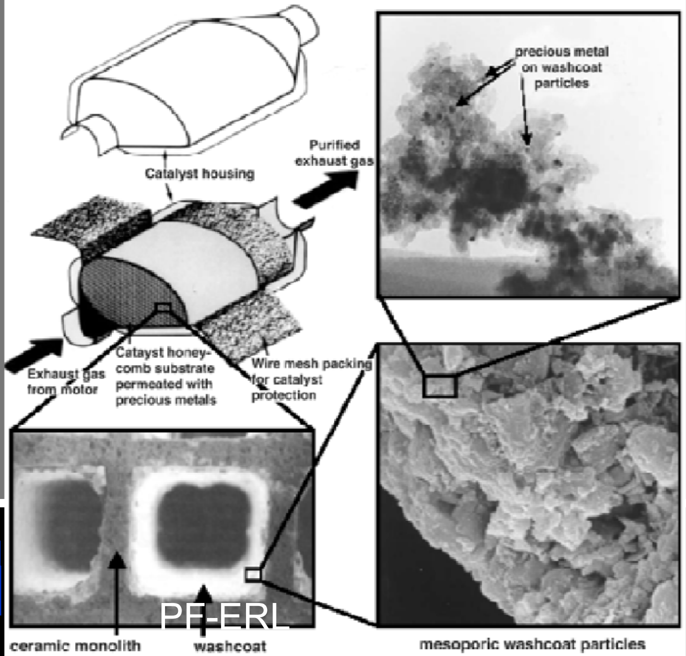


Fig. 2 Z-scheme system using two semiconductor photo-catalysts (two step system).



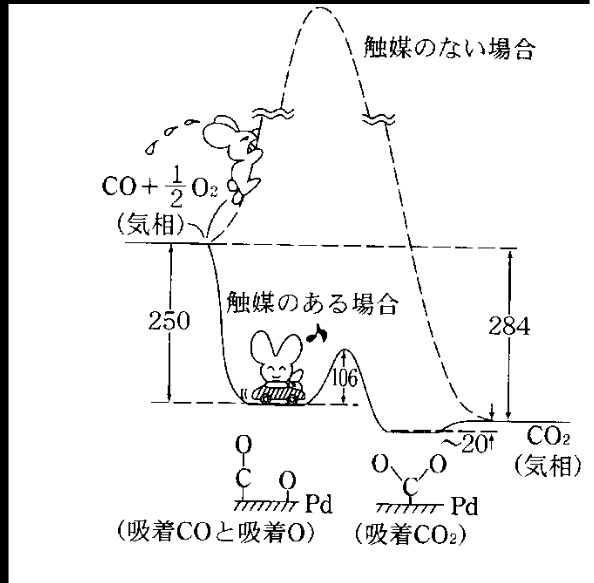
Automobile catalyst
To remove NOx
From exhausted gas

Three important factors in catalysis

- Activity
- rate determining step
- Slowest process.

- Selectivity
- ex. Propane oxidation
  - No selectivity CO_2
  - High selectivity CH_2CHCHO

- Life time



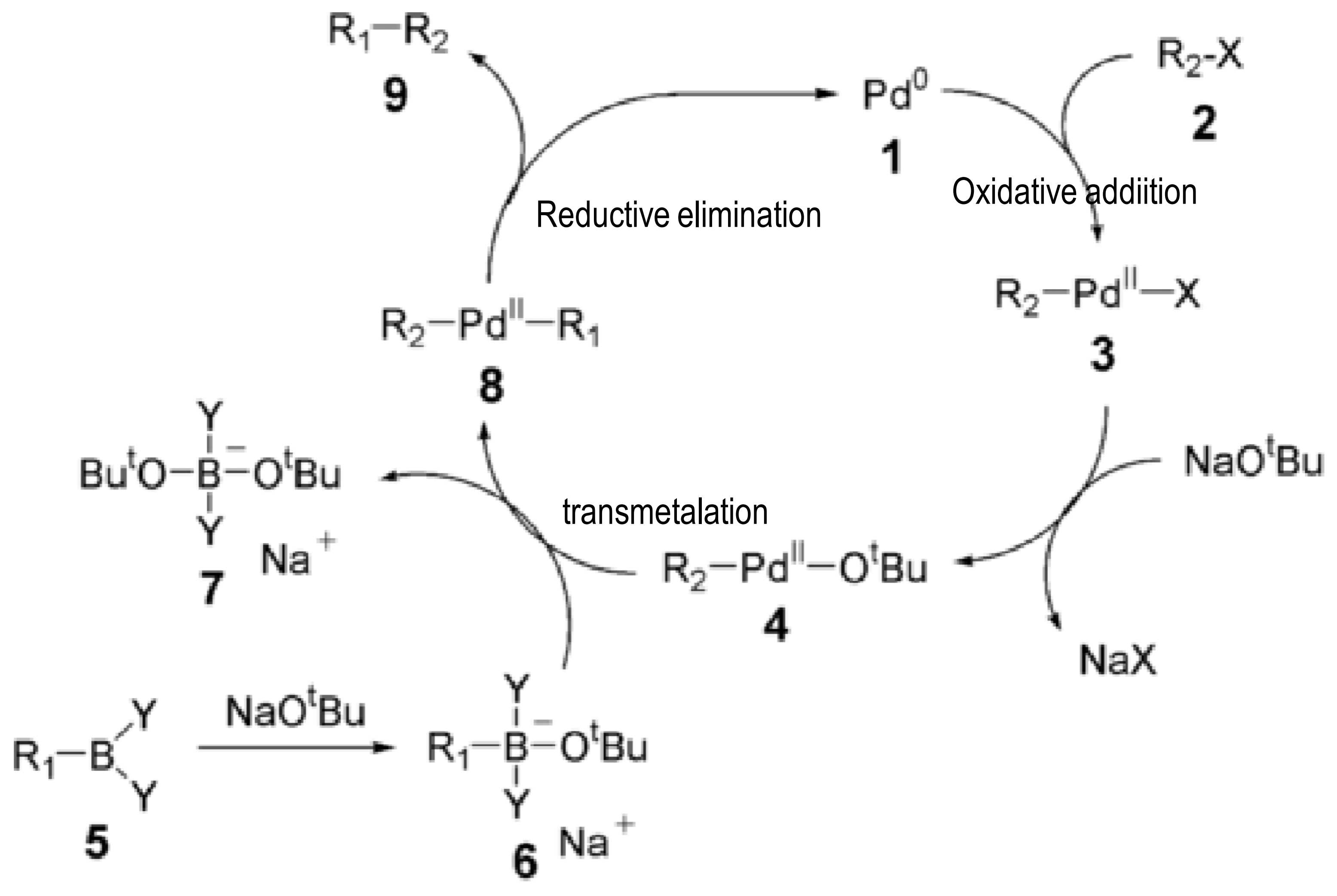
Classification of Catalysts

- Solid State Catalysts-Heterogeneous catalysts
  - Pt-Rh-Pd/Al2O3
  - Solid surface plays an important role

- Catalyst in Solution **Homogeneous catalysts**
  - Cross coupling catalysts, Enzyme
  - Chiral synthesis, Metatheses
  - Metal active site is important

→ Special Active Site Plays an important role.

Miyaura-Suzuki Reaction



Classification of Catalysts

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  - Pt-Rh-Pd/Al2O3
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- Catalyst in Solution **Homogeneous catalysts**
  - Cross coupling catalysts, Enzyme
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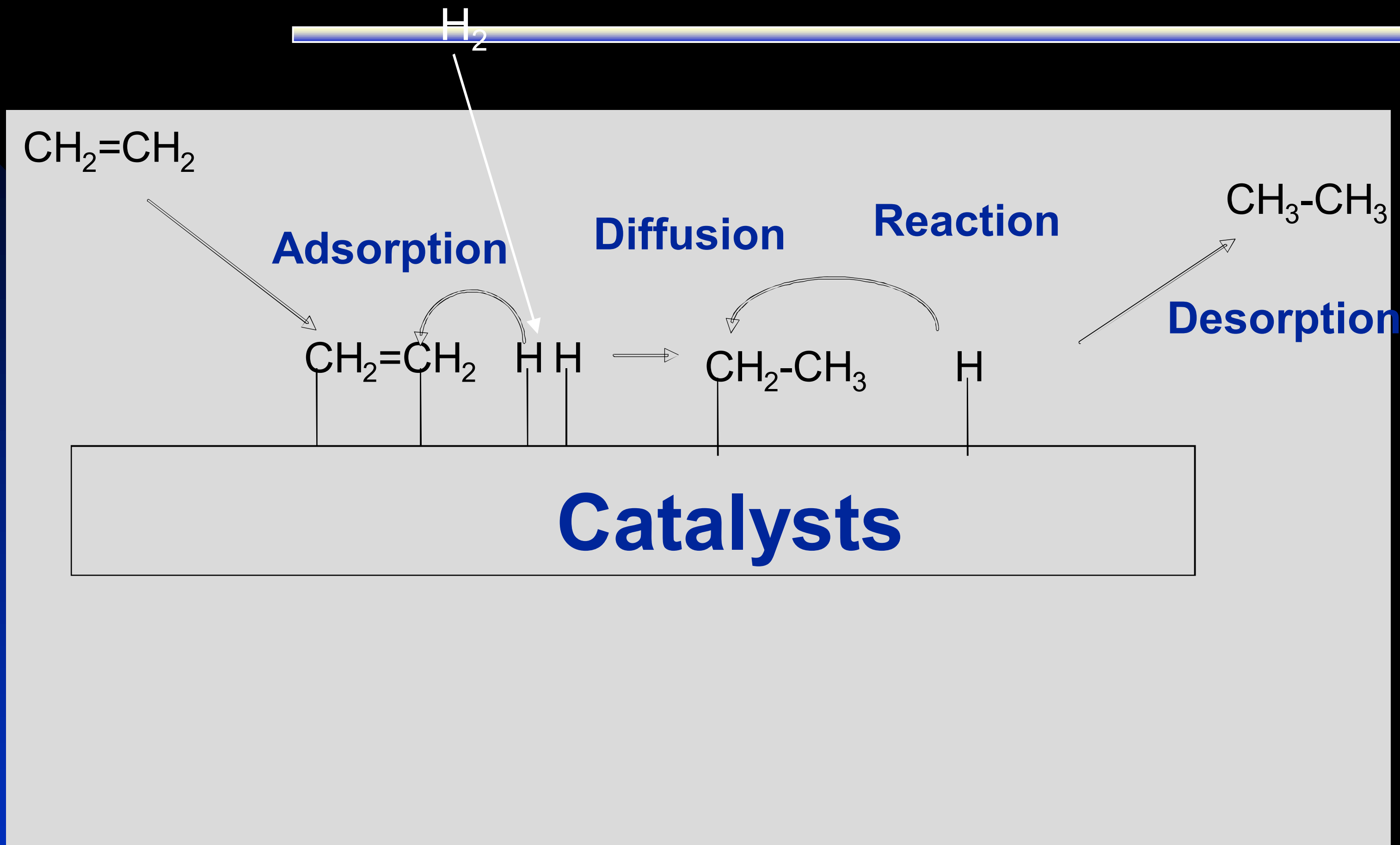
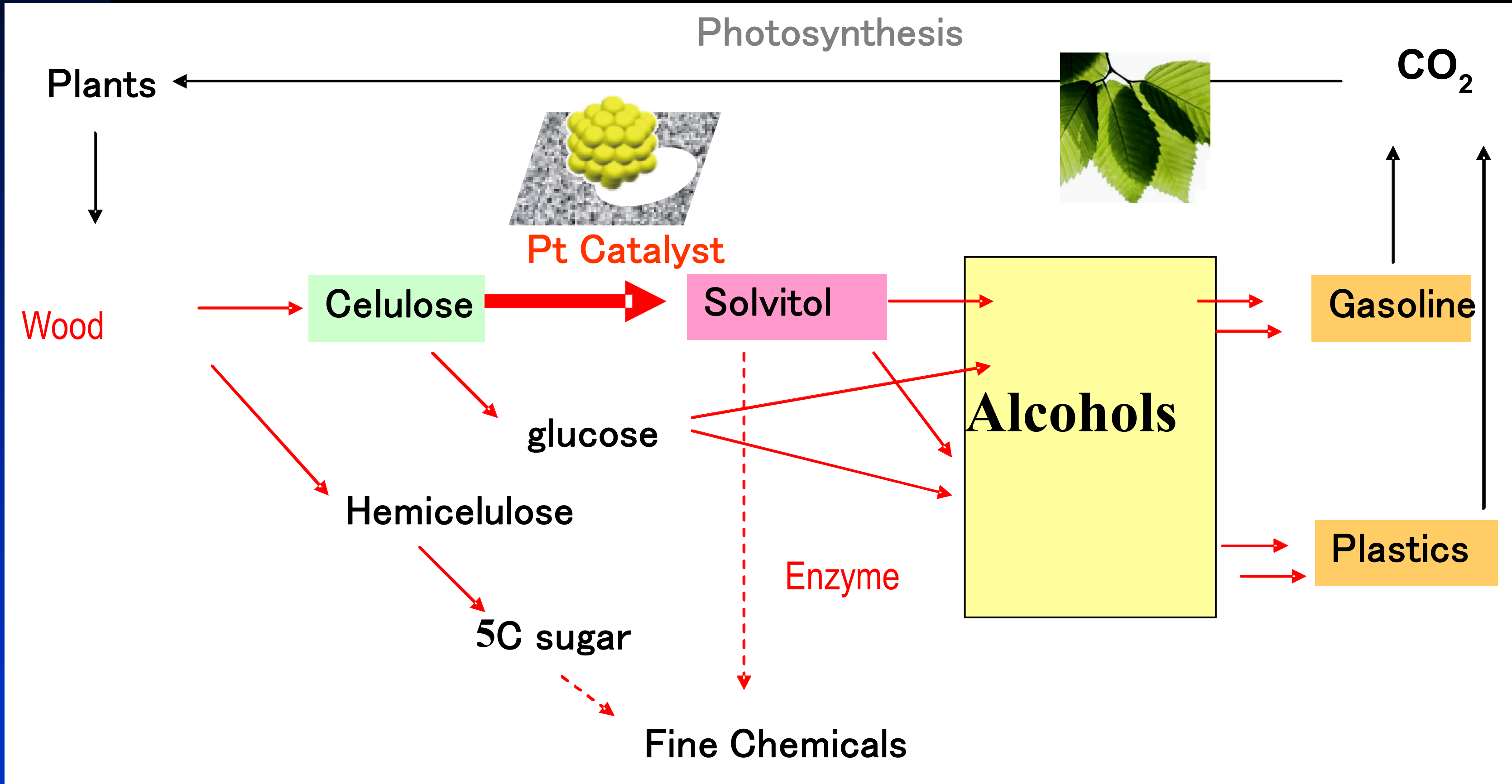
Heterogenous Catalysts



