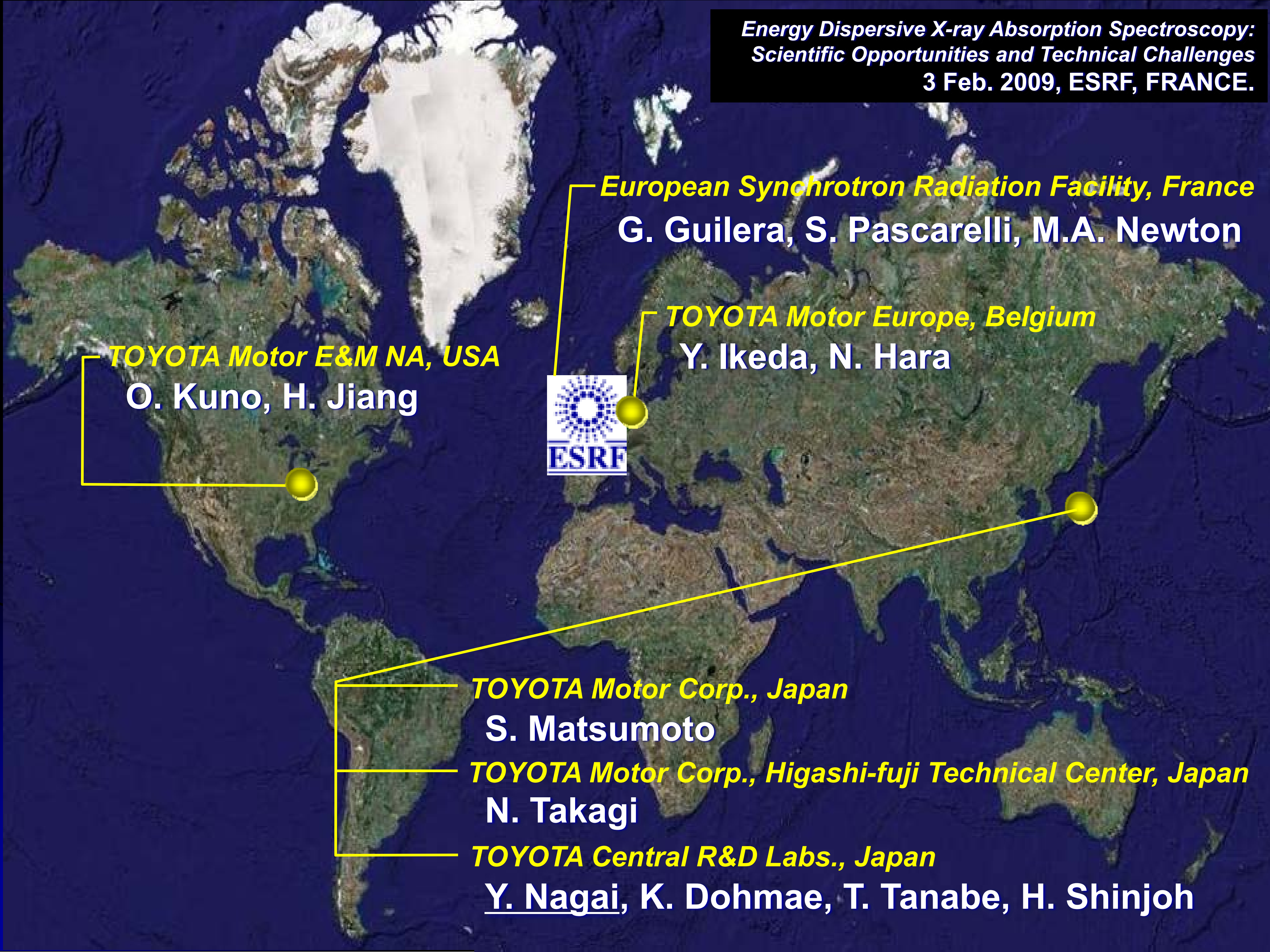
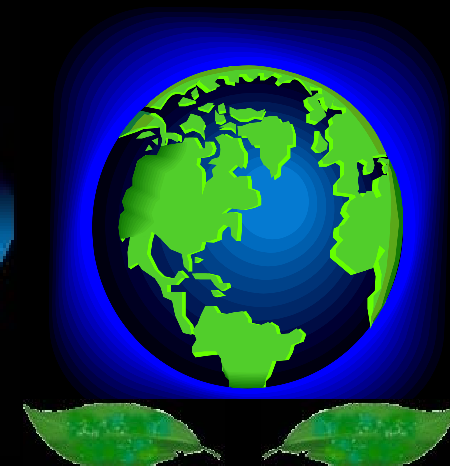

