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共同利用共同研究公募中　1／6締め切り
http://www.cat.hokudai.ac.jp/r2_kyoten.html

In situ XAFS in Catalysis – merit, demerit and measurement.

Kiyotaka Asakura
Institute for Catalysis, Hokkaido University, Sapporo, Japan

Scope

Physical Chemistry Chemical Physics (PCCP) is an international journal for the publication of cutting-edge original work in physical chemistry, chemical physics and biophysical chemistry. To be suitable for publication in *PCCP*, articles must include significant innovation and/or insight into physical chemistry; this is the most important criterion that reviewers and the Editors will judge against when evaluating submissions.

The journal has a broad scope which includes spectroscopy, dynamics, kinetics, statistical mechanics, thermodynamics, electrochemistry, catalysis, surface science, quantum mechanics and theoretical developments. Interdisciplinary research areas such as polymers and soft matter, materials, nanoscience, energy, surfaces/interfaces, and biophysical chemistry are welcomed if they demonstrate significant innovation and/or insight into physical chemistry.

In situ(その場）and operando （反応中）　in-operandoは誤用

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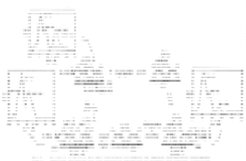
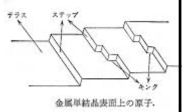
https://youtu.be/ugzqLxiOISM?t=11



反応が起こっているところの構造



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3

なぜXAFS?

高い透過力があること

　　ガス共存下での測定が可能

濃度が低くても測定できる。

アモルファスも**OK**

　　Photon –in Photon Out

様々なオペランド手法

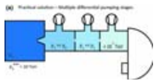
　赤外、**Raman,**可視紫外

　NMR,ESR（ただし本当のフローは難しい）

　XPS（窓、差動排気）

　TEM(窓、差動排気）

　反応物解析、**TAP**



Ambient pressure XPS

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Operando XAFS

まさに反応中の構造を知ることができる。

過渡応答・振動反応なら、時間分解能が必要とされる。

　QXAFS,DXAFS

定常条件なら、

Demerit

解析が複雑。

ガス漏れ、爆発など注意が必要。

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高時間分解能

Step Scan XAFS　　10min

Quick XAFS　　　　ms－s

透過法、蛍光法、など様々な手法に対応、

DXAFS　　　　　　マイクロs-s

透過法のみ、

サンプルの均一性を要求する

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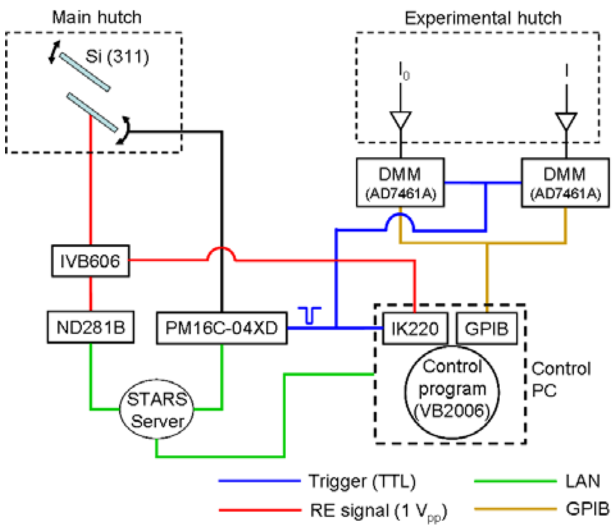
QEXAFS

A technique that can measure one EXAFS spectrum in a short time (a few seconds in our system) by sampling signals from ionization chambers and monochromator continuously with scanning the monochromator (on the fly).



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Change during the reduction.

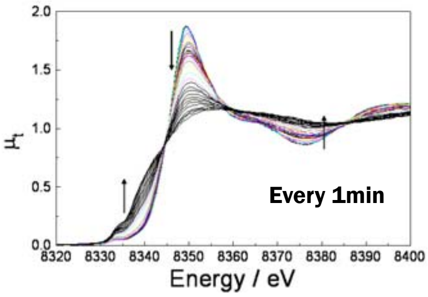
7

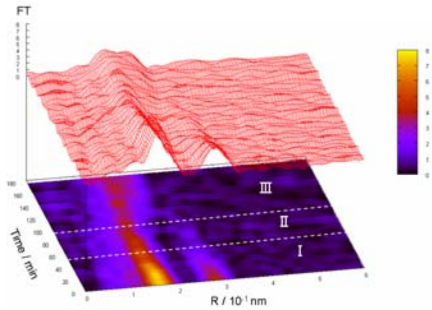
Slow but high quality and Fluorescence XAFS is applicatble.

1 K. K. Bando, Y. Koike, T. Kawai, G. Tateno, S. T. Oyama, Y. Inada, M. Nomura, K. Asakura, *J. Phys. Chem. C* 2011, 115, 7466-7471 10.1021/jp11657z.

XANES

Every 1min





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QXAFS Studies in SP8 (2004-)

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1. K. Okumura, K. Yoshino, K. Kato and M. Niwa, *Quick XAFS studies on the Y-type zeolite supported au catalysts for CO-O-2 reaction. J Phys Chem B.* ***109,12380-12386(2005).***

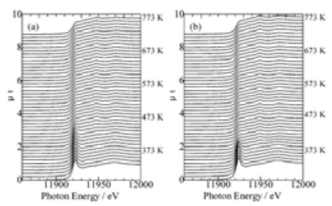

Figure 2. Au L_3-edge XANES of 5 wt % Au loaded on (a) H−Y and (b) Na−Y zeolite measured in a 10% H_2 flow. Temperature ramping rate, 5 K min^{-1}.

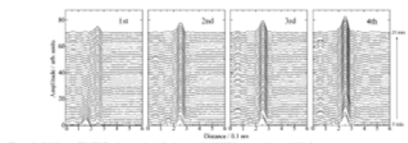

Figure 2. Pd K-edge EXAFS Fourier transforms for 0.4 wt % Pd/H-USY measured in an 8% H_2 flow.

K. Okumura, T. Honma, S. Hirayama, T. Sanada and M. Niwa, *Stepwise Growth of Pd Clusters in USY Zeolite at Room Temperature Analyzed by QXAFS. J.Phys.Chem.C.* ***112,16740-16747(2008).***

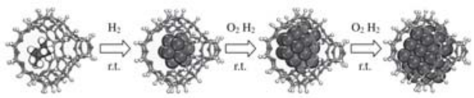

Fig. 1. Stepwise growth of Pd clusters in the supercage of USY zeolite.

K. Okumura, T. Honma, S. Hirayama, T. Sanada and M. Niwa, *Stepwise Growth of Pd Clusters in USY Zeolite at Room Temperature Analyzed by QXAFS. J.Phys.Chem.C.* ***112,16740-16747(2008).***