- Langmuir Hinshellwood mechanism
- Horiuchi-Polanyi Mechamism

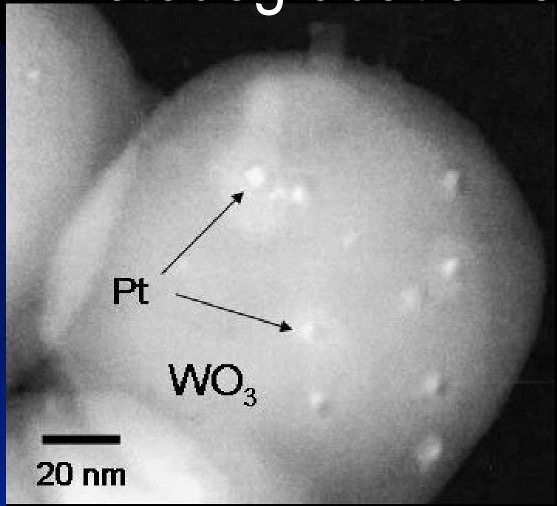
From Unused Biomass to Fuel
(A.Fukuoka Angewandte Chem. 2007)

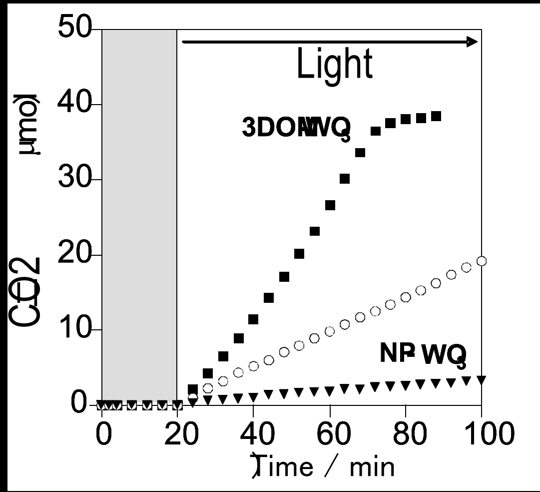


New Chemical industry based on biomass

Environment Improvement Catalysts

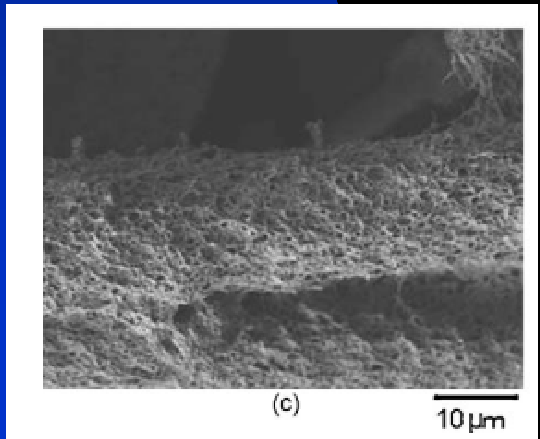
Photodegradation of VOC

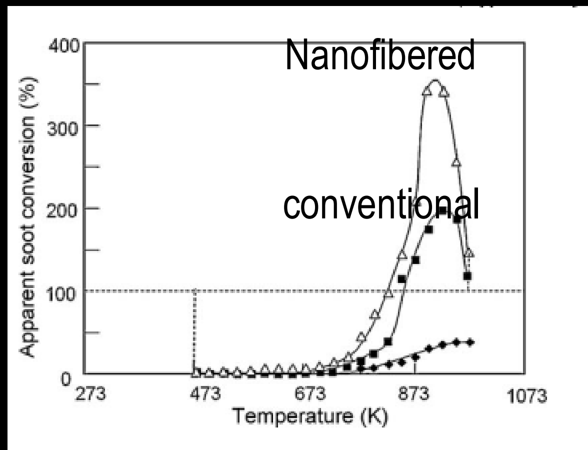




Ueda Ohtani et al.
J.Material Chem. (2010)

Soot combution on nanofibered $LaMnO_3$



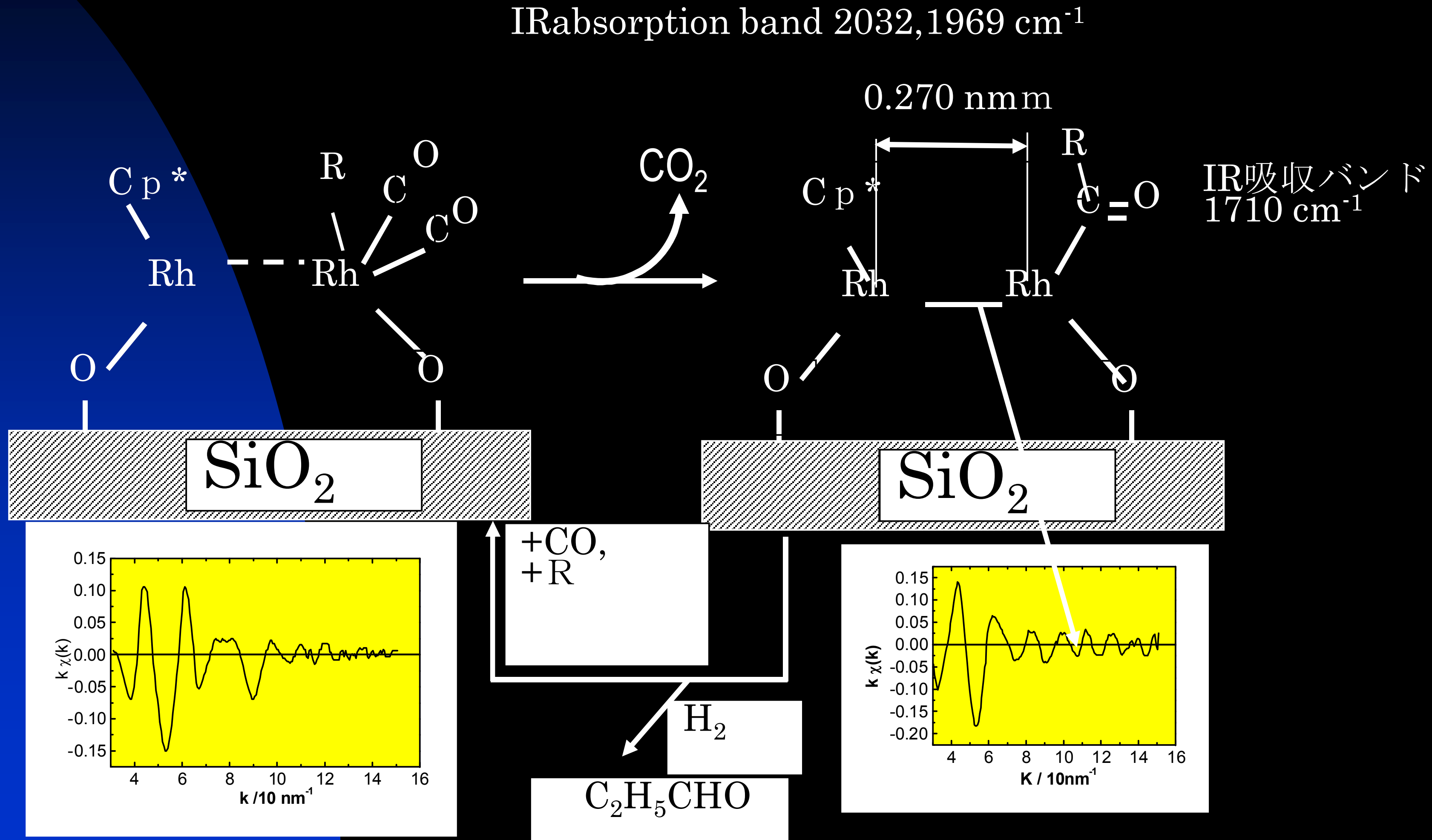


Li, S.; Kato, R.; Wang, Q.; Yamanaka, T.; Takeguchi, T.; W., U. *Applied Catalysis B: Environmental* ***2010, 93, 383.***

Rh dimer catalysts（Active for ethylene hydroformylation reaction）

K. Asakura, K.K. Bando, Y. Iwasawa, H. Arakawa, K. Isobe, J.Am.Chem.Soc 112 (1990) 9096.

- C2H4+CO+H2→ C2H5CHO



EXAFS before the reaction

EXAFS after the adsorption

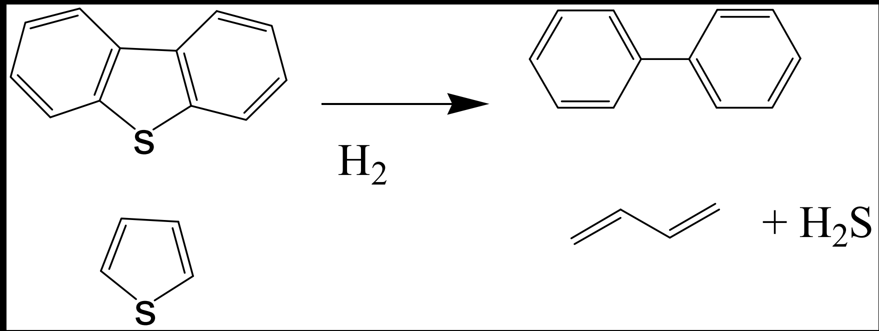
.In-situ studies

- Active site is dynamically changed during the reaction
- In-situ studies are necessary to determine the reaction mechanisms.
- High temperature and high pressure.

Introduction

Sulfur compounds in fossil fuel.

1. Sulfur is oxidized to sulfurous or sulfuric acids and is an origin for acid rain.
2. It poisons the $deNO_X$ catalysts equipped in cars.
3. Demand for use of low quality oil with high sulfur contents.



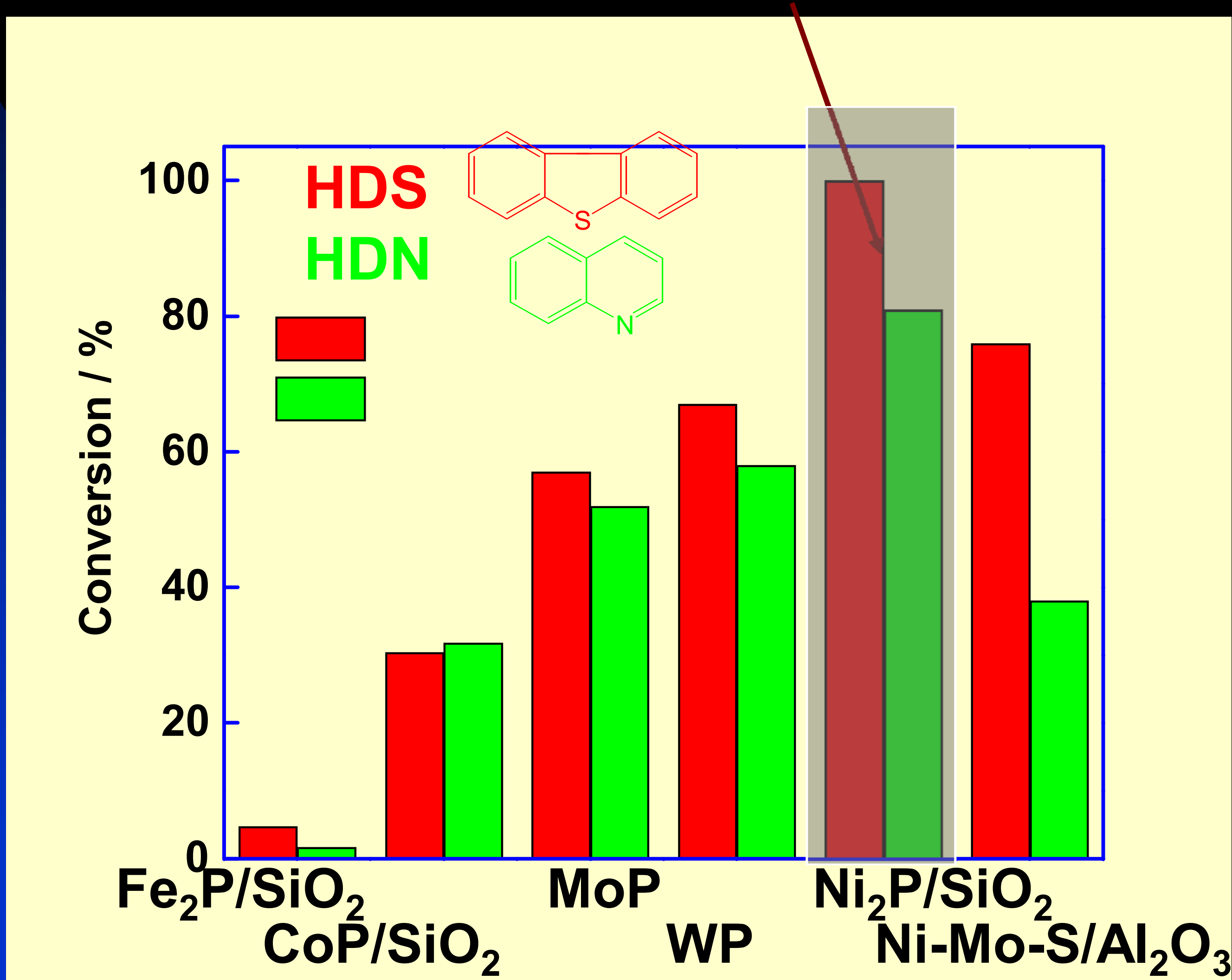
http://www.epa.gov/apti/course422/ap7b1.html

Sulfur in fuel is legally restricted more and more strictly.

	1990-1994	1995-2000	Post 2000
USA	500 ppm	500 ppm	**15 ppm by 2006**
Europe	500 ppm	500 ppm	**50ppm by 2005** **10 ppm by 2008**
Japan	0.2 wt%	500 ppm	**50 ppm by 2005** **10 ppm by 2007**

Metal phosphides

More active than commercially avaialbe NiMoS



In situ EXAFS

X-ray windows are set far away from sample.

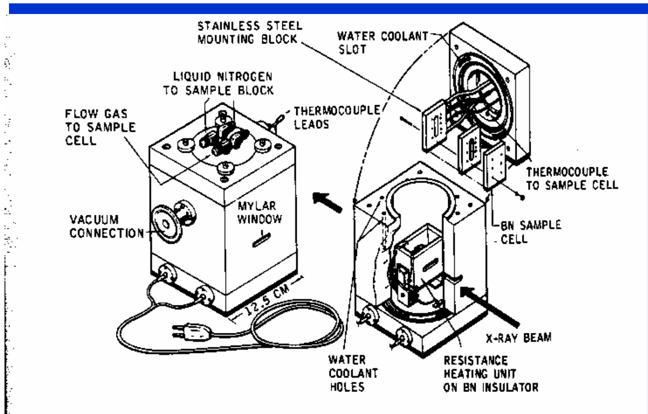
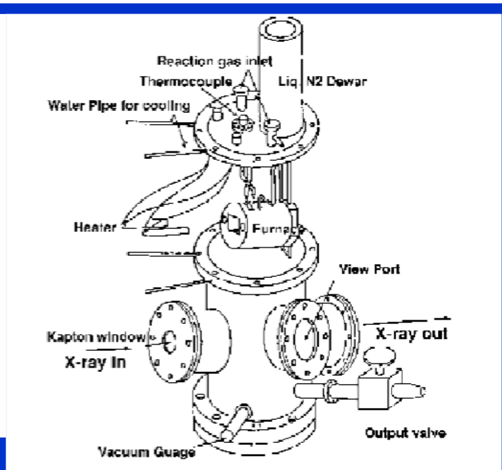
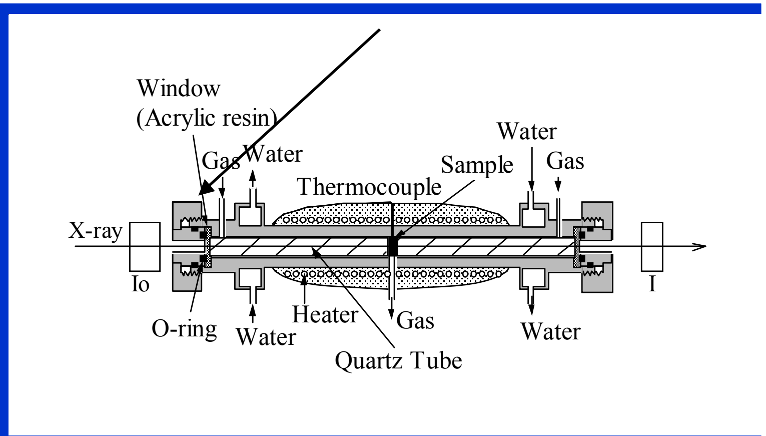


Figure 8.1. *In situ* cell of Lytle et al. (6).