Energy Dispersive X-ray Absorption Spectroscopy:
Scientific Opportunities and Technical Challenges
3 Feb. 2009, ESRF, FRANCE.
European Synchrotron Radiation Facility, France
G. Guilera, S. Pascarelli, M.A. Newton
TOYOTA Motor Europe, Belgium
Y. Ikeda, N. Hara
TOYOTA Motor E&M NA, USA
O. Kuno, H. Jiang
ESRF
TOYOTA Motor Corp., Japan
S. Matsumoto
TOYOTA Motor Corp., Higashi-fuji Technical Center, Japan
N. Takagi
TOYOTA Central R&D Labs., Japan
Y. Nagai, K. Dohmae, T. Tanabe, H. Shinjoh

In Situ Redispersion of Platinum Nanoparticles Supported on Ceria-Based Oxide for Auto-Exhaust Catalysts

Improving The lifetime of auto-exhaust catalysts?



Automotive Catalyst

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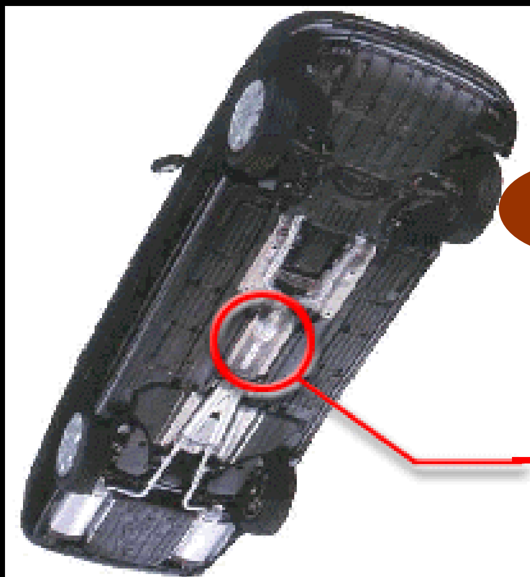
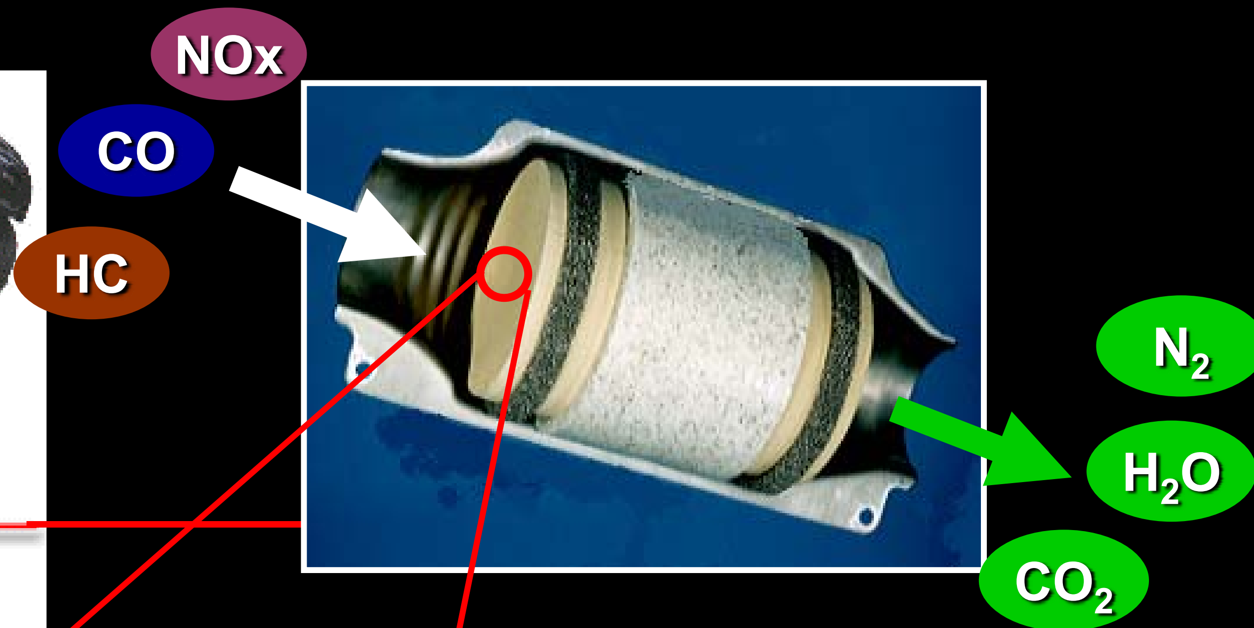
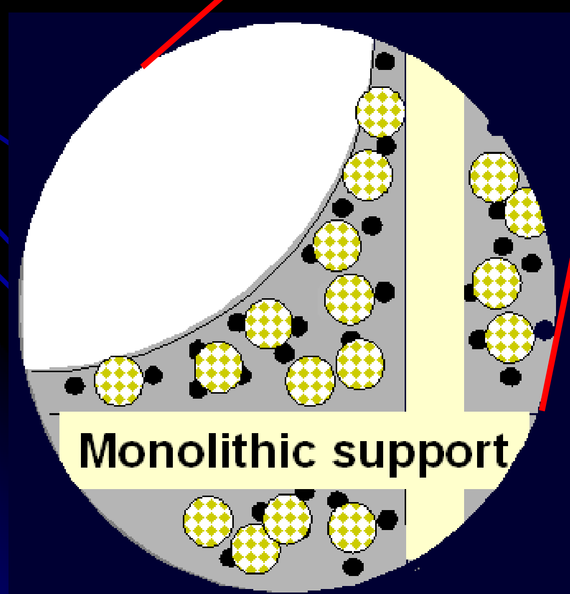
Automotive Three-way Catalyst (TWC)