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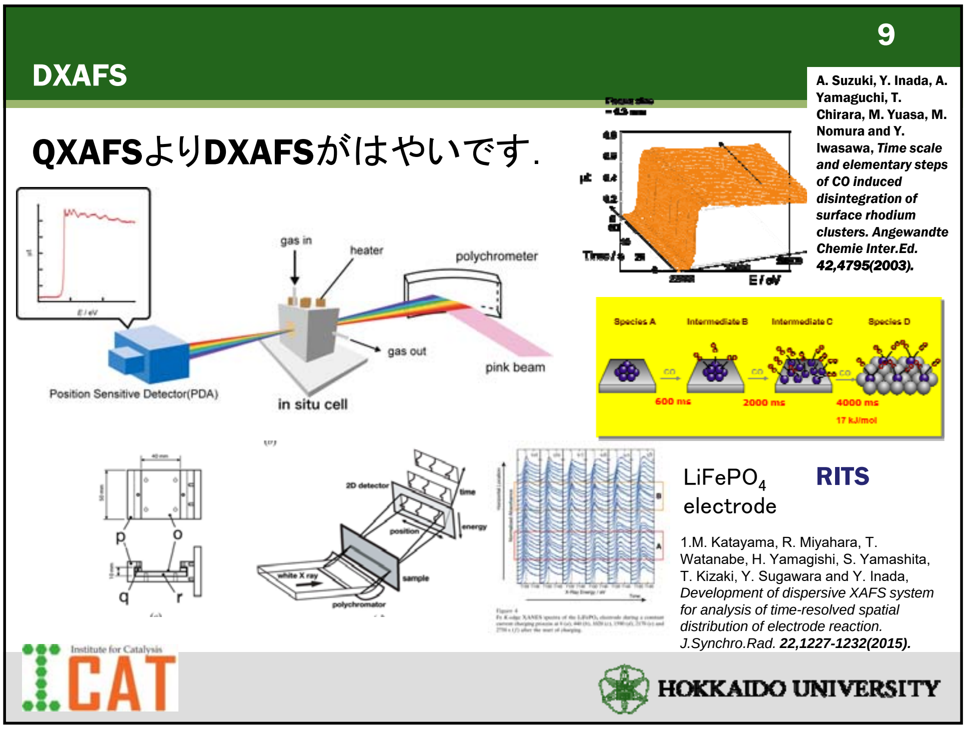
9
DXAFS
QXAFSよりDXAFSがはやいです.
gas in
heater
polychrometer
gas out
pink beam
Position Sensitive Detector(PDA)
in situ cell
A. Suzuki, Y. Inada, A. Yamaguchi, T. Chirara, M. Yuasa, M. Nomura and Y. Iwasawa, Time scale and elementary steps of CO induced disintegration of surface rhodium clusters. Angewandte Chemie Inter.Ed. 42,4795(2003).
E / eV
Species A
Intermediate B
Intermediate C
Species D
600 ms
2000 ms
4000 ms
17 kJ/mol
2D detector
white X ray
sample
polychromator
LiFePO4 electrode
RITS
1.M. Katayama, R. Miyahara, T. Watanabe, H. Yamagishi, S. Yamashita, T. Kizaki, Y. Sugawara and Y. Inada, Development of dispersive XAFS system for analysis of time-resolved spatial distribution of electrode reaction. J.Synchro.Rad. 22,1227-1232(2015).
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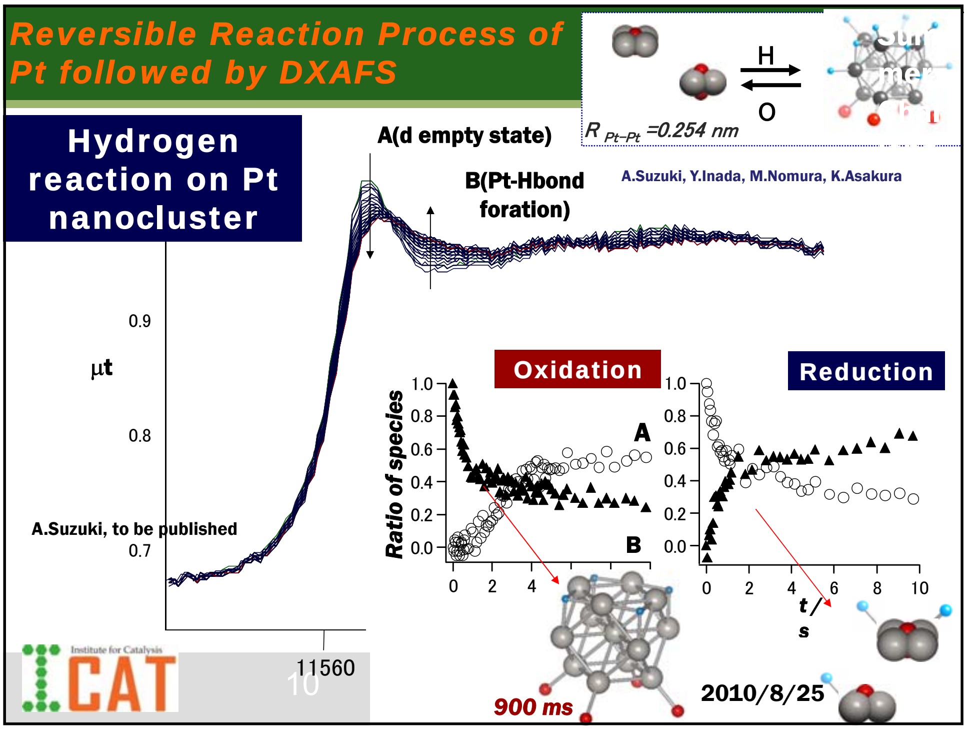
Reversible Reaction Process of Pt followed by DXAFS
H
O
R Pt-Pt =0.254 nm
Hydrogen reaction on Pt nanocluster
A(d empty state)
B(Pt-Hbond foration)
A.Suzuki, Y.Inada, M.Nomura, K.Asakura
0.9
μt
0.8
A.Suzuki, to be published
0.7
11560
Oxidation
Reduction
Ratio of species
A
B
t / s
900 ms
2010/8/25
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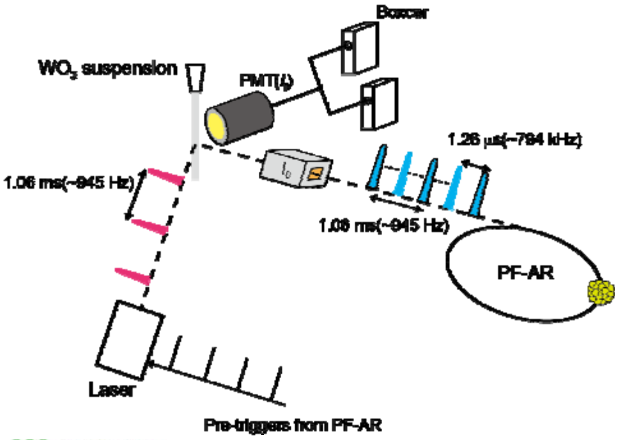
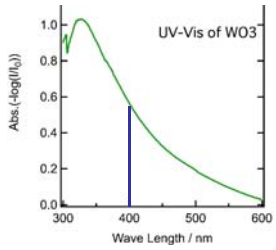
Pump Probe XAFS setup for Photocatalyst

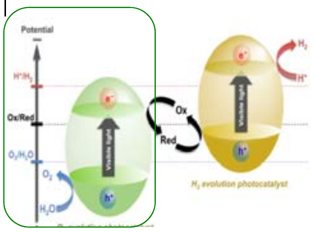
Honda-Fujishima effect

可視光応答型光触媒

Sample: 0.6 mM WO_3 suspension
pump laser: 400 nm 270 mJ/cm^2@945 Hz
X-ray pulse width: 100 ps(FWHM)







J. Synchrotron Radiat. 2007, 14, 313.
J. Synchrotron Radiat. 2009, 16, 110.

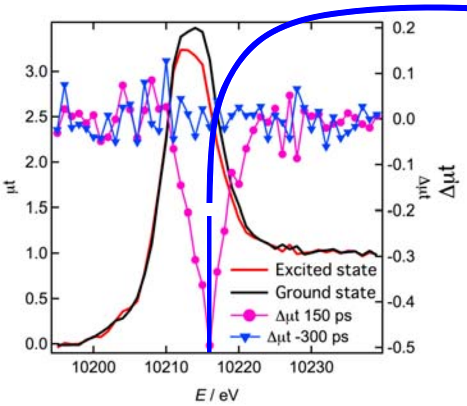
R. Abe, et. al. *J. Am. Chem. Soc.* **2008, 130, *7780-7781***

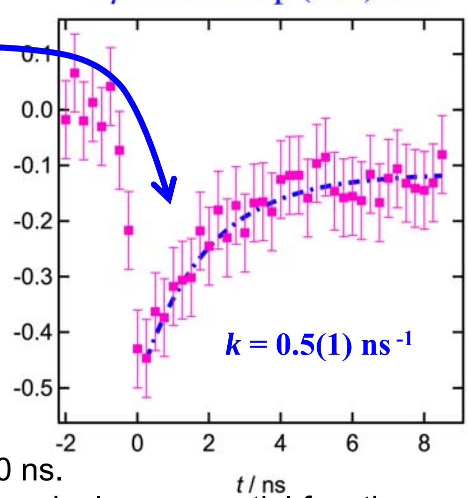
through two-step photoexcitaion

Decay of X-ray absorption

Uemura, Y.; Uehara, H.; Niwa, Y.; Nozawa, S.; Sato, T.; Adachi, S.; Ohtani, B.; Takakusagi, S.; Asakura, K. *Chem. Lett.* ***2014, 43 977.***

$$\Delta\mu t = A \cdot \exp(-kt) + B$$





The excited state decayed in 10 ns.
→It was successfully fitted with a single exponential function.

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Assignment

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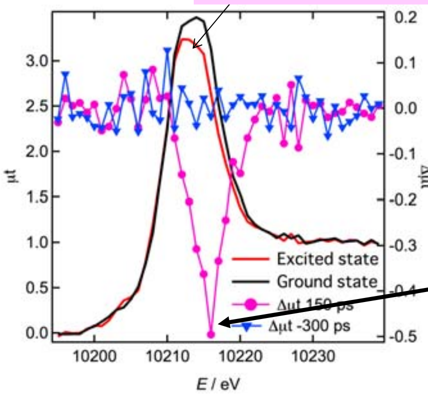
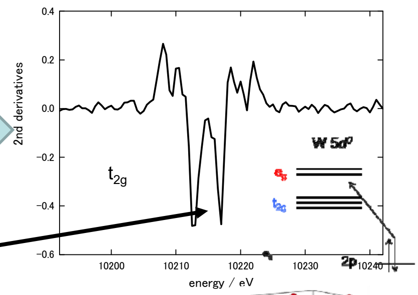
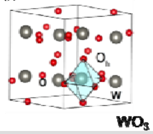
White line
This is a dipole transition from 2p3/2 to 5d state.
Intensity is related to 5d empty state.
If 5d is occupied, white line decreases.
Low valence gives smaller white line