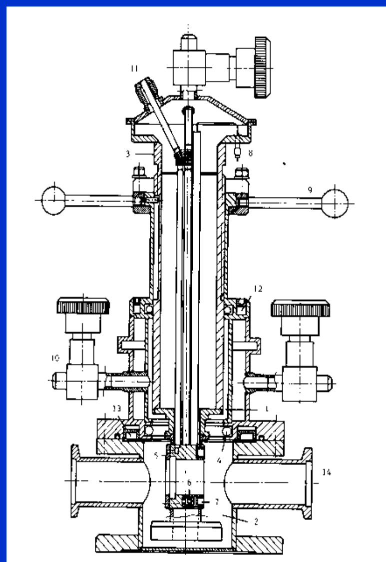


J.Chem.Phys. 70 (1979) 4849.

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.



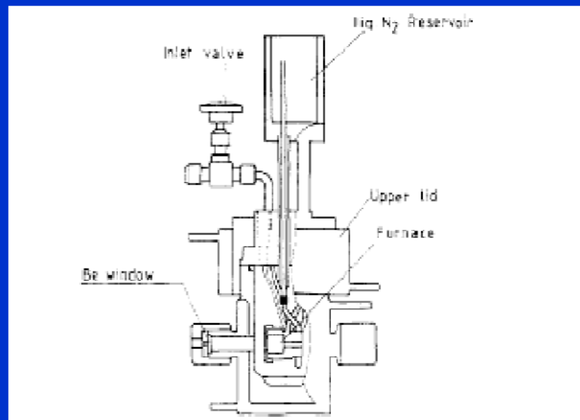
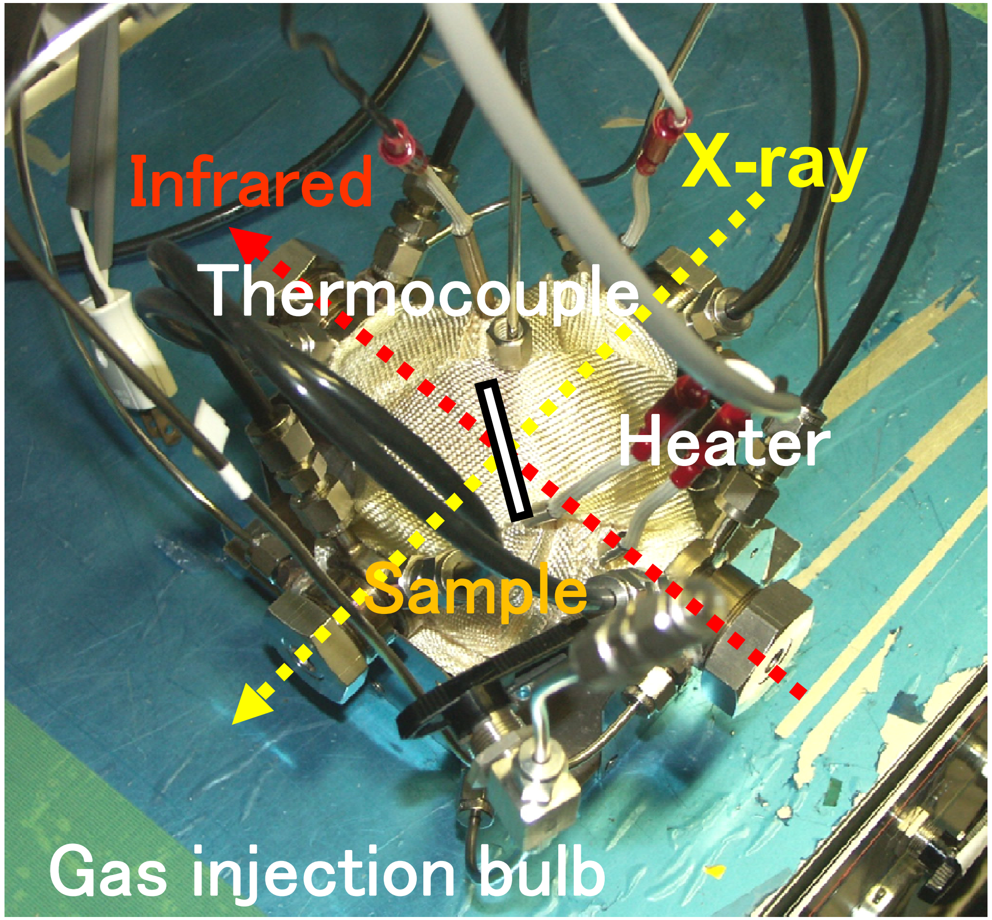


Figure 2. Chamber for the EXAFS measurements under vacuum and at high pressures.

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

PF-ERL

Experimental Setup

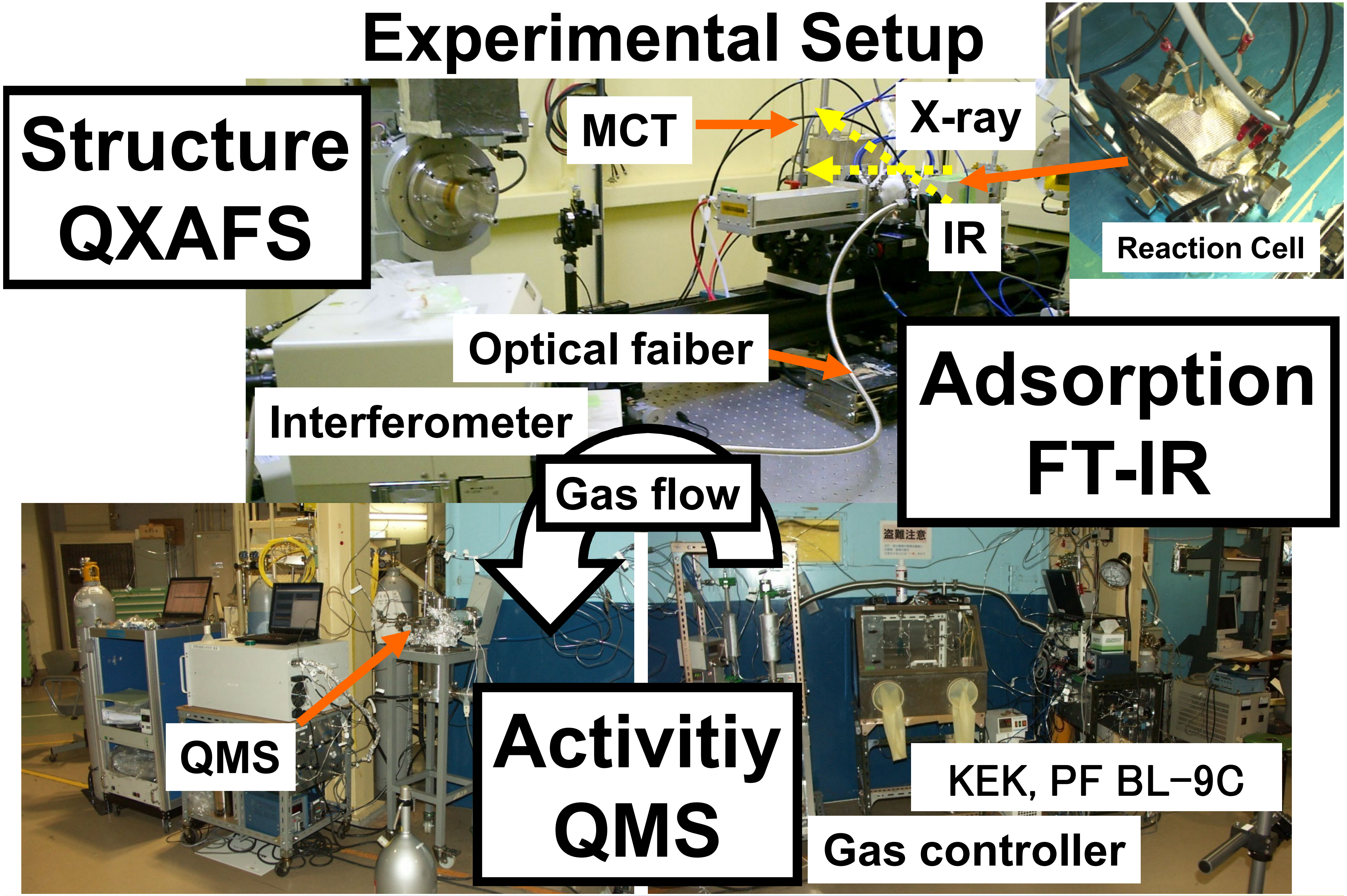


IR and X-ray hit the sample
Sample : Ni_2P/MCM-41
35 mg,15 mm in diameter

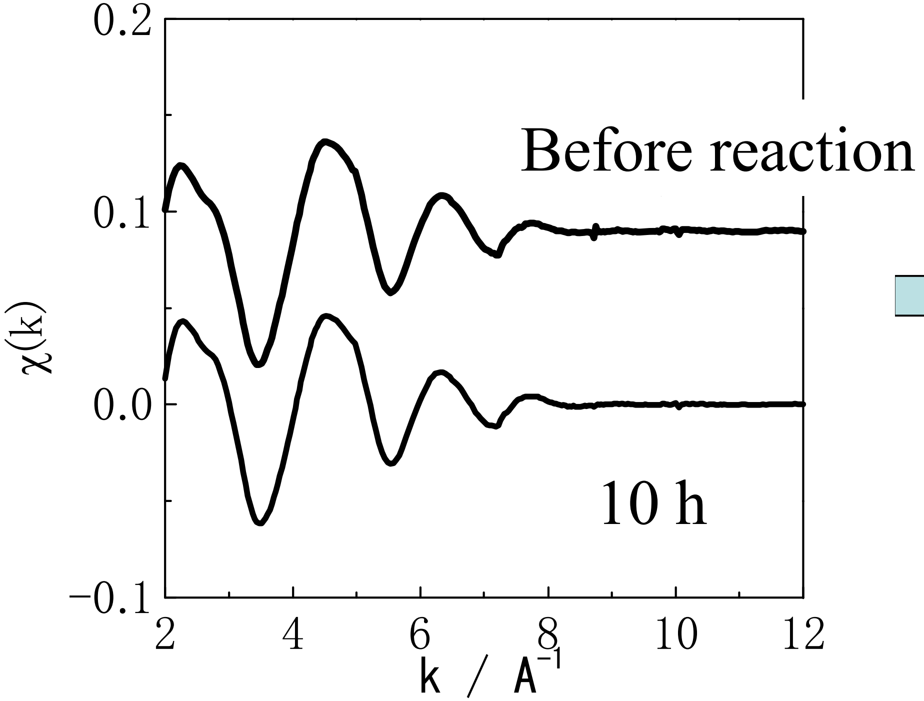
Heating
803 K by heater
Gas introduction

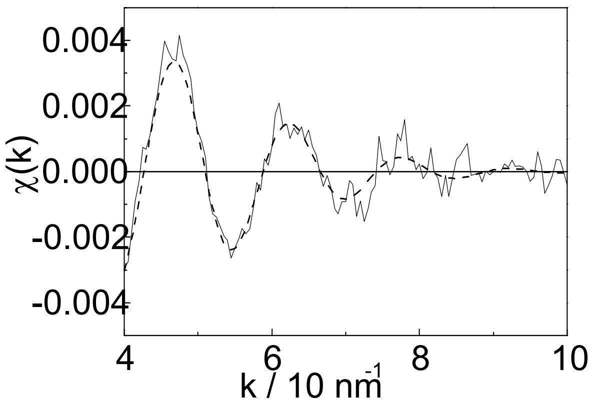
反応 : $C_4H_4S + 2H_2 \rightarrow C_4H_8S$
$C_4H_8S + H_2 \rightarrow H_2S + C_4H_8$