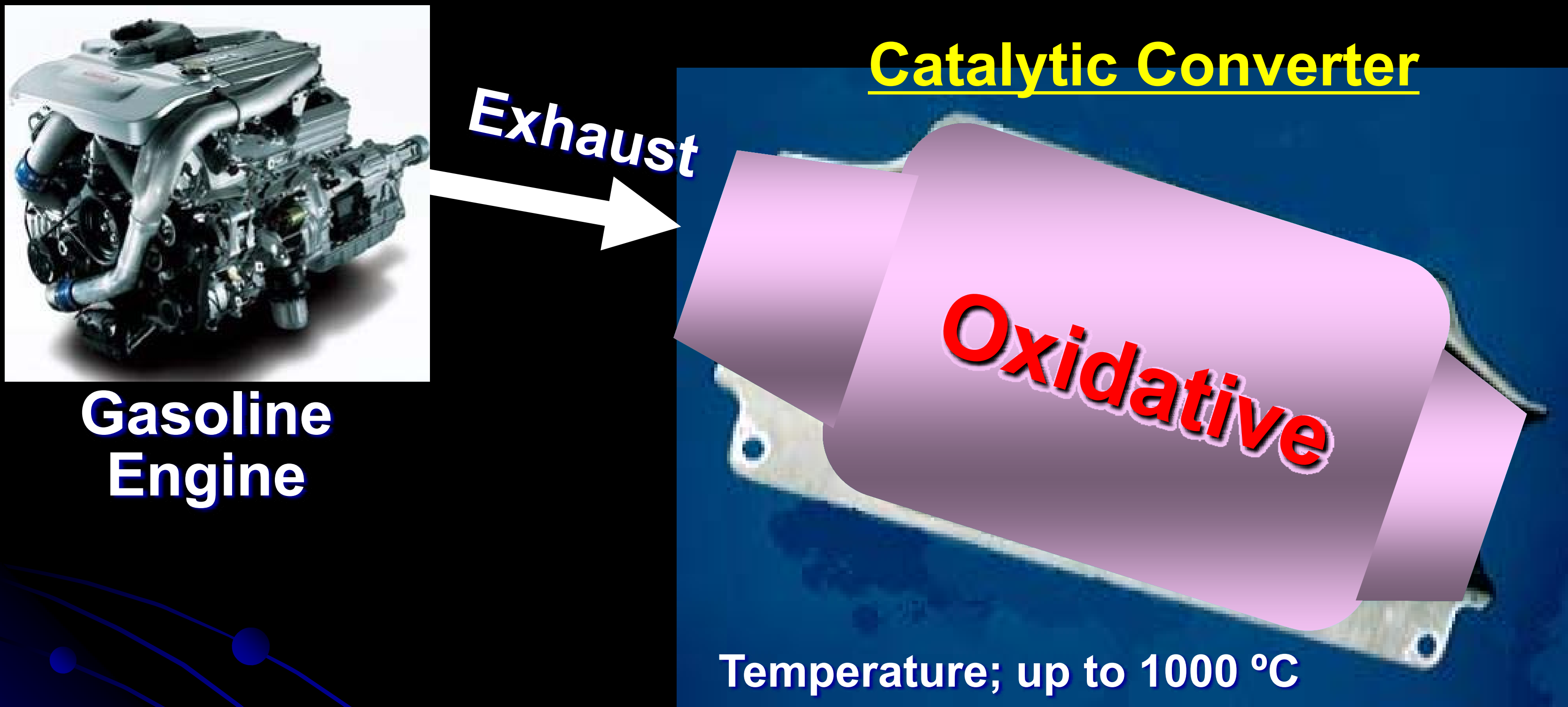






- Active site : Pt, Rh, Pd
- Support : alumina, etc
- Additives : CeO_2, etc

Exhaust Condition from Gasoline Engine



***In-situ dynamic observation of precious metals** is important to the development of advanced catalysts.*

Pt Sintering/Redispersion (Static study)

Our Goal:

In-situ dynamic observation of the Pt Sintering/Redispersion in simulated exhaust flowing.

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Experimental

- **Catalyst**
  2 wt% Pt/ γ-Al_2O_3
  2 wt% Pt/CZY(Ce-Zr-Y mixed oxide)