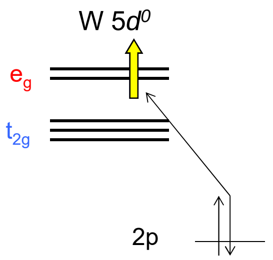
2nd derivative

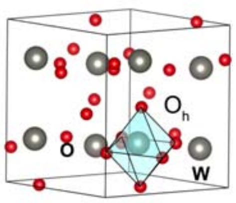


Eg orbitals are occupied by excited electron

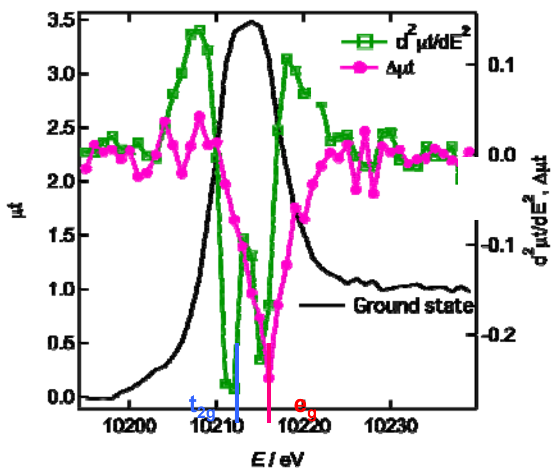
Photoexcited State of WO_3 : L_{III} XANES

Uemura et al. *Chem. Lett.* **2014**, 43, 977-979





WO_3



Oxygen 2p is excited to 5d eg ortbital not the bottom of d band

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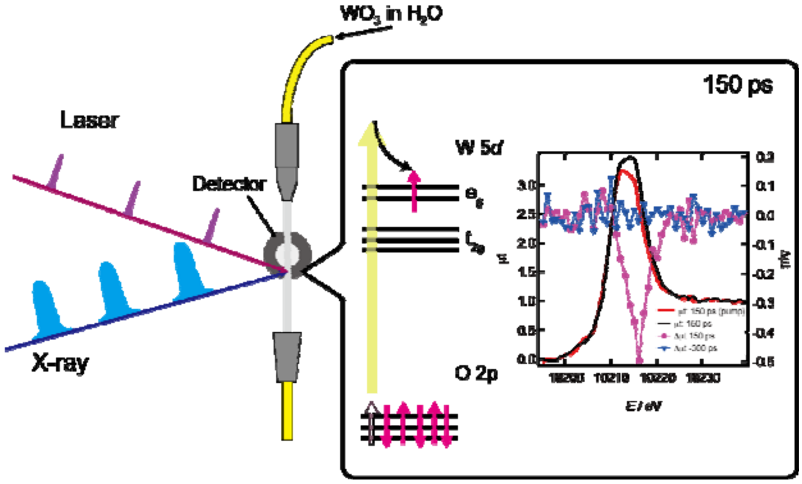
Conclusions from XANES



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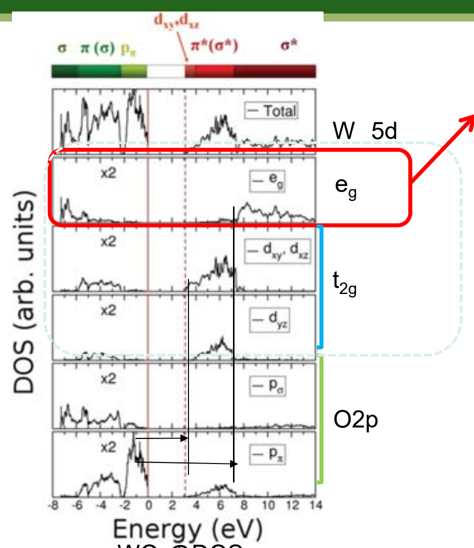
Is it possible to excite the electron to e_g?



WO_3のDOS

Energy is necessary
>6.0 eV!!

Excitation energy of laser
3 eV

F. Wang, C. D. Valentin, G. Pacchioni, *J. Phys. Chem. C.* **2012**, *116*, 8901

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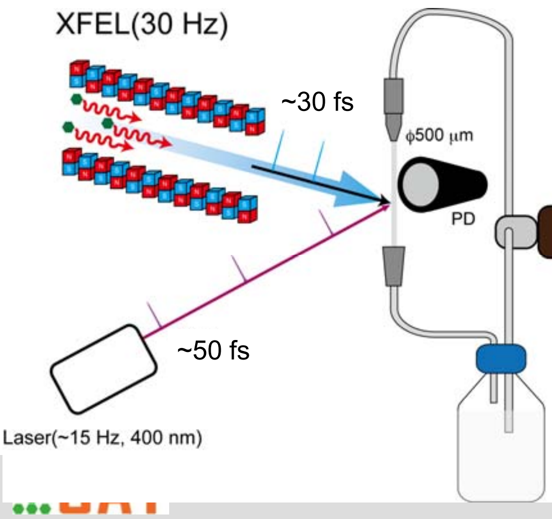
SACLA : X-ray Free Electron Laser

Experiments at SACLA



Sample: 4 mM WO_3 suspension
pump laser: 520 mJ/cm^2@15 Hz
X-ray pulse width: 30 fs(FWHM)
Time resolution: 700 fs

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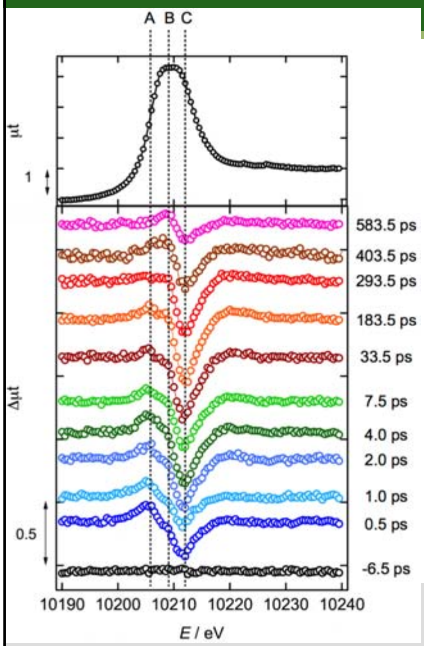
Photoexcitation of WO_3 : XFEL

Uemura, Y.; Kido, D.; Wakisaka, Y.; Uehara, H.; Ohba, T.; Niwa, Y.; Nozawa, S.; Sato, T.; Ichiyanagi, K.; Fukaya, R.; Adachi, S.; Katayama, T.; Togashi, T.; Owada, S.; Ogawa, K.; Yabashi, M.; Hatada, K.; Takakusa, S.; Yokoyama, Y.; Ohtani, B.; Asakura, K. *Angew. Chem.Int.Ed* ***2016, 55, 1364.***



➡ Three distinct peaks were found in the differential spectra.

peaks A ,B, C : decrease of absorption from e_g orbitals ~ 200 ps

⬇

peak B which was not found in the previous experiments was observed.

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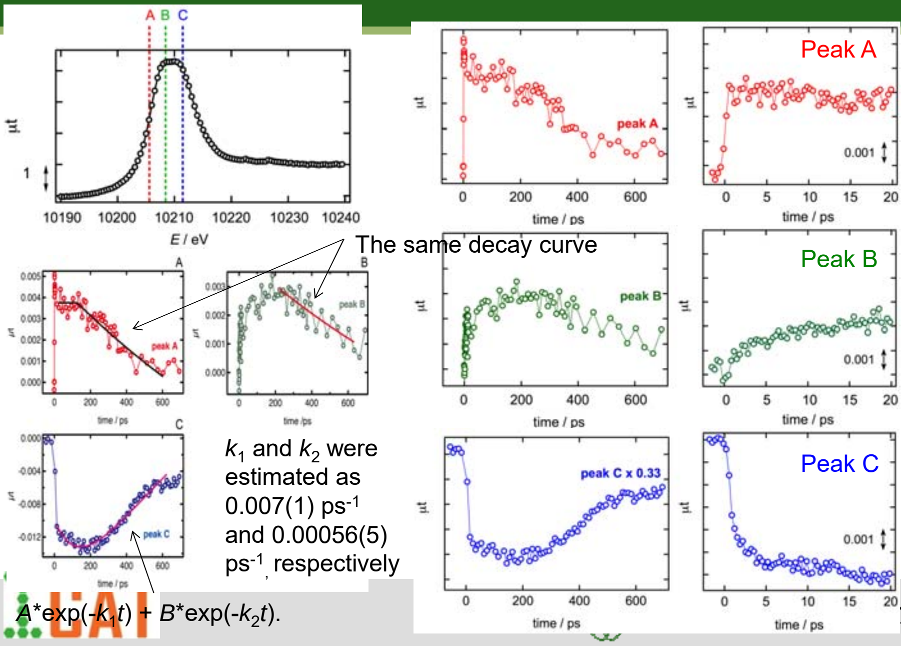
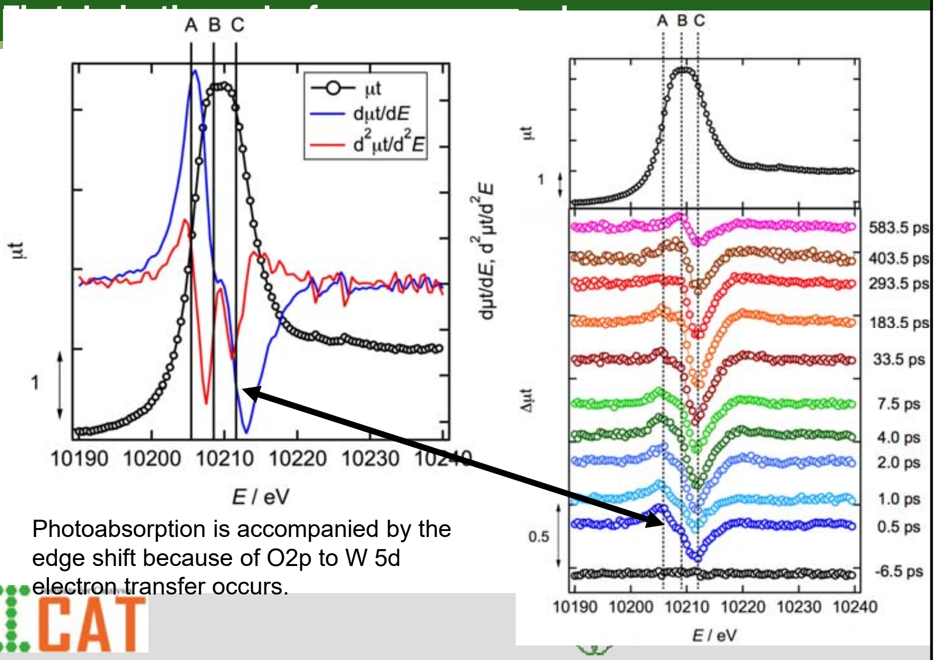
Changes of X-ray absorption at Peak A, B and C



k_1 and k_2 were estimated as 0.007(1) ps^{-1} and 0.00056(5) ps^{-1}, respectively

$A*\exp(-k_1 t) + B*\exp(-k_2 t)$.