Experimental Setup



EXAFS of Ni_2P under reaction





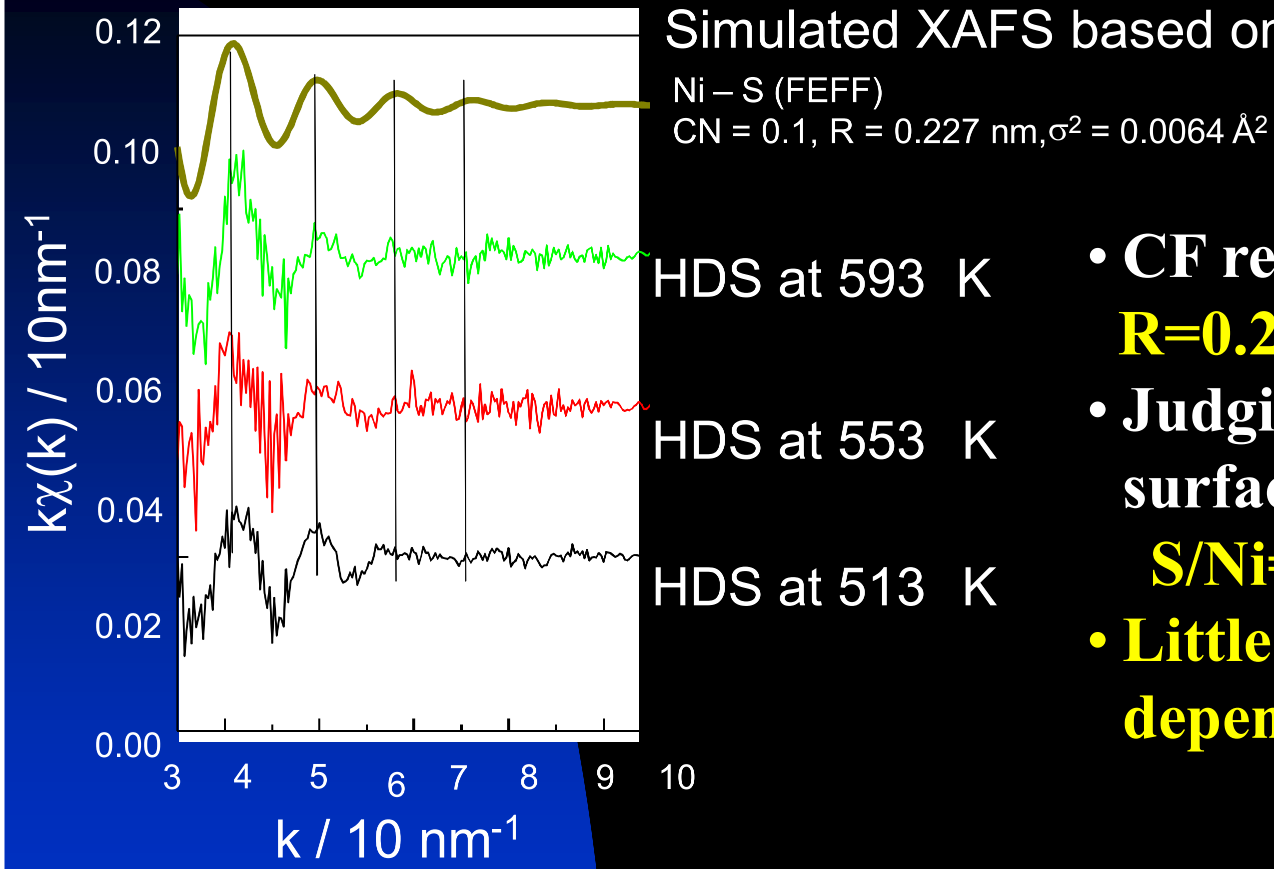
Difference Spectrum

- Ni_2P Ni K−edge XAFS

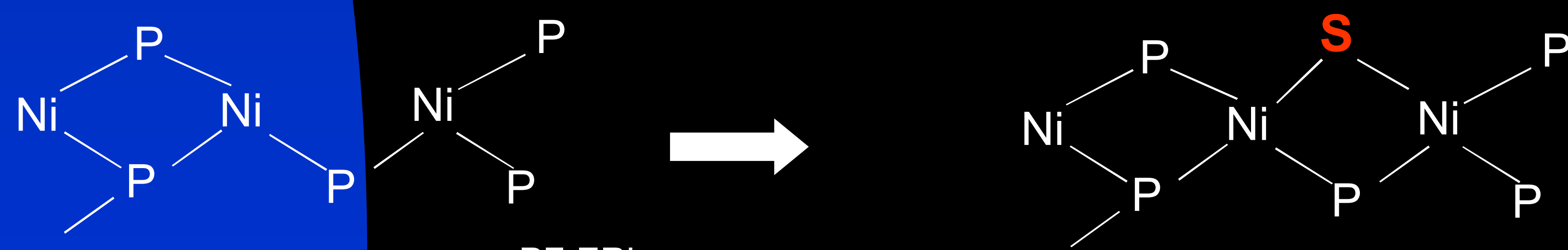
•Ni-S at 0.227 nm

• with N=0.1.

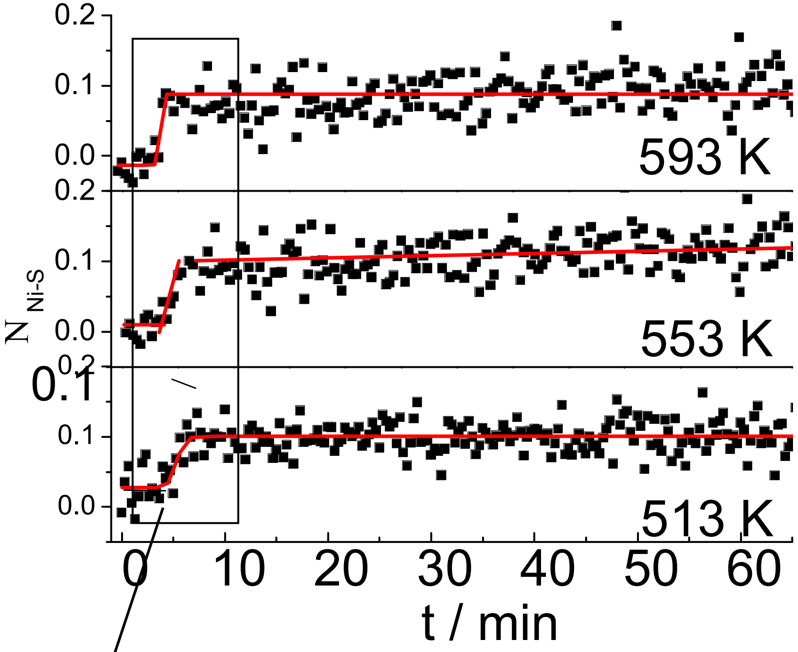
Difference spectra in HDS – before reaction

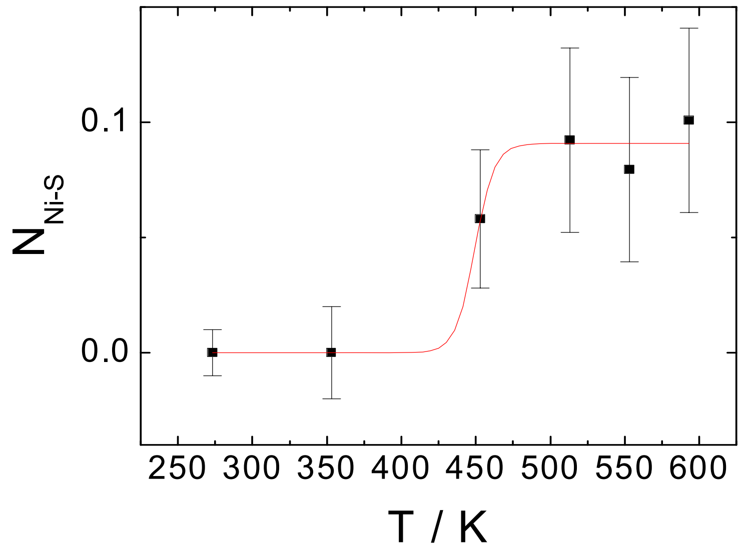


- **CF results of Ni-S**
  R=0.227 nm; CN=0.1.
- **Judging from the ratio of surface Ni to the bulk ~0.5**
  S/Ni=0.2±0.2
- **Little reaction temperature dependence**



How does Ni-S bond change?



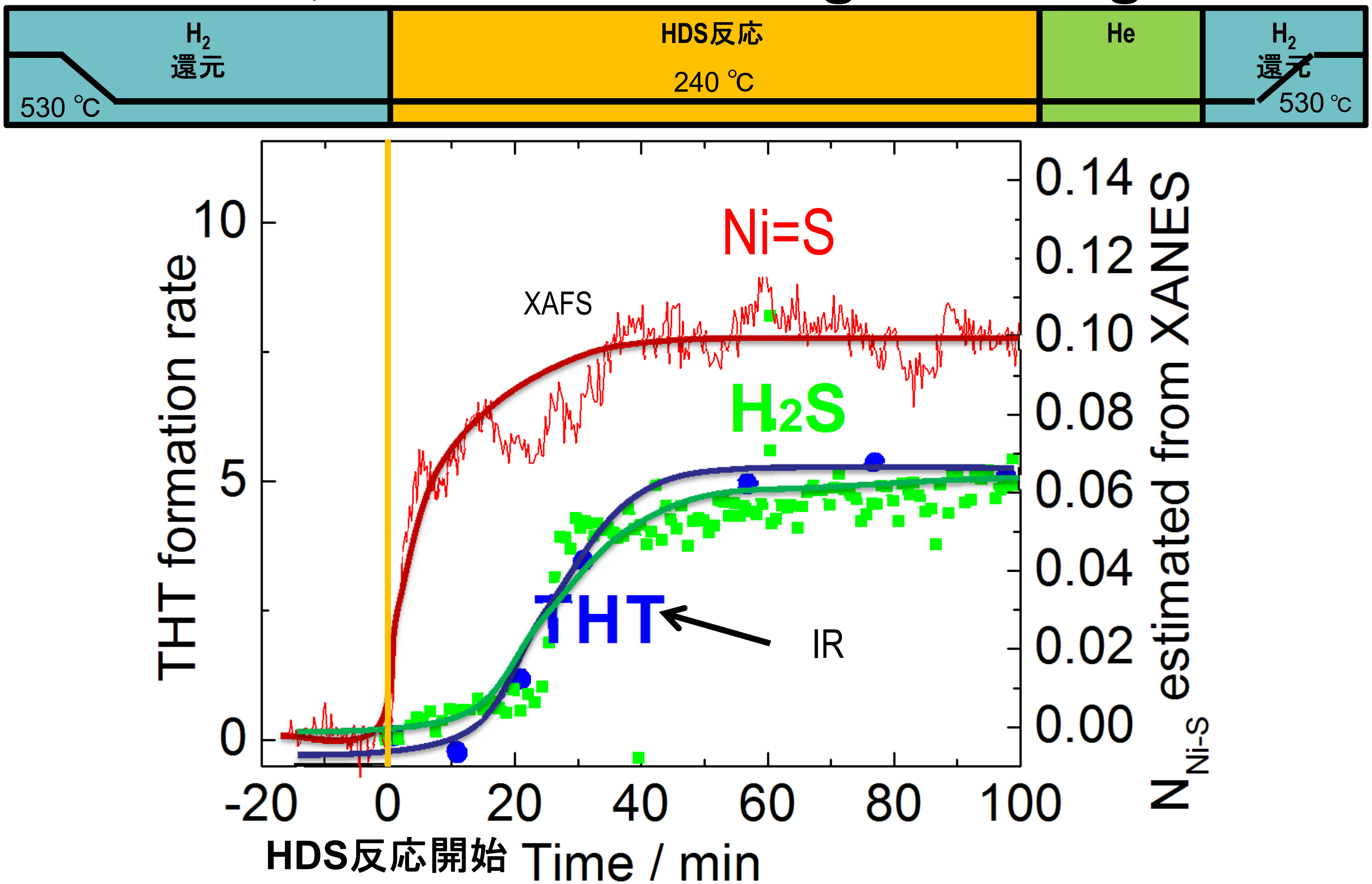


Formation rate

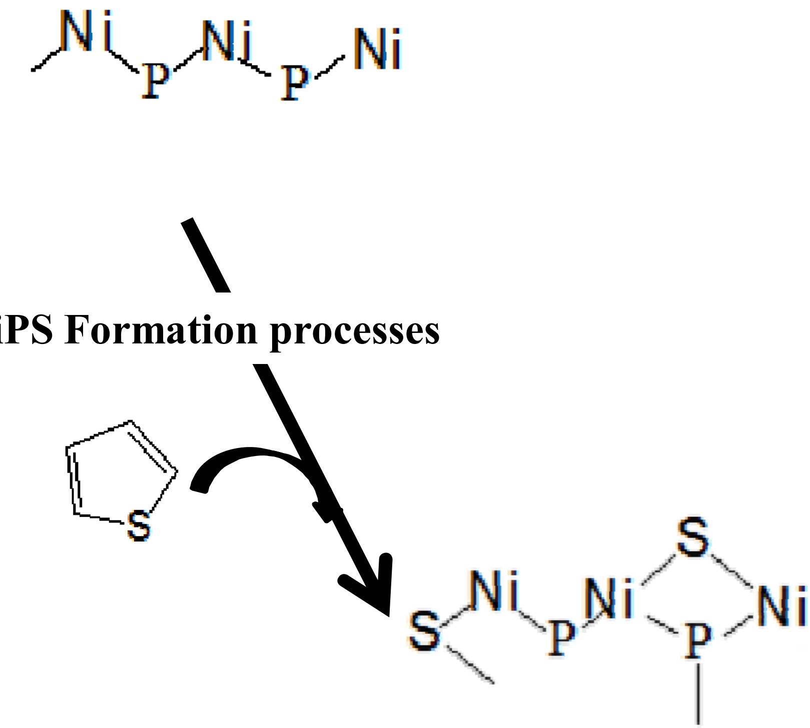
T / K	513	553	593
v/min^{-1}	0.47(3)	0.8(3)	2.5(3)

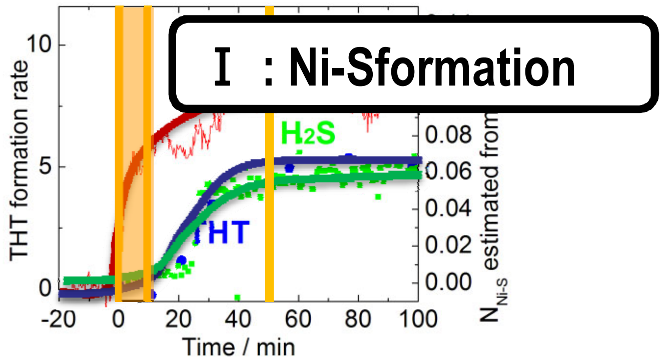
•Ni-S is rapidly formed and saturated.
•Saturation number is 0.1
•Ea=53 kJ/mol for formation reaction of Ni-S