  CZY:50 wt% CeO_2, 46 wt% ZrO_2 and 4 wt% Y_2O_3

- **XAFS measurement**
  Pt L_3-edge XANES every 1~6 sec
  ESRF ID24
  Turbo-XAS (variant of DXAFS) in fluorescence mode
  in-situ: Simulated gas
  O_2(4 or 20%)/He ↔ H_2(3%)/He cyclically, at 400~800ºC

- **In situ TEM Observation**
  Univ. Arizona
  820 ºC, 10 torr O_2 ,

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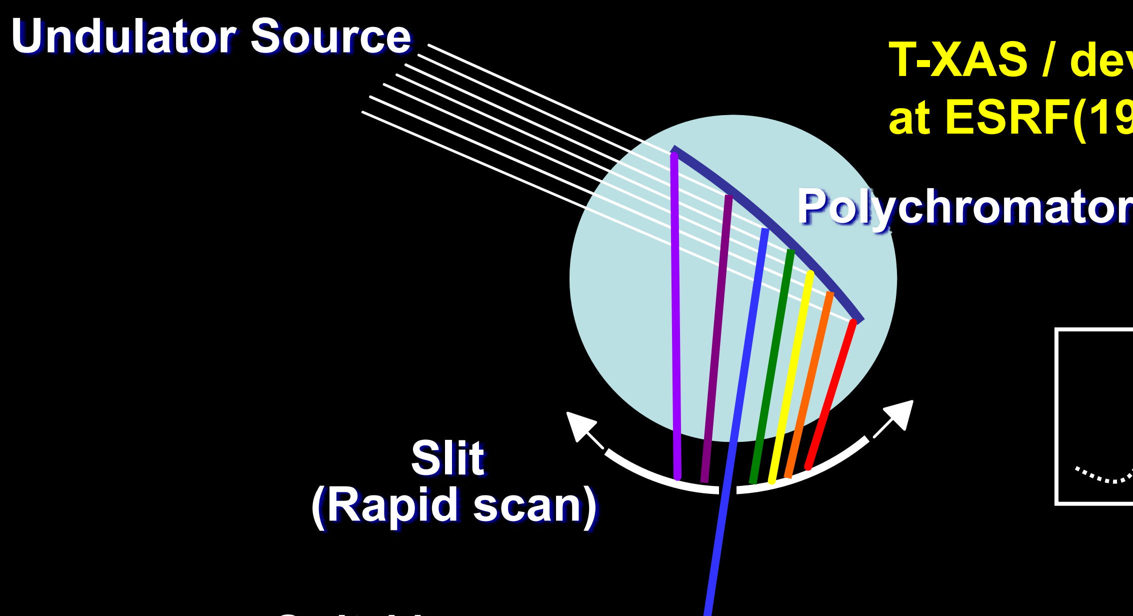
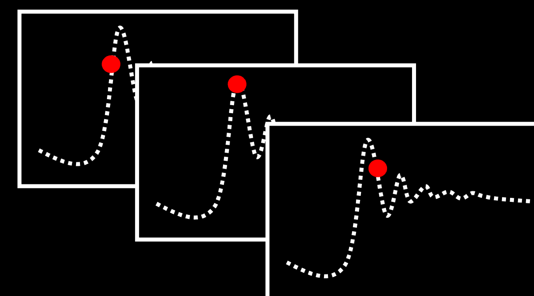
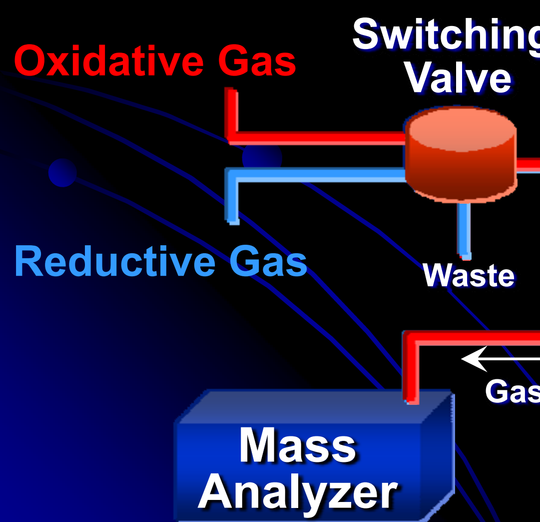
in-situ Turbo-XAS in Fluorescence Mode