Photoabsorption is accompanied by the edge shift because of O2p to W 5d electron transfer occurs.

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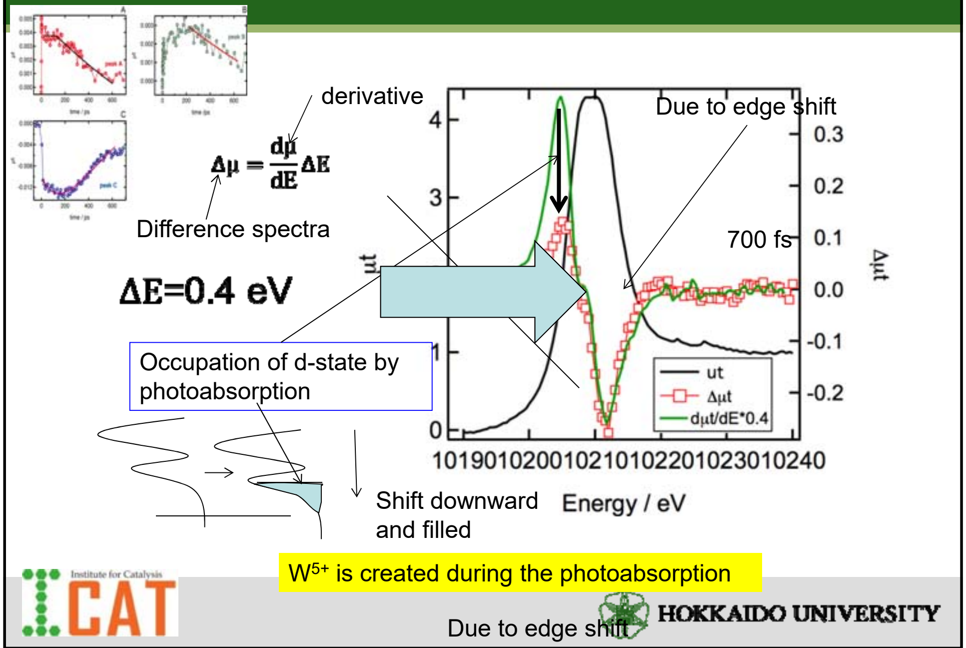
Comparison of derivative and difference spectra



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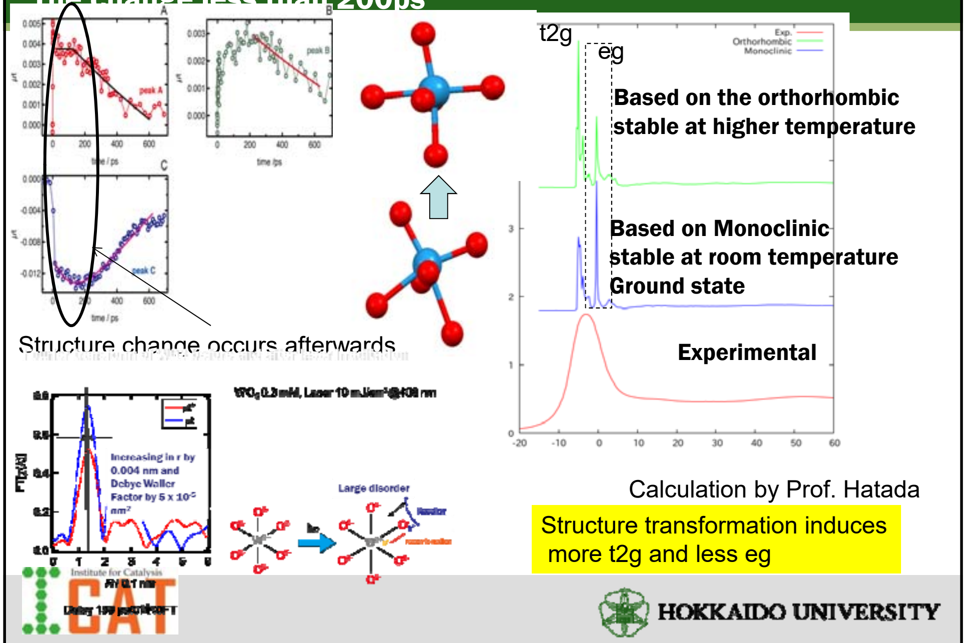
The change less than 200ps



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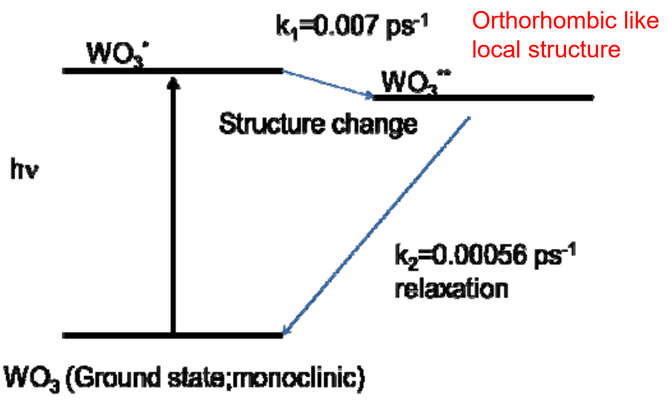
Scheme after the photoabsorption.



In situ EXAFS
principlple put window away from furnace.

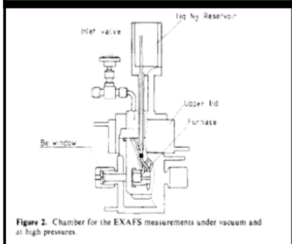
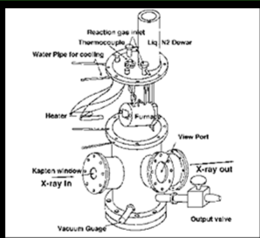
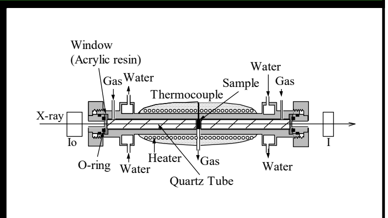


Figure 2. Chamber for the EXAFS measurements under vacuum and at high pressures.



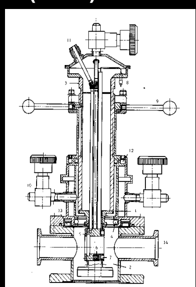


J.Synchro.Rad.8, 581(2001).

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

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

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



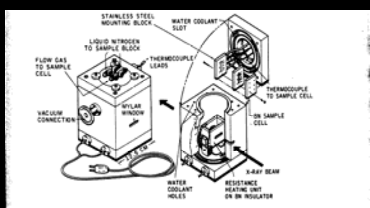


Figure 8.1. In situ cell of Lytle et al. (8).

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

Conversion reaction of methane to hydrocarbons.

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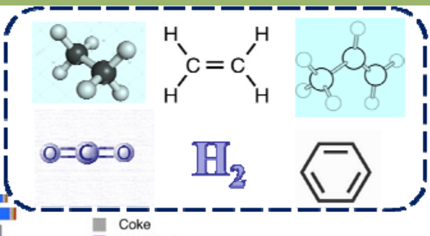
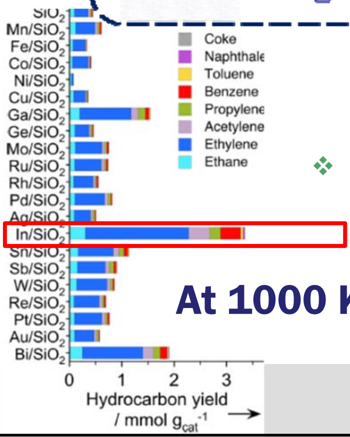
Methane





At 1000 K

Mo/HZSM-5	Wang et al. Catal. Lett. 21, 35 (1993)
Pt-SO_4/ZrO_2	Arata et al. J. Catal. 179, 28 (1998)
Single-site Fe/SiO_2	Bao et al. Science 344, 616 (2014)
In/SiO_2	Yamanaka et al. ChemistrySelect, 16, 4572 (2017)
Pt-Sn/HZSM-5	Dumesic et al. ACS Catal. 7, 2088 (2017)
Pt-Bi/ZSM-5	Verma et al. ACS Catal. 8, 2735 (2018)
Single-atom Pt/CeO_2	Wang et al. ACS Catal. 8, 4044 (2018)

❖ In/SiO_2 is a prominent catalyst for non-oxidative coupling of CH_4 [2].