XANES, IR and MS changes during 513 K

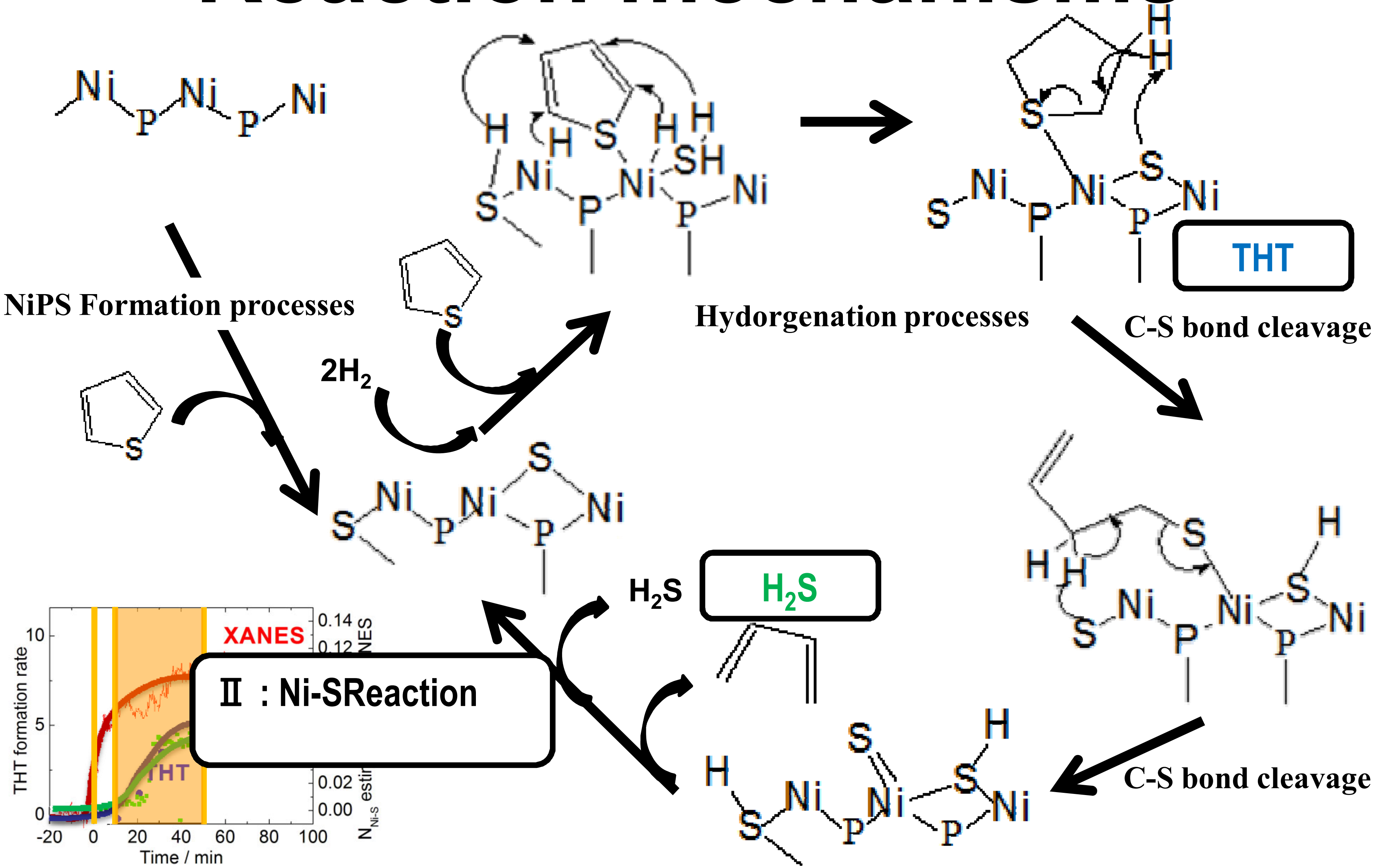


Reaction mechanisms

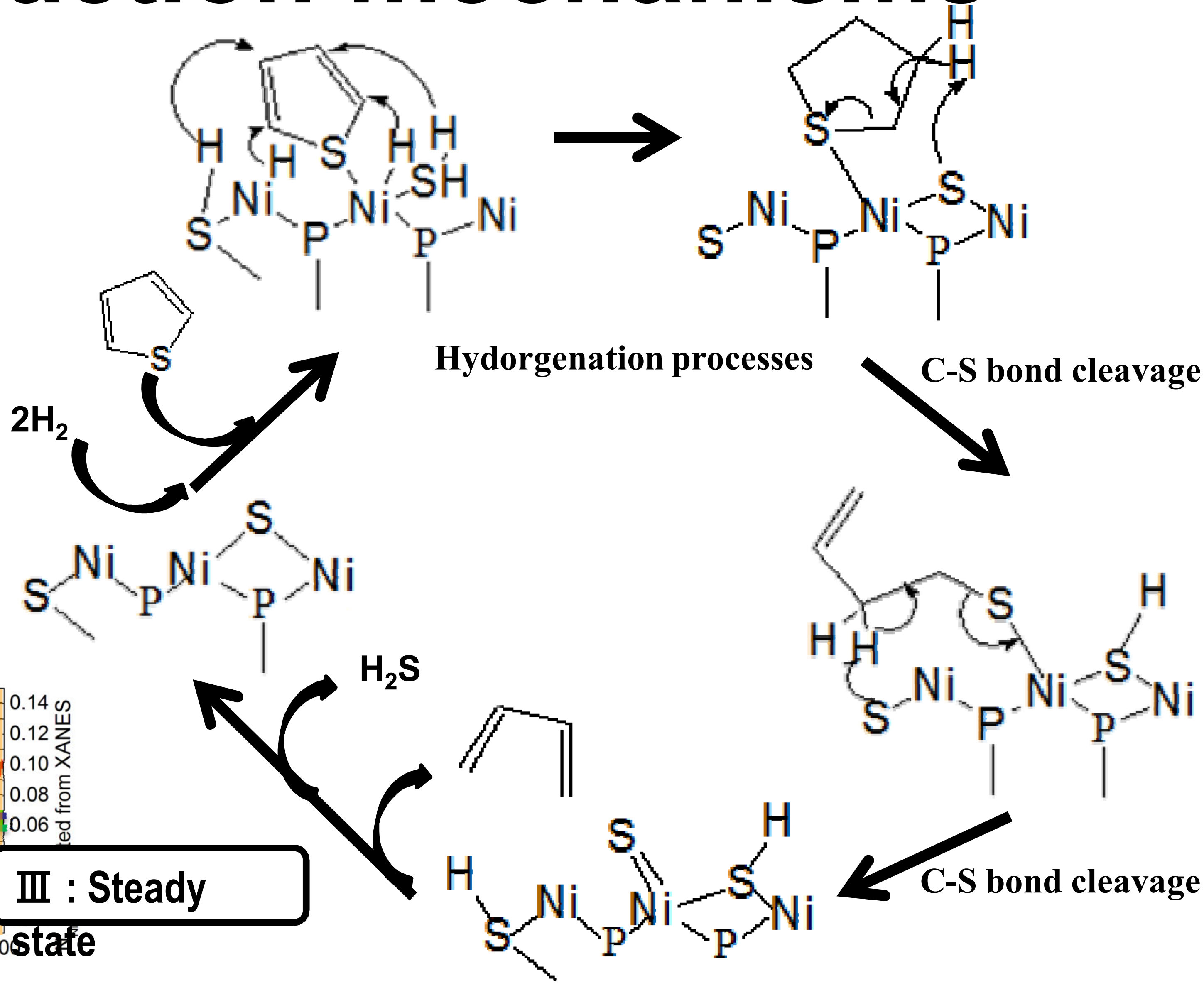


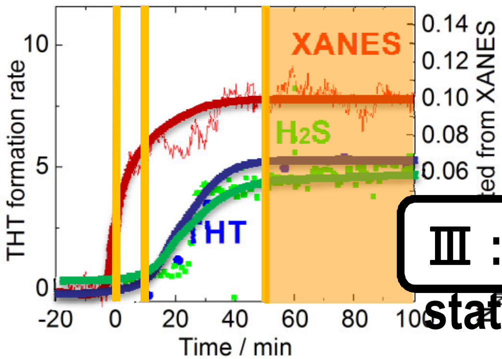


Reaction mechanisms



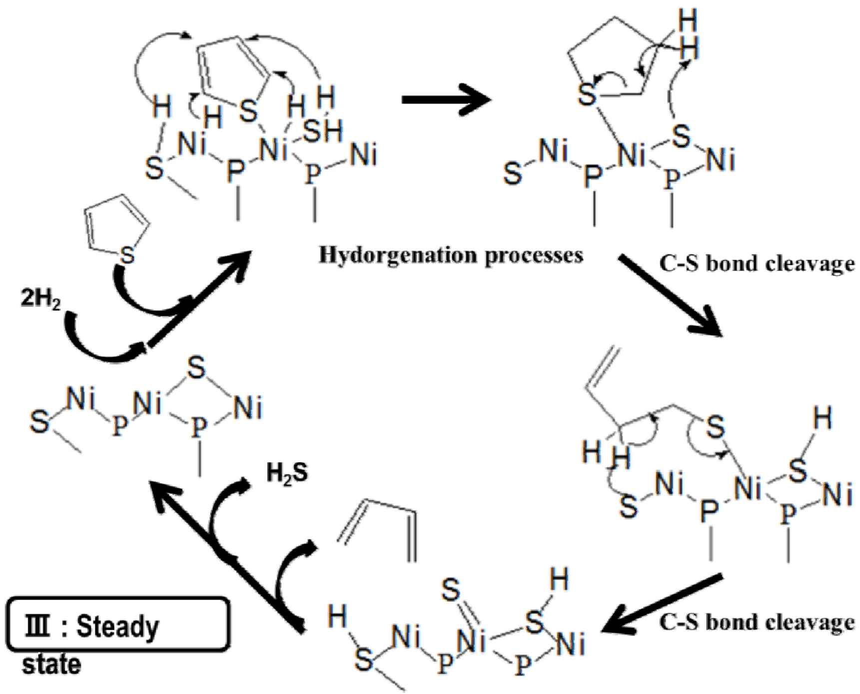
Reaction mechanisms



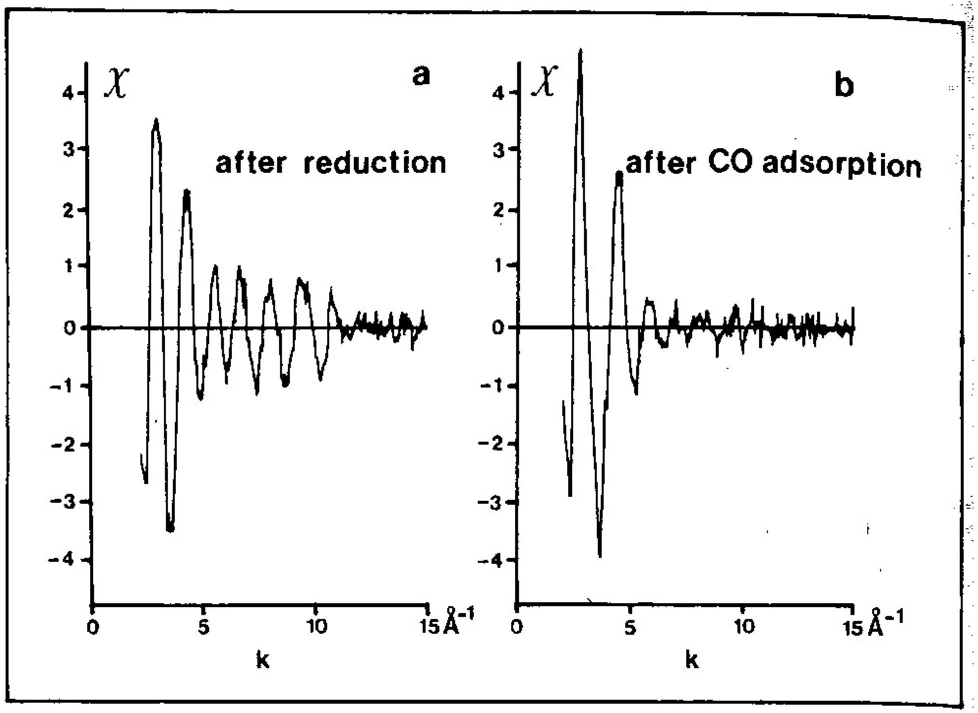


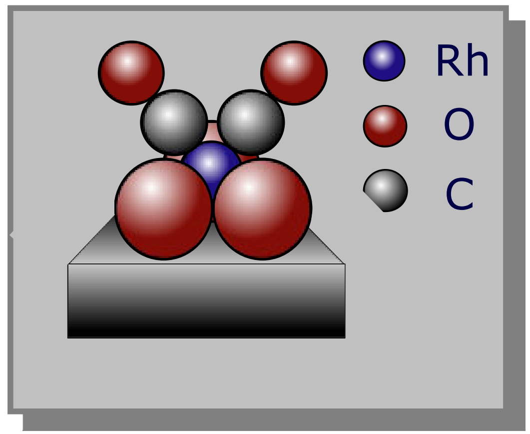
Time resolved studies=>DXAFS

- Stedy state
  - Mixture
- Reaction starts at once
  - Pump-probe
  - T-jump, P-Jump
  - Isotope change



Disruption of Rh clusters on Al2O3 surface by CO at RT





EXAFS Parameter Values for the 0.57 wt % Rh/γ-Al_2O_3 Catalyst after Reduction and CO Admission[a]

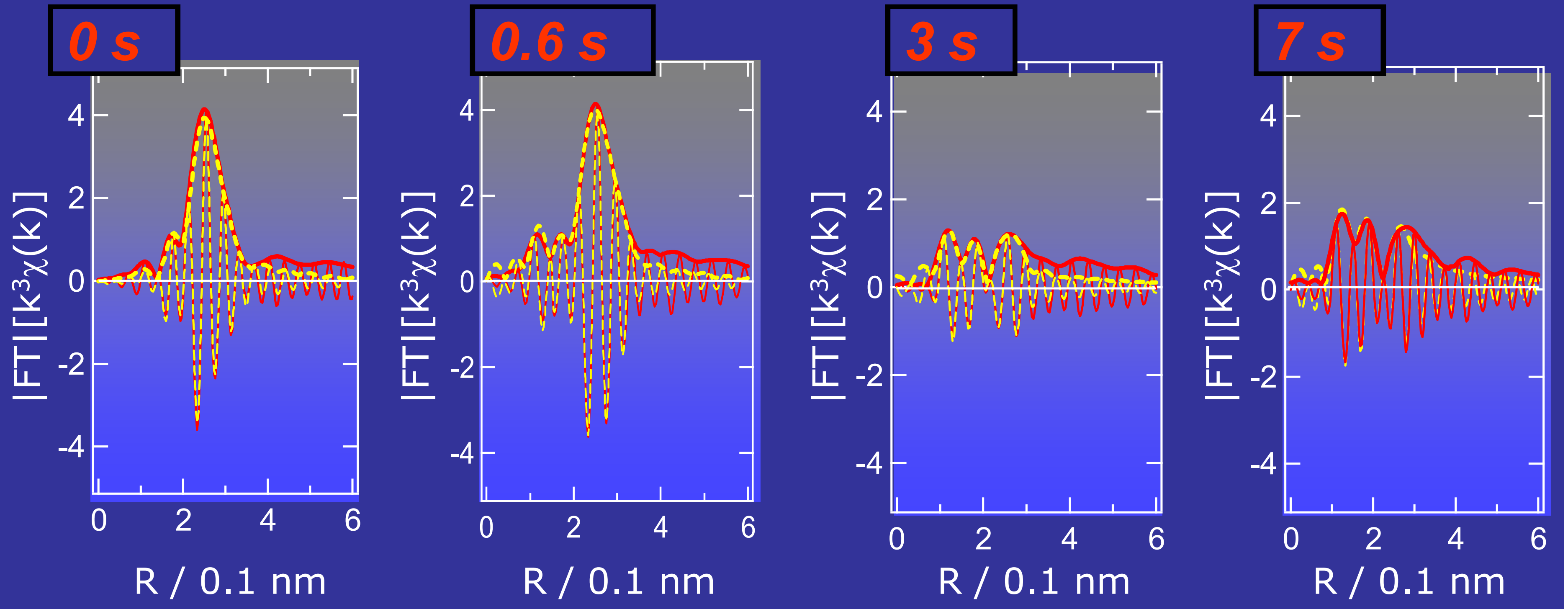
treatment	Rh–Rh N	Rh–Rh R (Å)	Rh–Rh $\Delta\sigma^2 \times 10^2$ (Å^2)	Rh–O N	Rh–O R (Å)	Rh–O $\Delta\sigma^2 \times 10^2$ (Å^2)	Rh–CO N	Rh–CO R (Å)	Rh–CO $\Delta\sigma^2 \times 10^2$ (Å^2)
reduction at 593 K	3.7	2.68	0.5	1.9	2.74	0.0			
reduction at 593 K, evacuation at 593 K, CO admission at 298 K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