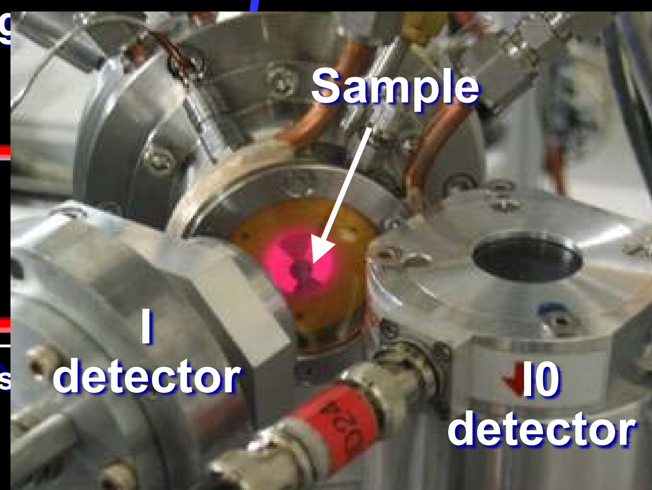
T-XAS / developed by S. Pascarelli et al. at ESRF(1998)





Very fine time resolution for fluorescence XANES





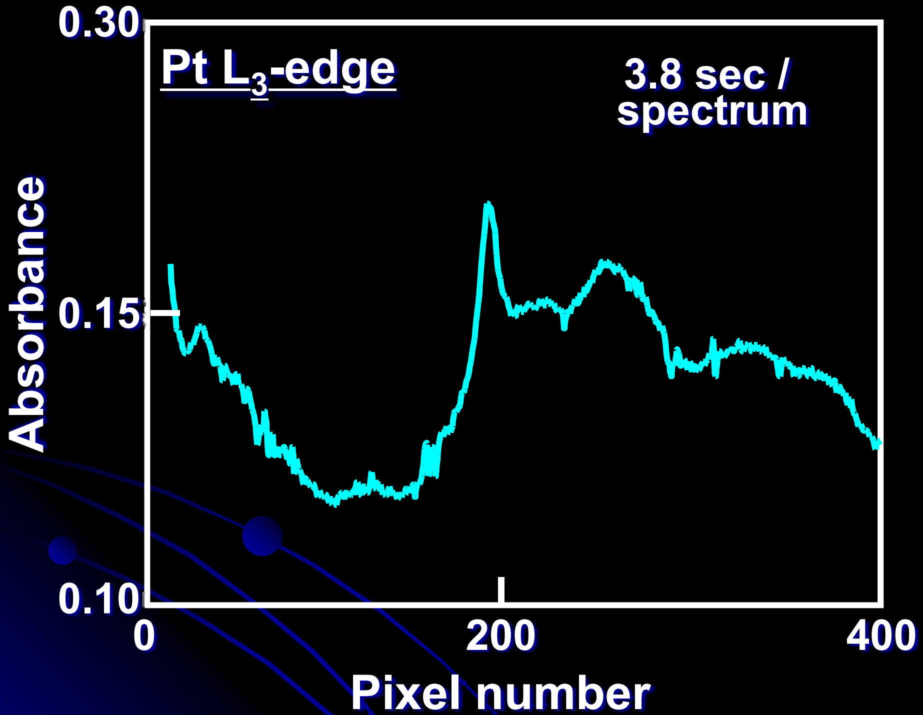
Manufactured by B. Gorges from the ESRF Sample Environ. Lab