1. Nishikawa, Y.; Ogihara, H.; Yamanaka, I., Liquid-Metal Indium Catalysis for Direct Dehydrogenative Conversion of Methane to Higher Hydrocarbons. ChemistrySelect 2017, 2 (16), 4572–4576.

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XAFS measurement cell

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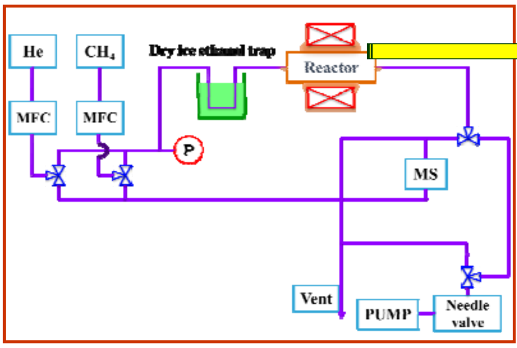

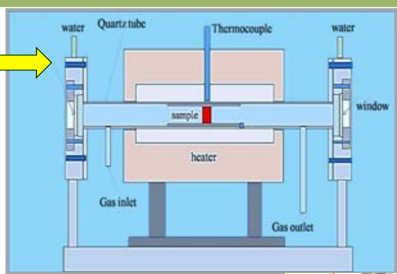

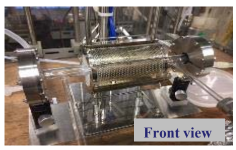

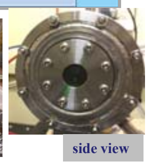

1. XAFS cell was made-up of quartz glass.
2. Resistance up to 1373 K even in H_2 or CH_4 gas flow.

Fabricated at Technical Division, Institute of Catalysis, Hokkaido University

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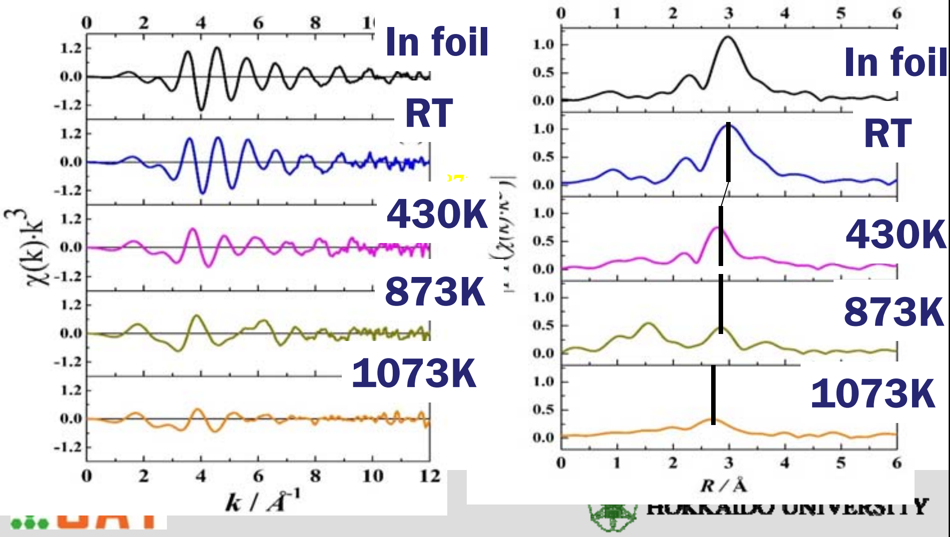
Activation process => Dynamic change occurs.

In catalysts are activated under the CH4 flow up to 1073 K



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Conclusions

❖ *In-situ* XAFS was used to identify the structural changes of In/SiO_2 during the activation process

At 300 K : In metallic particles

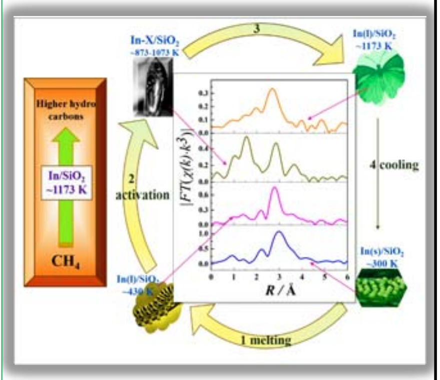
At 430 K : liquid In

At 873 K : In-X/SiO_2
In-X might be the Indium carbide

At 1073 K : In-X was disappeared and CO_2 appeared in QMS

At 1173 K : Fresh liquid In phase

Metamorphosis like



Kashaboina, U.; Nishikawa, Y.; Wakisaka, Y.; Sirisit, N.; Nagamatsu, S.; Bao, D.; Ariga-Miwa, H.; Takakusagi, S.; Inami, Y.; Kuriyama, F.; Dipu, A. L.; Ogihara, H.; Iguchi, S.; Yamanaka, I.; Wada, T.; Asakura, K. *Chem. Lett.* **2019, 48, 1145.**

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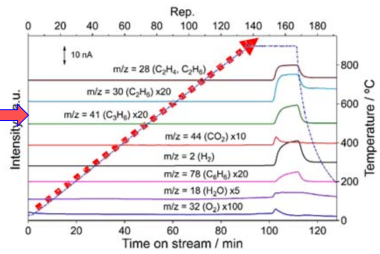
Activated under different conditions.

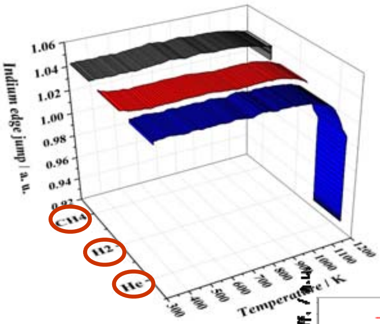
29

10wt% In/SiO_2 under CH_4 , H_2 and He flow activation

We increased the temperature with 10 K / min, from 300- 1173 K.

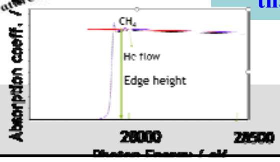
Temperature profile





- We found strong reduction of In K-edge jump in He flow activation.
- Reproduced 3 times.
- It indicates more In loss in He flow than that of others.

Edge jump of In K-edge



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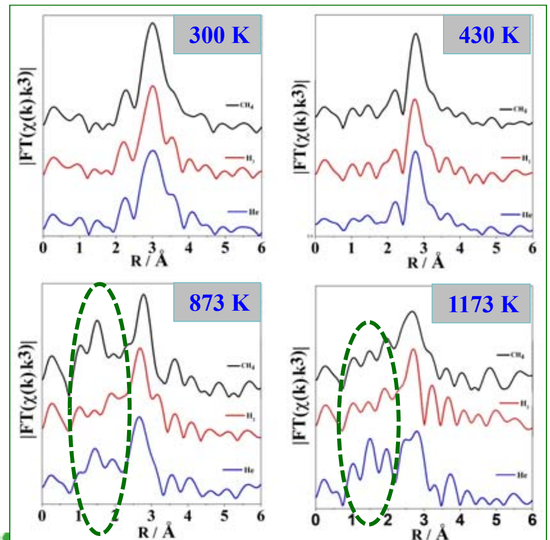
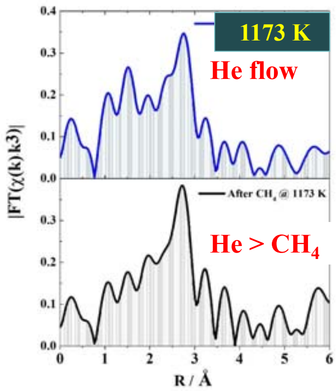
Fourier Transforms of k^3-weighted EXAFS

30



- Peak at 1.5 Å related to lighter element (O/C) attached to In.



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Hypothesis

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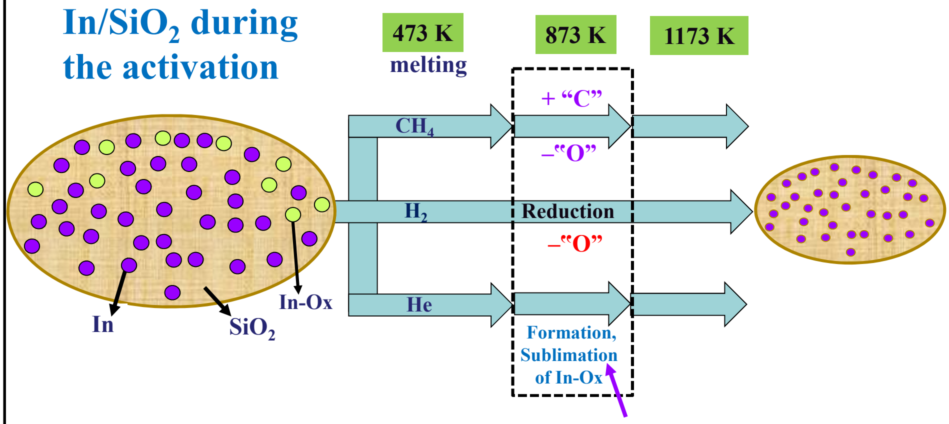
In/SiO_2 during the activation



Plausible pathway.. In2O3 is volatile at 1173 K (http://www.Americanelement.com)
Vapor pressure of In at 1173 K is 8 * 10-3 mbar.