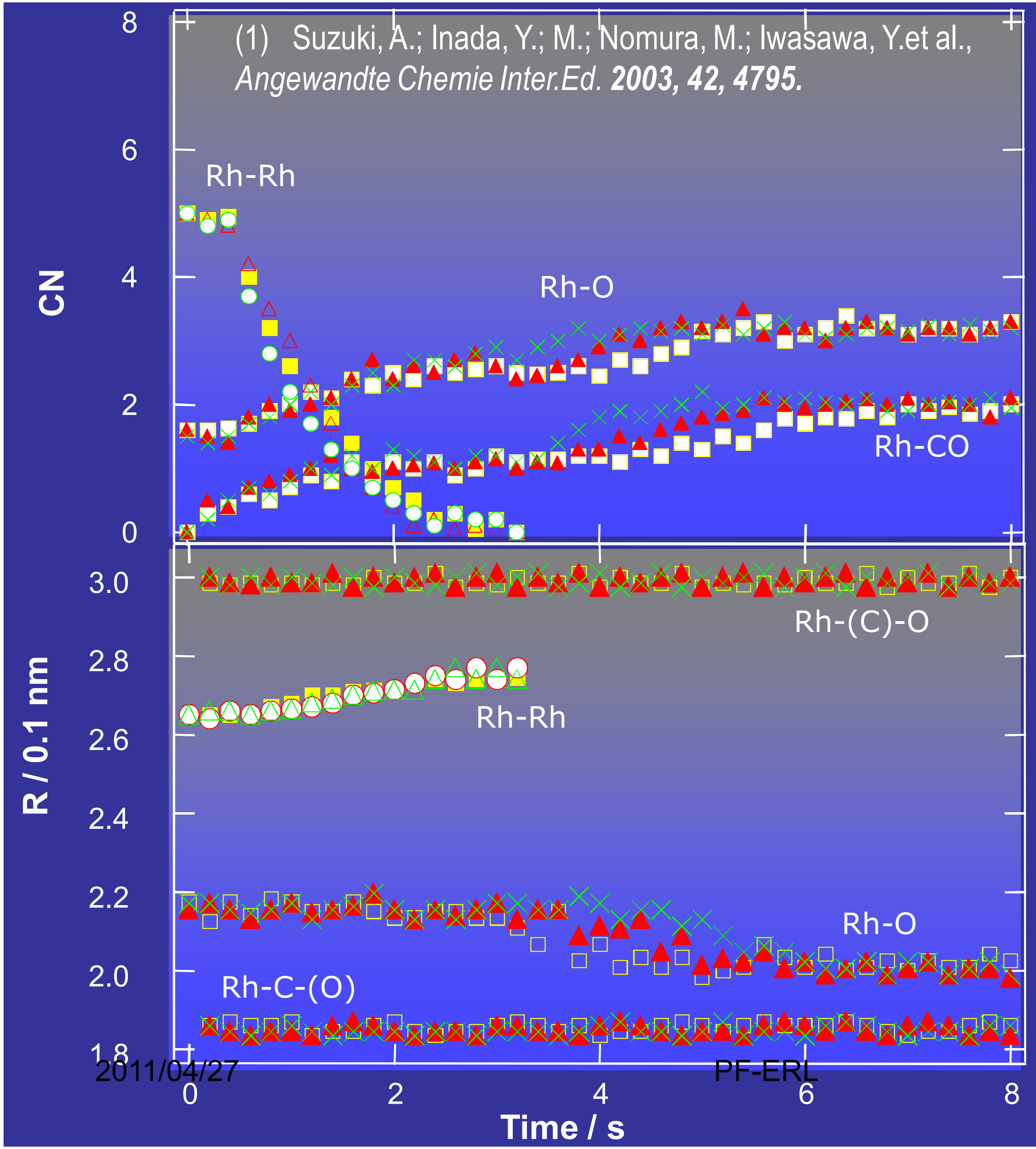
[a] Accuracies: N, ±15%; R, ±1%; $\Delta\sigma^2$, ±15%.

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.

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

(1) Suzuki, A.; Inada, Y.; M.; Nomura, M.; Iwasawa, Y.et al.,
Angewandte Chemie Inter.Ed. ***2003, 42, 4795.***





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

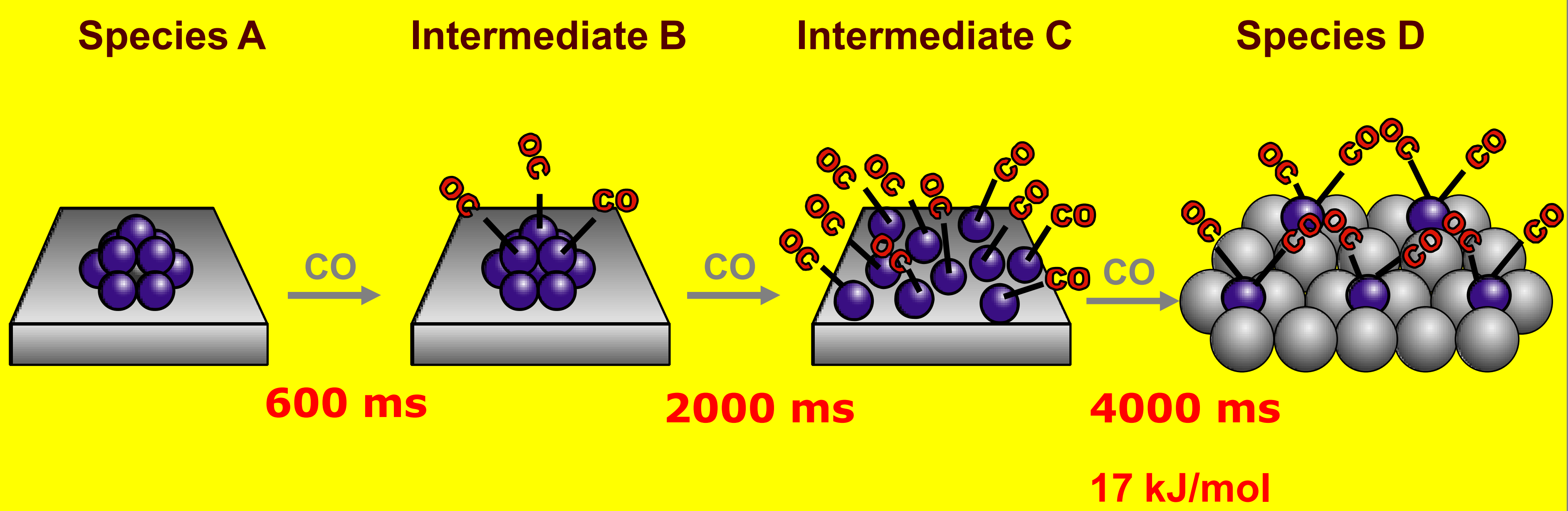
298 K

333 K

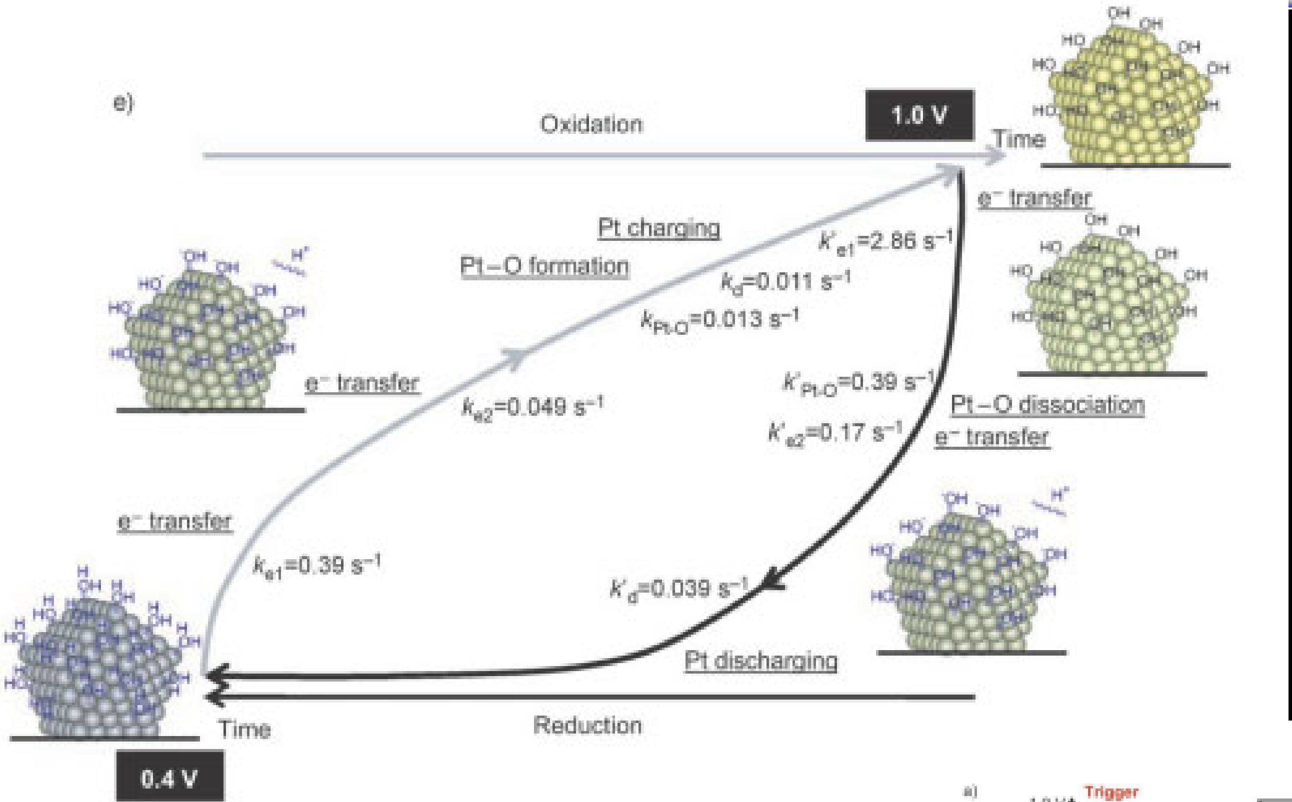
353 K

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

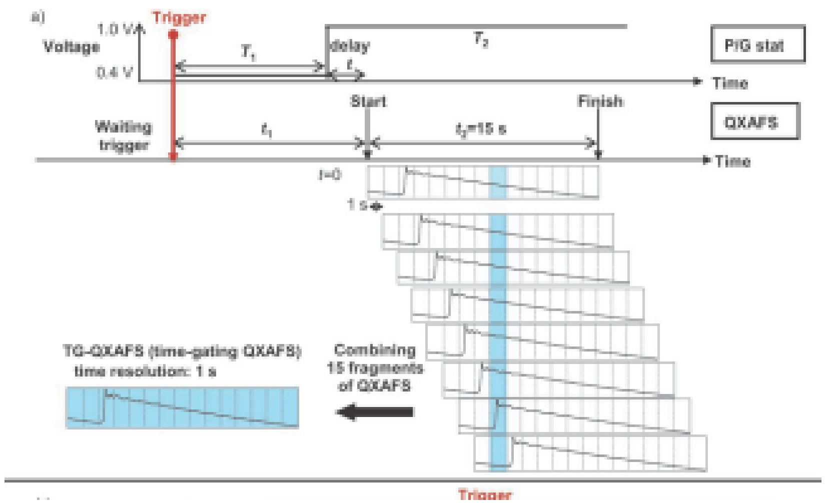
(1) Suzuki, A.; Inada, Y.; M.; Nomura, M.; Iwasawa, Y.et al. *Angewandte Chemie Inter.Ed.* ***2003, 42, 4795.***



Electrochemical trigger

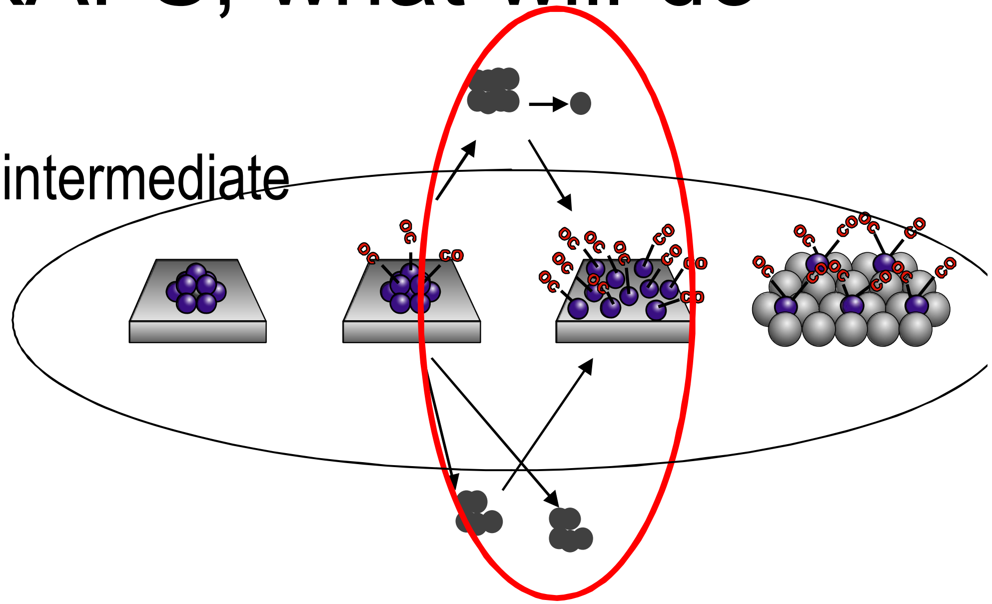


Tada, M., S. Murata, et al. (2007). Angewandte Chemie-International Edition **46(23): 4310-4315.**



IF we have faster XAFS, what will do we obtain?