Rapid gas s

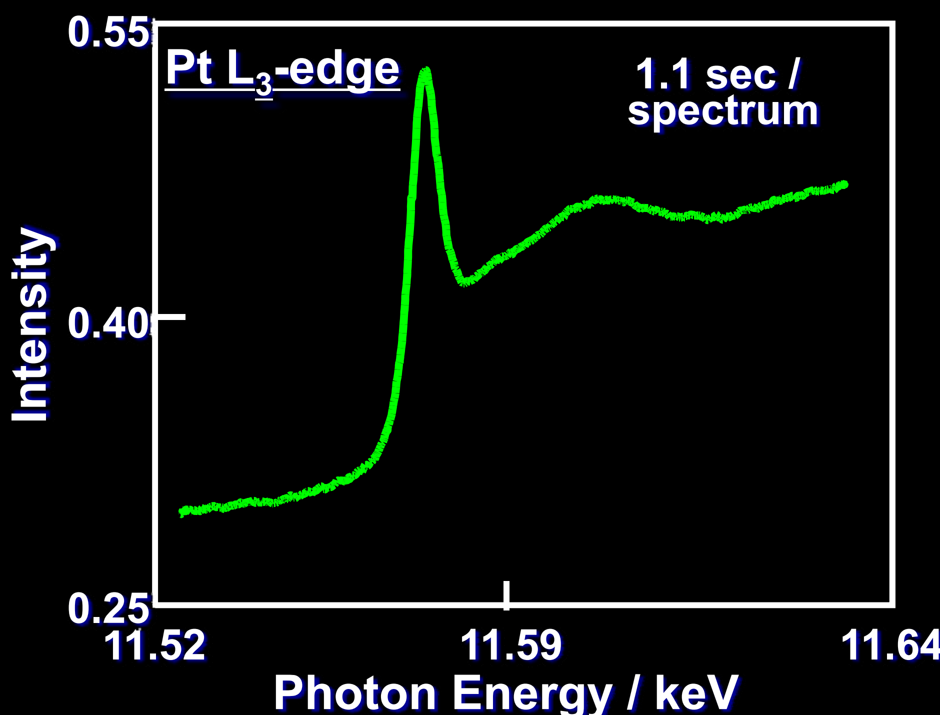
Comparison of Spectra on Pt/CZY

2 wt% Pt/CZY (Ce-Zr-Y mixed oxide)

DXAFS in Transmission mode at ESRF ID24



T-XAS in fluorescence mode at ESRF ID24



High loading amount of heavy elements such as Ce and Zr in this sample strongly absorbs the X-ray.

Fluorescence T-XAS permits time-resolved measurements.