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High pressure cell under high pressure gas.

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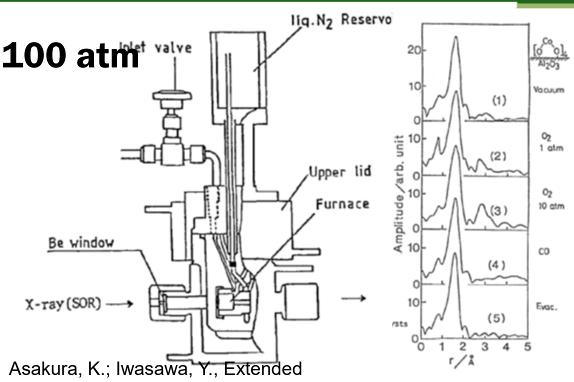
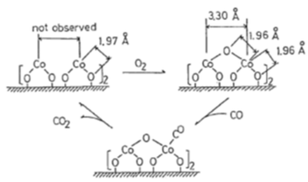
100 atm





Asakura, K.; Iwasawa, Y., Extended X-ray Absorption Fine Structure Studies on the Structure Change of the Al2O3-attached [CoII]4 Catalyst during a CO Oxidation Reaction. *J.Phys.Chem.* ***1989, 93, 4213-4218***

Cool down the windows so that we can use Be window or thick Plastic window

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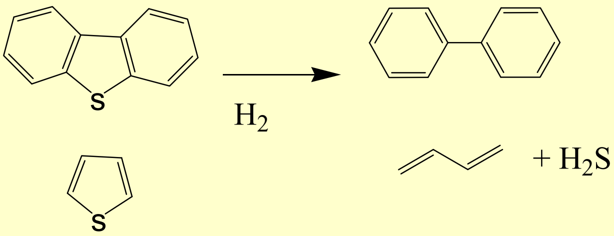
Hydrodesulfurization(HDS) catalyst

Oyama, S. T.; Wang, X.; Lee, Y.-K.; Chun, W.-J. *J.Catal* *2004, 221, 263.*

It removes sulfur compounds from fossil fuel.



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

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高温高圧に耐える窓材は？

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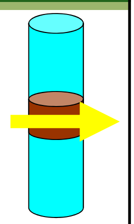
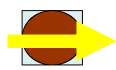
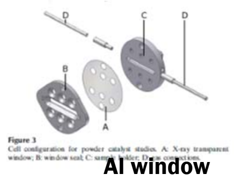
Demands are “window materials must stand for high pressure and high temperature at the same time”.

- **Capillary cells**
  - **But curved window causes thickness effects**
- **Diamond, Be and Al Flat windows.**
  - **Expensive (diamond) or toxic (Be)**
  - **Diamond, Be and Al are chemically and thermally not so stable.**

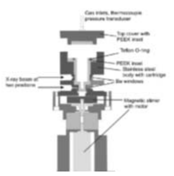




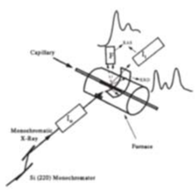


Al window

N. Weiher et.al., J. Synchrotron Rad. 12 (2005) 675.



J. D. Grunwaldt, et al. *Rev. Sci. Instrum.* 76, (5), 054104 (2005).



G. Sankar, and J. M. Thomas, *Topics.in Catal.* 8, 1 (1999).

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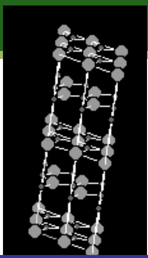
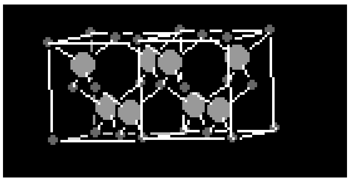
Cubic BN　2番目に硬い物質

35





Cubic BN is Second hardest material

Tensile strength = 1078.7 MPa

Diamond=2000 Mpa;Be=260 MPa

Sumiya, H.; Uesaka, N., High purity cBN polycrystalline its high pressure synthesis and its fieature. *New Diamond* **1999, 15 (4), 14.**

Previously cBN was made using binders and stregths was reduced.

Recently direct formation of cBN without binders by directly conversion at high pressure (7.7 GPa) and high temperature(2400 K).

(Sumitomo Electro Engineering Co. Dr. Sumiya)

It is thermally stable upto 1273 K and chemically also stable.

600 μmの厚みで十分な透過性と30気圧の耐久性

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A cell drawing .

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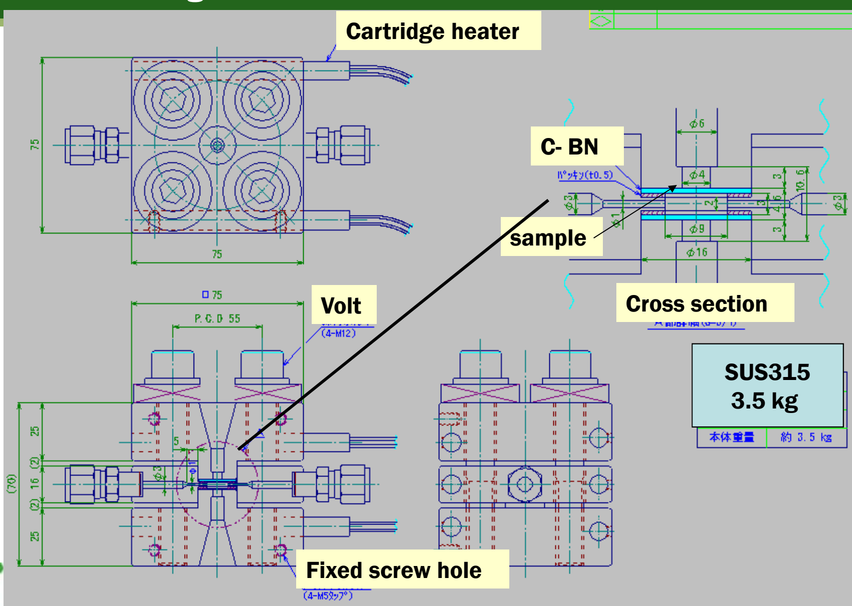
Kawai, T.; Chun, W. J.; Asakura, K.; Koike, Y.; Nomura, M.; Bando, K. K.; Oyama, S. T.; Sumiya, H. Review of Scientific Instruments 2008, 79, 014101.1.d



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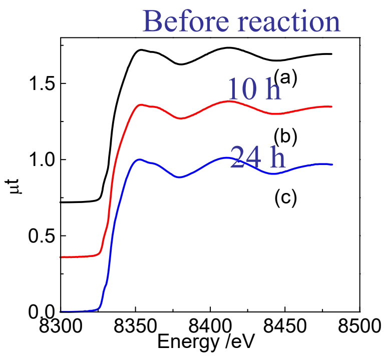
XANES of Ni_2P under reaction conditions.



30気圧613K　モデル油中のXAFS

20 wt% tetralin, 77 wt% tetradecane, and 3 wt% DBT, 80cc /min H_2

χ(k) oscillations of Ni K-edge XANES for Ni_2P on SiO_2 before (a) and during the HDS reaction 10 h and 24 h after the introduction of oil (b) and (c), respectively. The Ni_2P was reduced at 723 K and cooled to room temperature. The HDS was carried out at 3 MPa and 613 K.

1.Kawai, T.; Chun, W. J.; Bando, K. K.; Oyama, S. T.; Sumiya, H.; Asakura, K., A high-temperature and high -pressure liquid flow cell to measure operando XAFS spectra under the hydrodesulfurization reaction. *Rev.Sci.Instrum* ***2005.***
2.Kawai, T.; Bando, K. K.; Lee, Y. K.; Oyama, S. T.; Chun, W. J.; Asakura, K., EXAFS measurements of a working catalyst in the liquid phase: An in situ study of a Ni2P hydrodesulfurization catalyst. *J.Cat.* ***2006, 241, 20-24.***
3.T.Kawai; S. Sato, K. K. B., W.-J.Chun, S.T.Oyama,Y.-K.Lee ; K.Asakura, Active Phase of Ni2P Observed by an Operando XAFS. In *TOCAT2006, Tokyo, 2006.*

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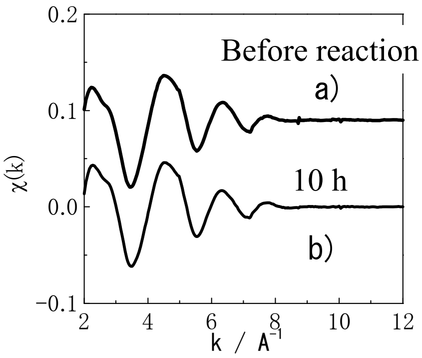
EXAFS of Ni_2P under reaction conditions.

χ(k) oscillations of Ni K-edge EXAFS for Ni_2P on SiO_2 before (a) druing the HDS reaction 10 h after the introduction of oil (b).