μs-s → Reaction intermediate

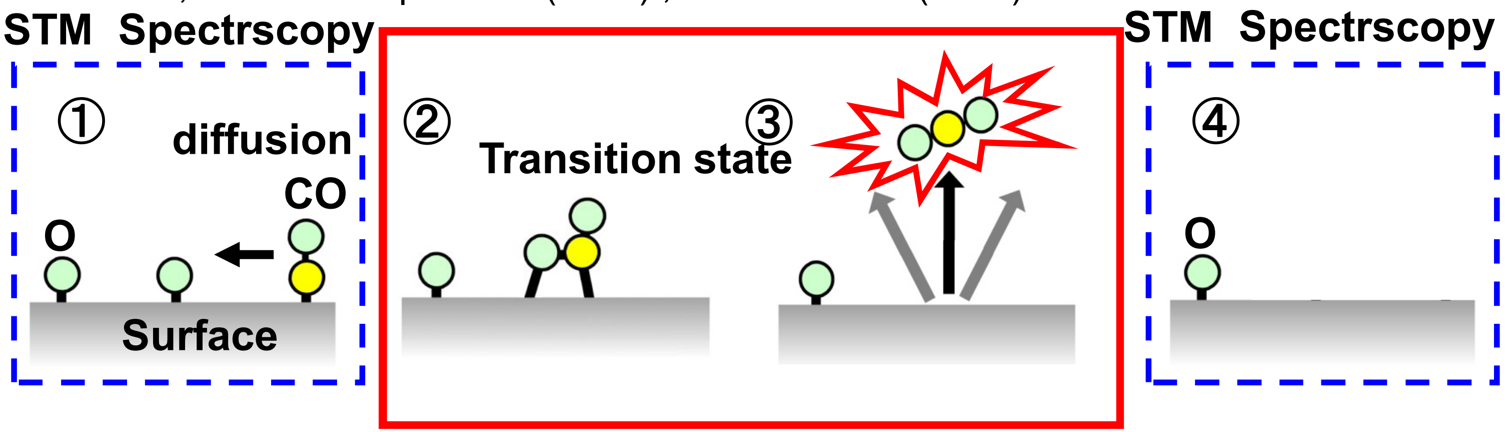


ps-ns → Atomic Dynamics

at-fs → Electron Dynamics

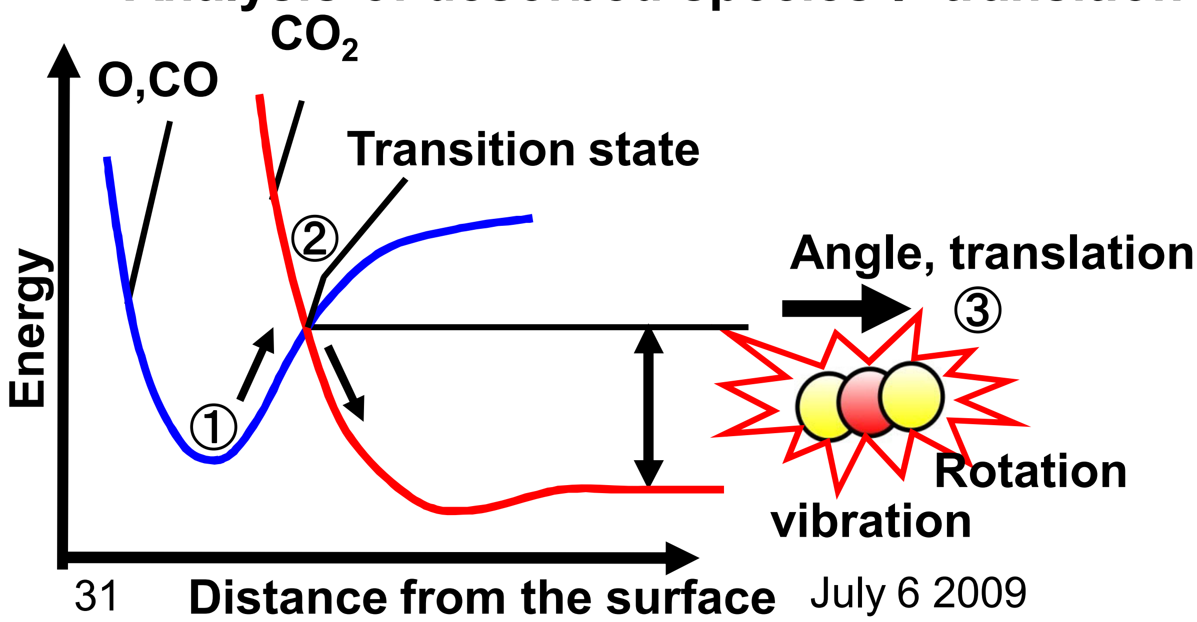
Spectroscopy and desorption analysis

T. Matsushima, Surf. Sci.Reports 52 (2003) ; Surf. Sci. 603 (2009) 1415.



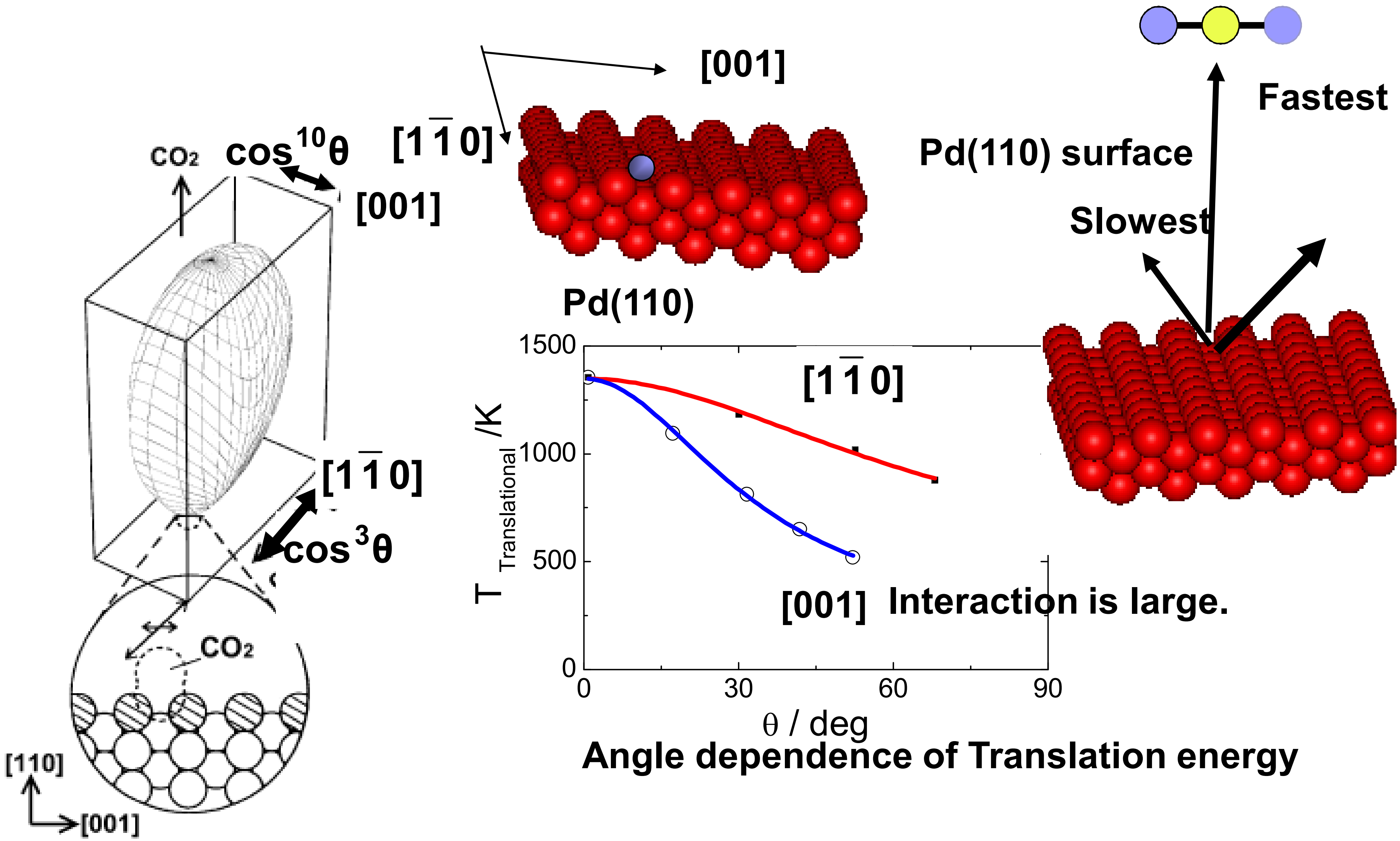
Repulsive desorption → No equillibrium and information after reaction is maintained.

Analysis of desorbed species→ transition state information



CO_2 Desorption profile during CO +O reaction

T. Matsushima, Surf. Sci.Reports 52 (2003) ; Surf. Sci. 603 (2009) 1415.

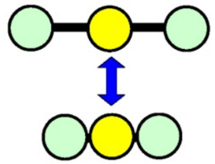


IR Emission

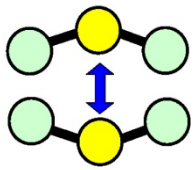
K. Nakao, K. Kunimori, et al. Catalysis Letters **85** (2003) 213; K. Nakao, K. Kunimori et.al., Catalysis Today **111** (2006) 316.

vibrational

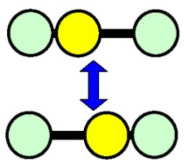
s mode **Symmetric stretch**



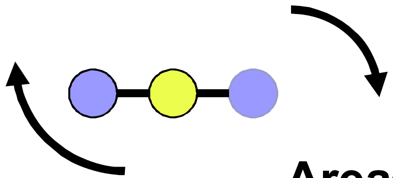
b mode **Bending**

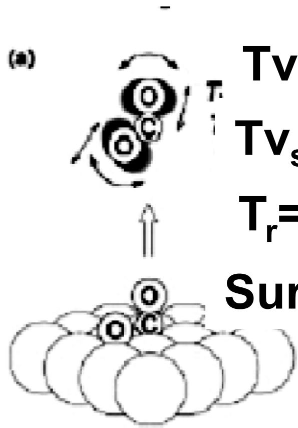


a mode **Antisymmetric stretch**



rotation





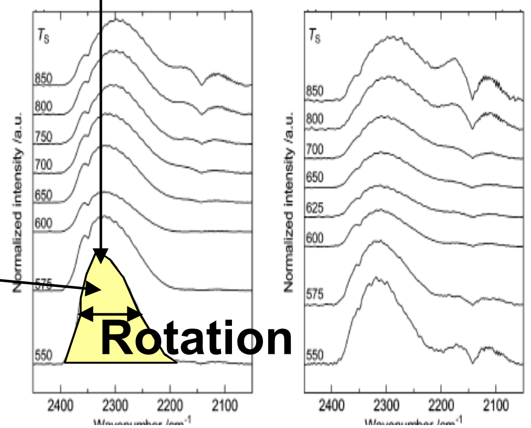
Tv_a=2090 K

Tv_{sb}=2200 K

T_r=1000 K

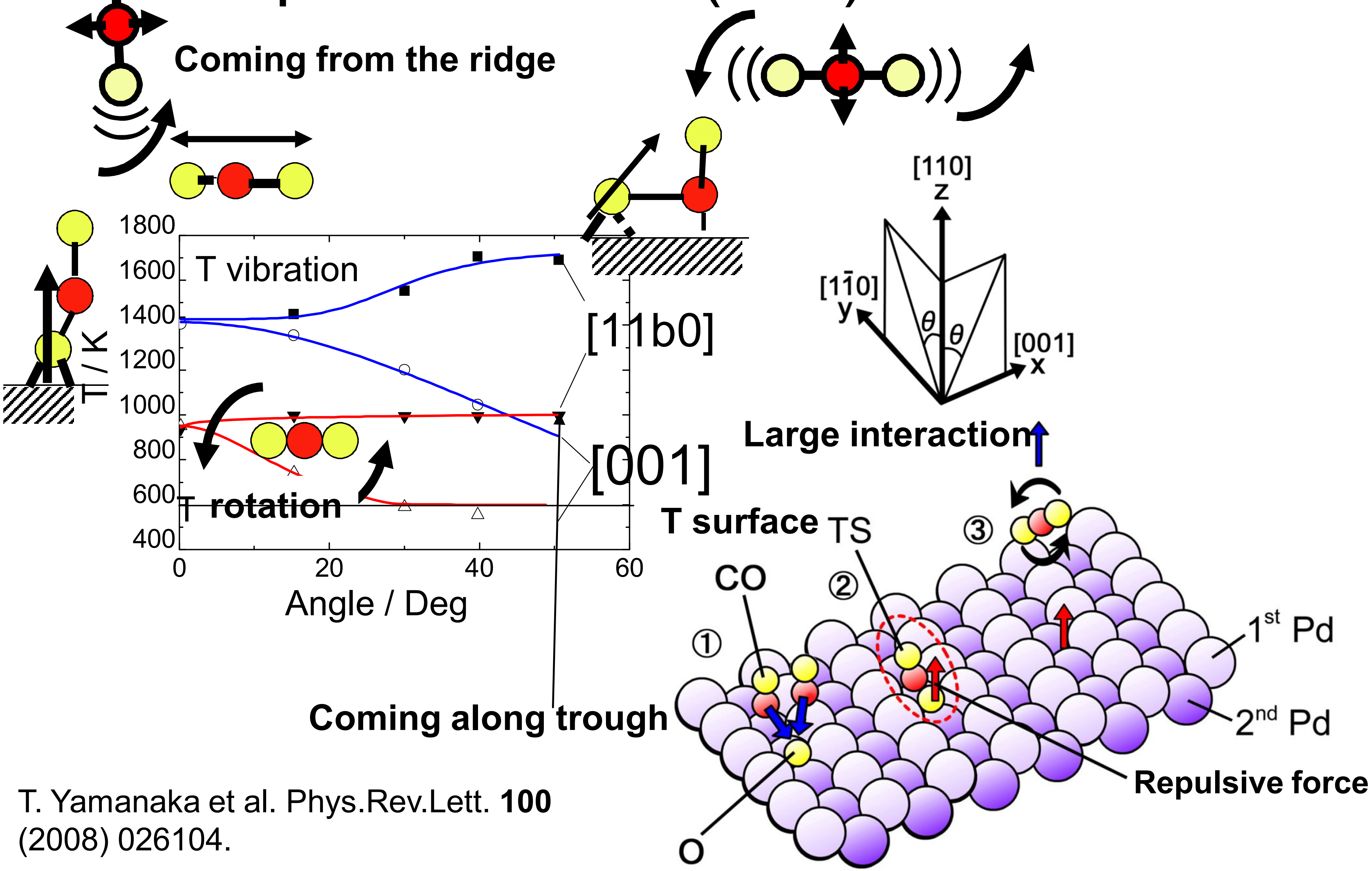
Surface temp=850 K

Position→ average of s and b



IR emission from desorbed CO_2 from Pd(111) with dirrerent surface temperatures

Desorption from Pd(110)

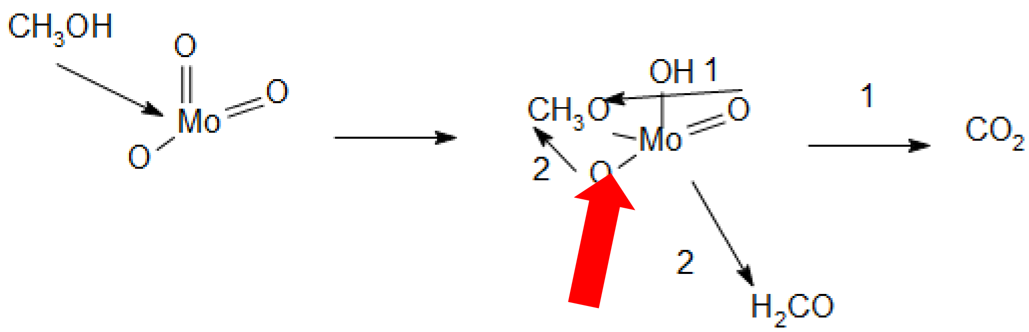


T. Yamanaka et al. Phys.Rev.Lett. **100** (2008) 026104.

Mmechanical catalyst

Gerhard Swiegers

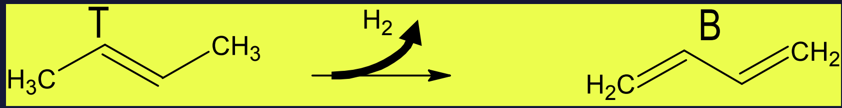
- Energy –control to timing- control

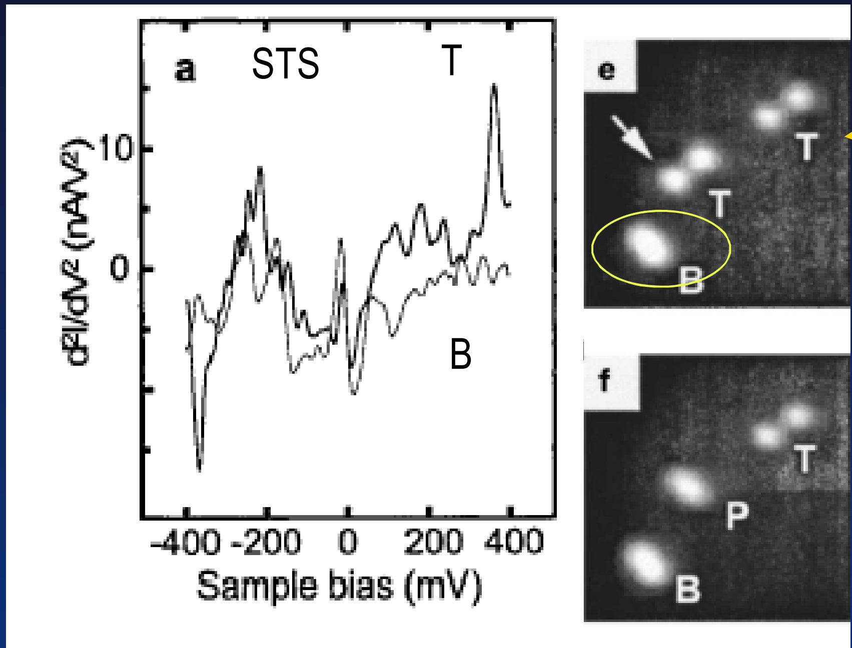


Selective excitation

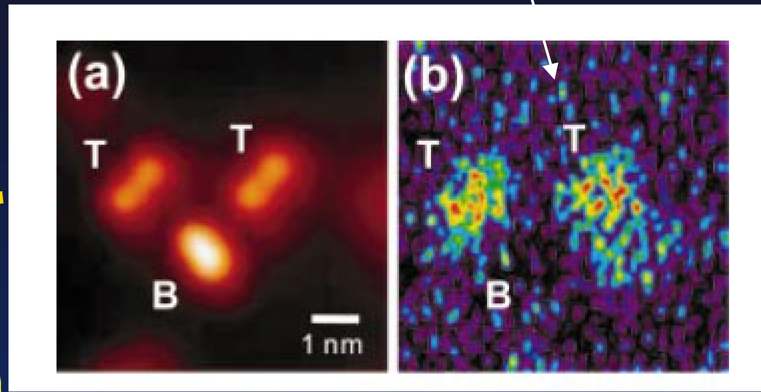
- Perfect Catalyst
  - 100 % acitivity, 100 % selectivity, Self-recovery(long life time)
  - Like Enzyme