Ni_2P structure のあらわな変化がない.
反応中安定である.

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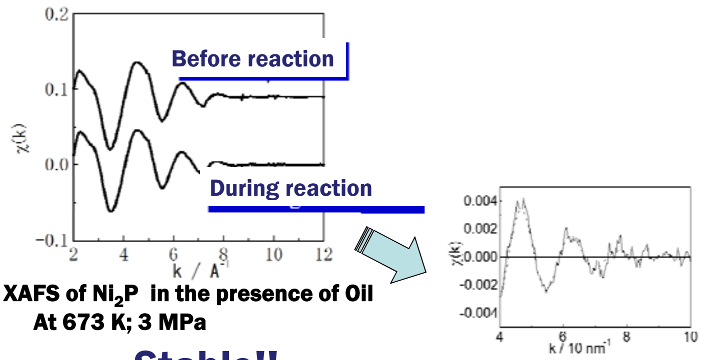
High pressure liquid cell 39
window must be tolerable against high pressure and temperature.

Cubic BN is Second hardest material
Tensile strength = 1078.7 MPa
Diamond=2000 Mpa;Be=260 MPa



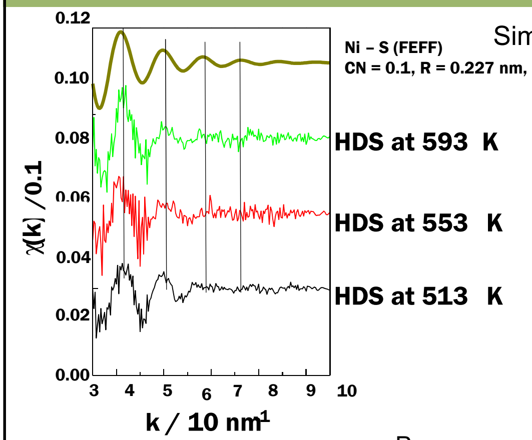
XAFS of Ni_2P in the presence of Oil
At 673 K; 3 MPa

Stable!!

Difference spectrum

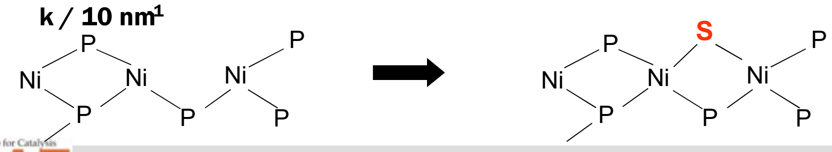
Ni-S=0.227 nm

チオフェン脱硫反応(1気圧)の脱硫反応 40



Simulated XAFS based on Ni-S bond

- 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_{surf}=0.2
- Little reaction temperature dependence



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But what is Ni-S for?

Ni-S is a spectator ?

Ni-S is a poison ?

Ni-S is included in an active site?

We carried out the simultaneous measurements of in situ quick XAFS,IR, and product analysis.

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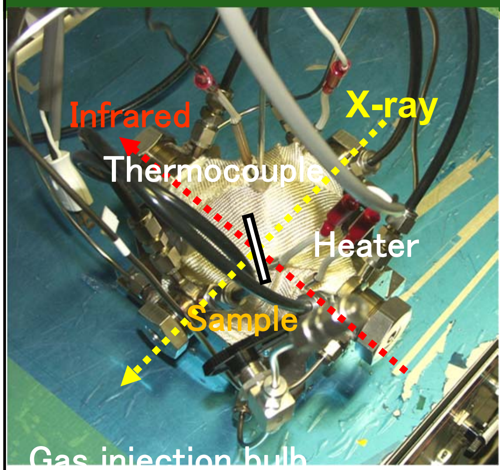
XAFS,IR,反応生成物分析同時測定



$C_4H_4S + 2H_2 \rightarrow C_4H_8S$

$C_4H_8S + H_2 \rightarrow H_2S + C_4H_8$

Sample：Ni_2P/MCM-41
35 mg, 15 mm Φ　disk

45 deg tilted against Xray and IR.

1. Bando, K. K.; Koike, Y.; Kawai, T.; Tateno, G.; Oyama, S. T.; Inada, Y.; Nomura, M.; Asakura, K., Quick X-ray absorption fine structure studies on the activation process of Ni2P supported on K-USY. *J. Phys. Chem. C* ***2011**, 115 (15), 7466-.*
2. Bando, K. K.; Wada, T.; Miyamoto, T.; Miyazaki, K.; Takakusagi, S.; Koike, Y.; Inada, Y.; Nomura, M.; Yamaguchi, A.; Gott, T.; Ted Oyama, S.; Asakura, K., Combined in situ QXAFS and FTIR analysis of a Ni phosphide catalyst under hydrodesulfurization conditions. *J Catal* ***2012**, 286 (0), 165-.*
3. Wada, T.; Bando, K. K.; Miyamoto, T.; Takakusagi, S.; Oyama, S. T.; Asakura, K., Operando QEXAFS studies of Ni2P during thiophene hydrodesulfurization: Direct observation of Ni-S bond formation under reaction conditions *J.Synchrotro.Rad.* ***2012**, 19 (2), 205-209.*
4. Wada, T.; Bando, K. K.; Oyama, S. T.; Miyamoto, T.; Takakusagi, S.; Asakura, K., Operando Observation of Ni2P Structural Changes During Catalytic Reaction: Effect of H2S Pretreatment. *Chem. Lett.* ***2012**, 41, 1238-1240.*

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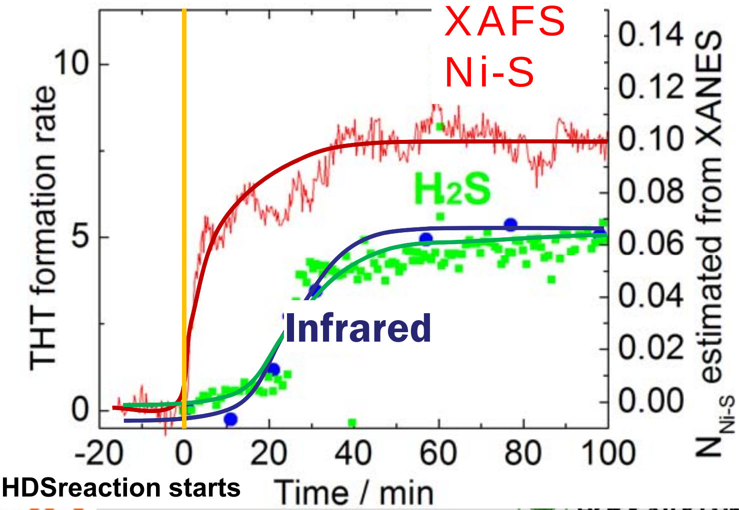
XANES, IR and MS changes during 513 K

Bando, K. K.;et al *J Catal* ***2012****, 286 (0), 165.*



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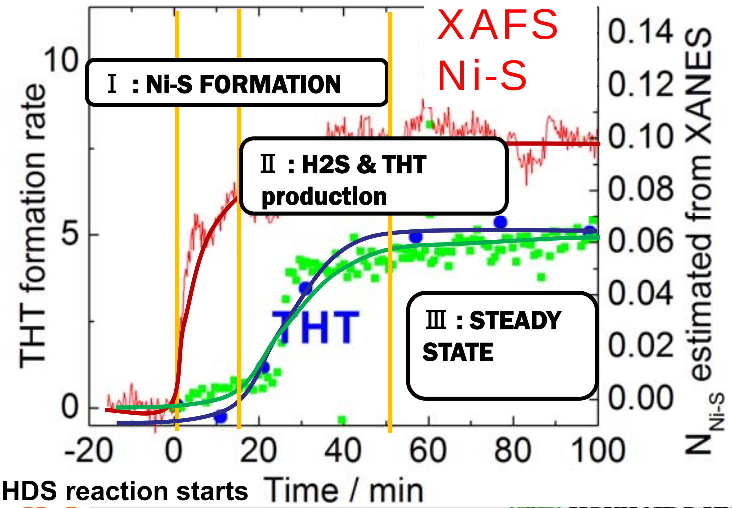
XANES, IR and MS changes during 513 K

Bando, K. K.;et al *J Catal* ***2012****, 286 (0), 165.*

THT=Tetrahydrofuran



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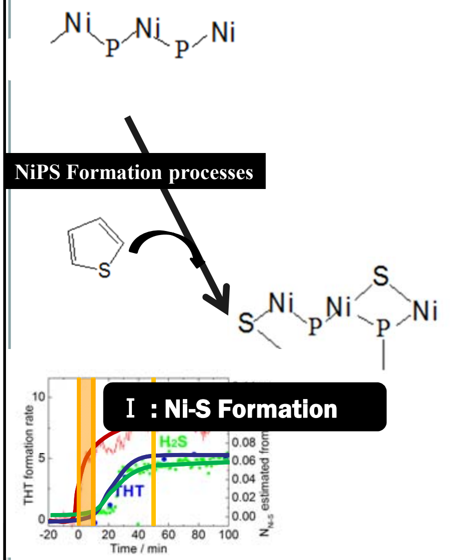
Reaction mechanisms

Bando, K. K.;et al *J Catal* **2012, 286 (0), 165.**



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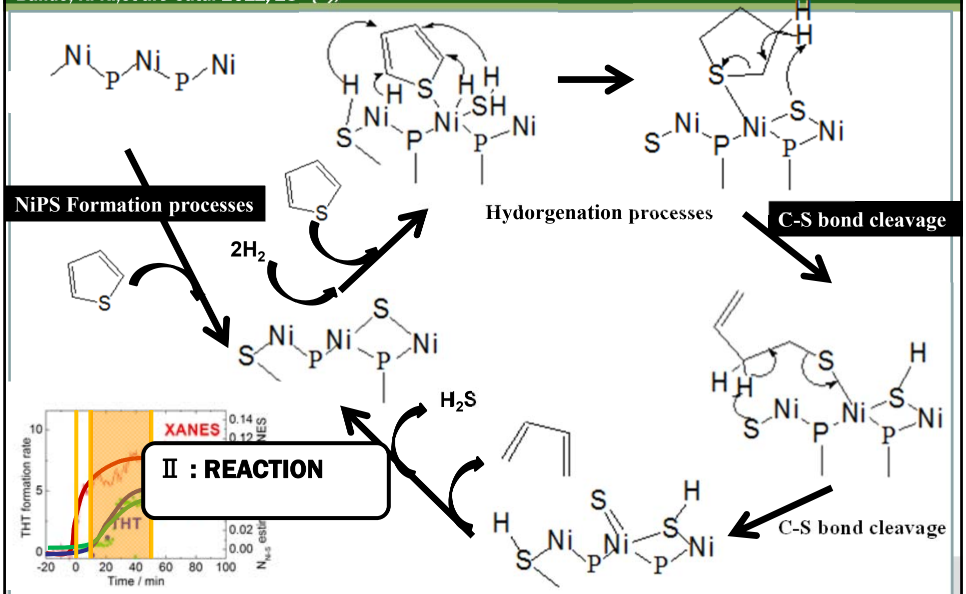
同時測定による反応機構提案

Bando, K. K.;et al *J Catal* **2012, 286 (0), 165.**



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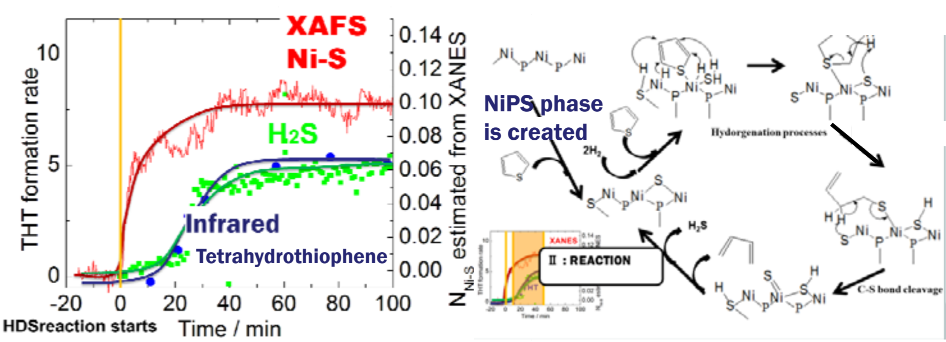
Simultaneously measurement of IR,XAFS and QMASS



NiPS structure is first formed and then reaction starts with formation of THT as intermedite

電池駆動型マイクロガスセンサの開発

Suzuki, T.; Soma, S.; Nagase, T. In *FujiElectric Review; Fuji electric: 2012; Vol. 58, p 37.*

●ガスの安全・安心に対する社会的要求高まる
⇒都市ガスの供給、ガス機器の両面での安全確保に加え、**都市ガス警報器の普及**が急務

●更なる普及推進のためには**ガス警報器のコードレス化(電池駆動化)**が必要
・停電時にも安全を確保可能
・台所ではAC電源が確保しにくい
・設置箇所に制約を受ける
・配線が美観を損ねる

高い信頼性を持ち、電池駆動できる超省電力型ガスセンサの開発が必要

MEMS技術により、
従来比**1/2000以下**の低消費電力を実現

開発中のガスセンサ概要

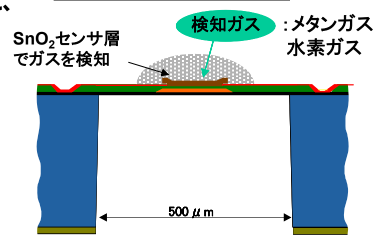
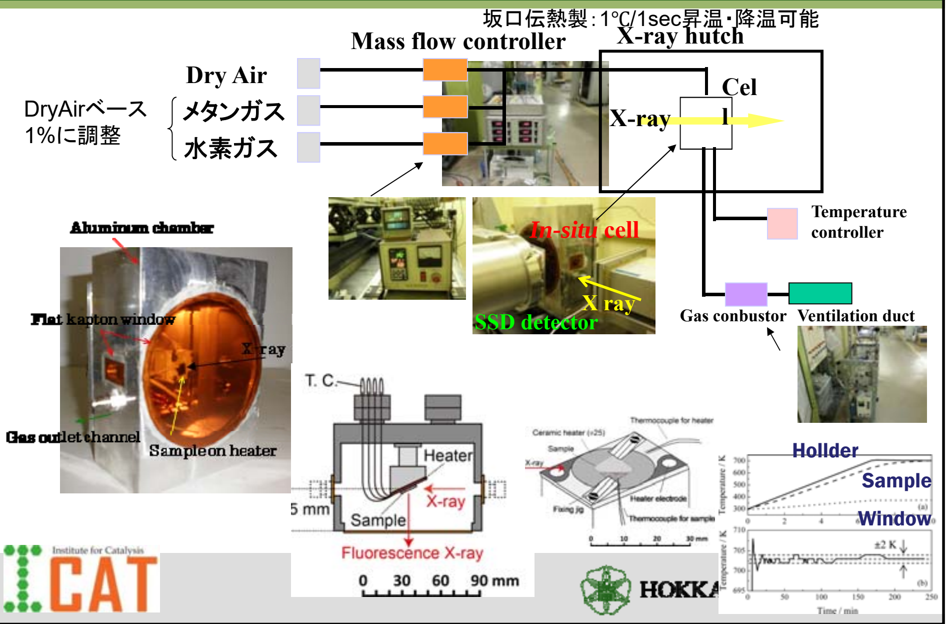


図 薄膜ガスセンサチップ概略

PtドープSnO_2触媒を採用することで特性が改善。

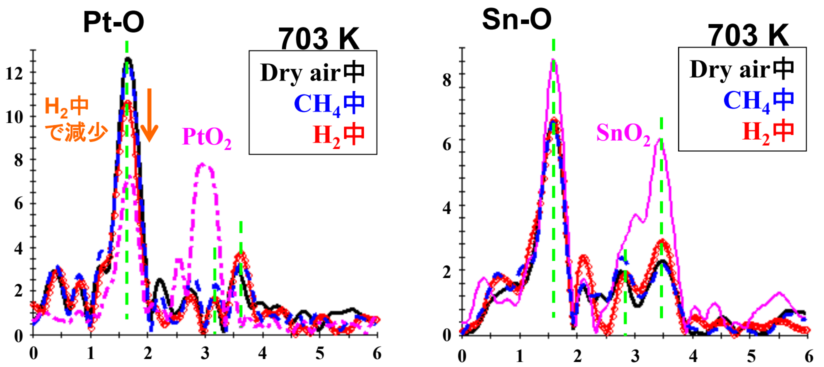
In-situ XAFS実験

1) Murata, N.; Kobayashi, M.; Okada, Y.; Suzuki, T.; Nitani, H.; Niwa, Y.; Abe, H.; Wada, T.; Mukai, S.; Uehara, H.; Ariga, H.; Takakusagi, S.; Asakura, K. *Review of Scientific Instruments* **2015, 86, 034102.**
2) Murata, N.; Suzuki, T.; Kobayashi, M.; Togoh, F.; Asakura, K. *Physical Chemistry Chemical Physic* ***2013, 15, 17938.***



動径分布関数の比較

☆CH_4、H_2ガス中のいずれもPt周囲とSn周囲の局所構造がSnO_2の構造に酷似
☆703 Kの水素ガス中において、Pt-Oの強度が減少



Pt 吸収端 EXAFS フーリエ変換　　Sn 吸収端 EXAFS フーリエ変換

➡ カーブフィッティング解析により、Pt-OとSn-Oの配位数、結合距離を明確し、構造について検証

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Summary

1. Operando XAFS—High penetration ability.
2. High pressure Less than 100 bar and high temperature less than 1200K are possible.

3. Future 時空間分析、高エネルギー分解、同時解析で、触媒そのものが働いているときにそのまま測定。
https://youtu.be/ugzqLxiOlSM?t=11
（https://www.youtube.com/watch?v=jljxDWb3ADs）

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Dr. M. Yabashi(SACLA)
Dr. T.Katayama(SACLA)
Dr. S.Nozawa(PF)
Prof. M.Kimura(PF)
Dr. H.Abe(PF)
Dr. Y.Niwa(PF)
Dr. H.Nitani(PF)
Dr. Murata(Fuji)
Dr. Suzuki(Fuji)
Dr. U.Kashabonia(HU)
Prof. S.Iguchi(TIT)
Prof. I.Yamanaka(TIT)
Financial Support from NEDO and JST

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