Reaction induced by STM on Pd(110)

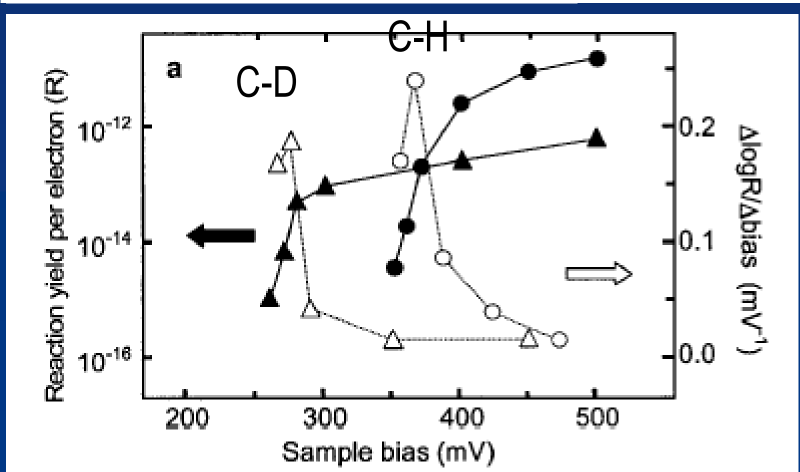




-360 mV dI2/dV2 image



Y. Sainoo, Y. Kim, M. Kawai, J. Chem. Phys.120 (2004) 7249.

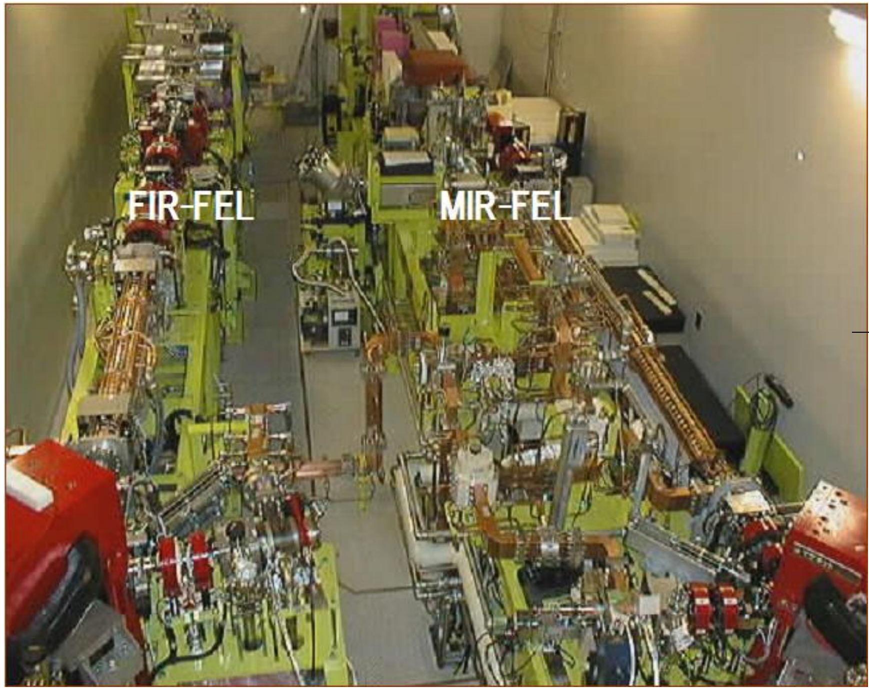


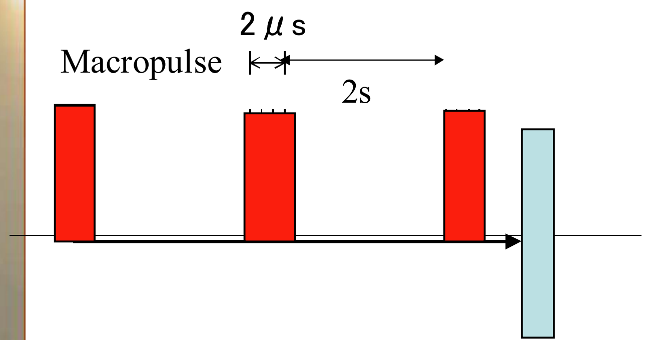
Dosing tunneling current on
7 nA, 450 mV, 1sec
—C-H excitation.

Y. Kim, M. Kawai, et. al.
PhysRev. Lett. 89 (2002) 126104.

FEL-IR-selective excitation of chemical bond

H. Kuroda,et.al. Free Electron Lasers 2002, 2003, pp. II.



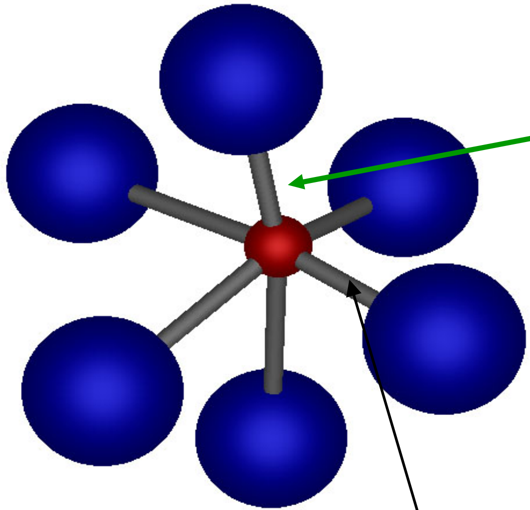


1. If one can use a strong **pulse source with long interval**, one irradiates the sample without heating the sample.

Ethanol decomposition reaction on MoO_3 induced by Pulse IR

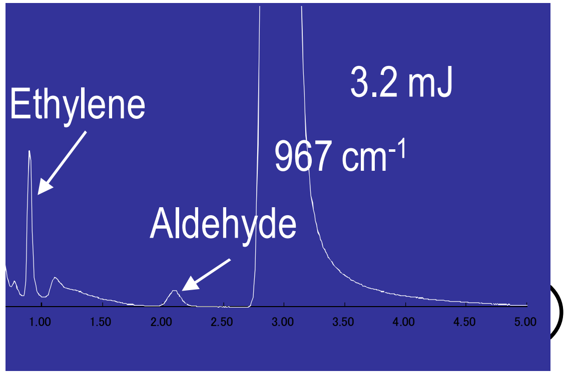
S.Sato, M.G.Moula Jpn.J.Appl.Phys. 41-1 (2002) 118; Chem.Lett 33 (2004) 558; Bull.Chem.Soc.Jpn., 81 (2008) 836.

C2H5OH → CH3CHO, CO2, C2H4

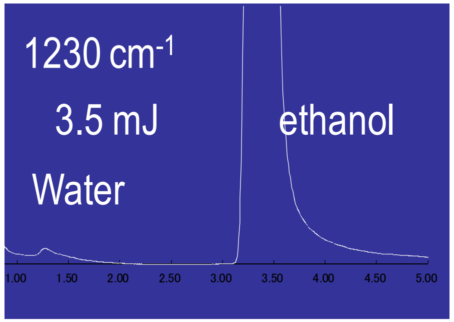


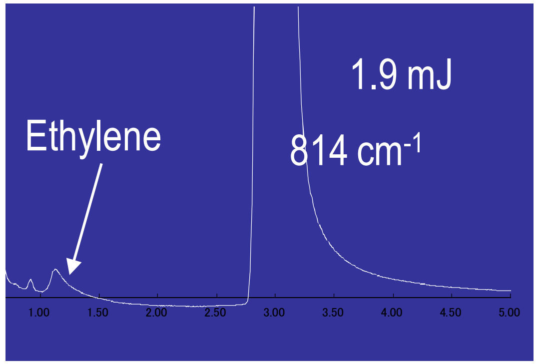
0.167 nm(967 cm^{-1})

0.173 nm(814 cm^{-1})



No resonance





Problems are

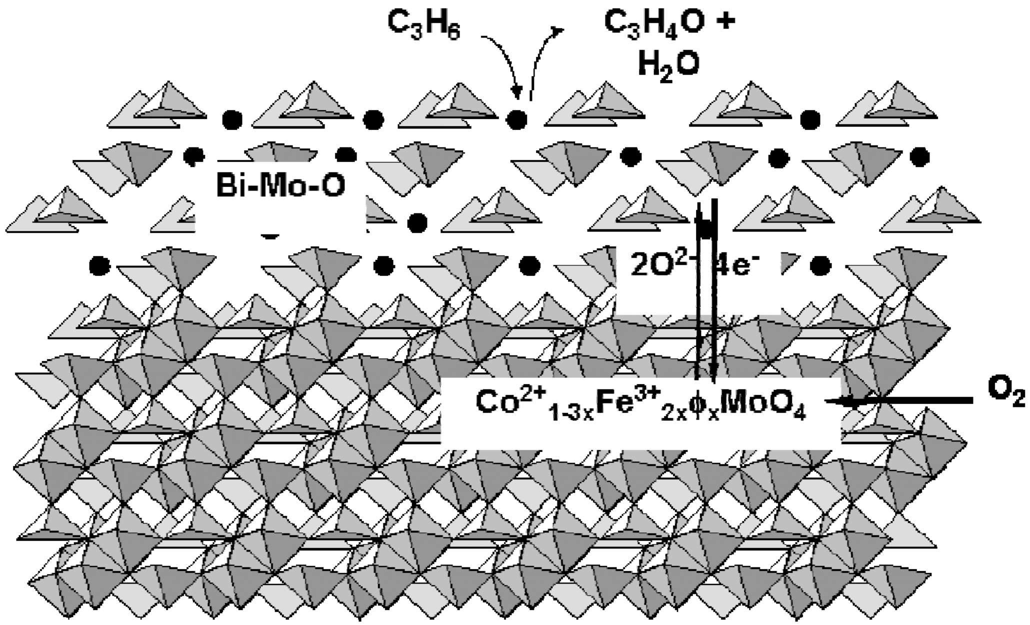
- How to control inhomogeneity of Catalysis
  - Time scale and Spatial scale.
  - Chaotic reaction process
  - Single shot

CO oxidation reactions on Pt(100)

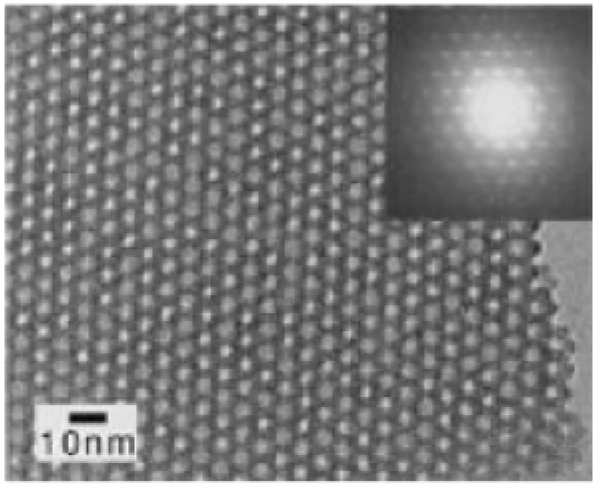
Surface is well-defined single crystal

Real catalysts are complicated

- Multifunctional
- Porus



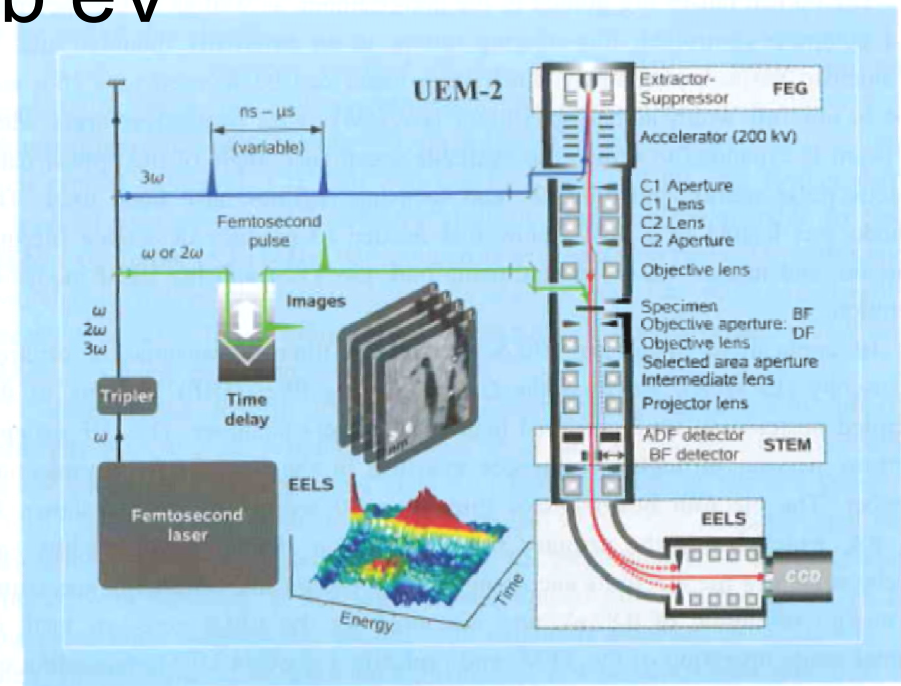
Moro-oka, Y. and W. Ueda (1994) Advances in Catalysis **40: 233.**



Kapoor, M. P.; Inagaki, S. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1463.FSM-16

4D (Time + spatial resolution) + spectroscopy

- Å ─mm の広いダイナミックレンジ
- ps- ms
- sub eV



Conclusions

- Ultra fast will help us understand the atom dynamics of surfaces
- Ultrafast monitoring may be helpful to control the surface reaction
- 4D is necessary to apply the ultarafast technique to catalysts.