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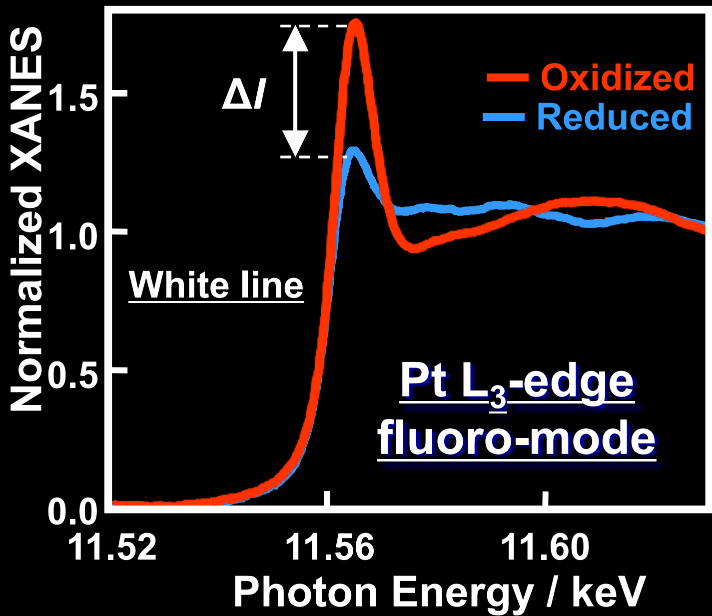
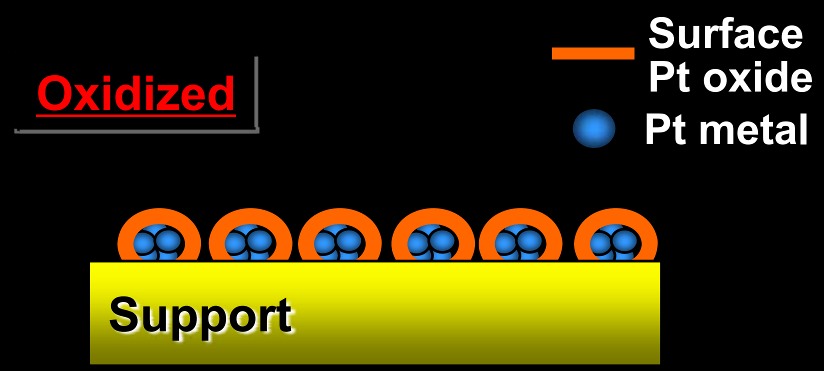
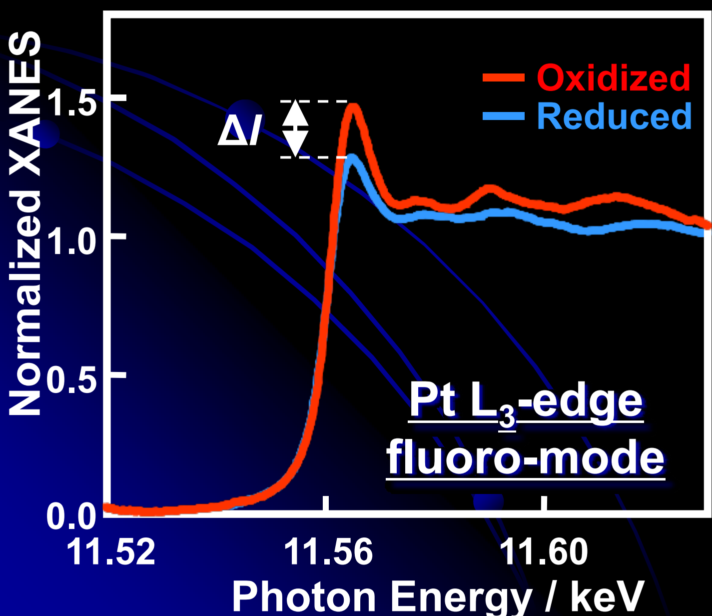
How to Analyze Pt Particle Size?

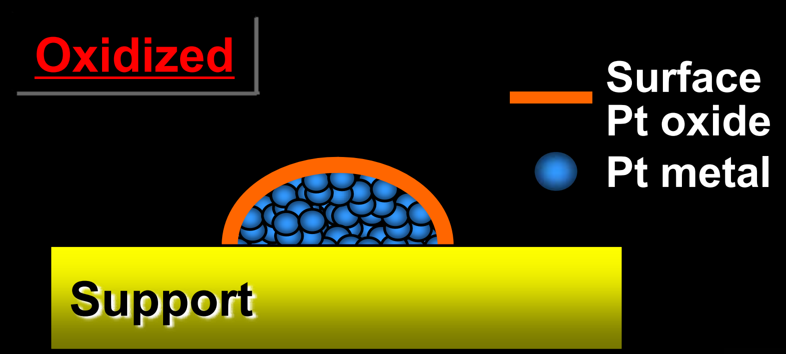


Small Pt particles ➡ Large ΔI





Large Pt particles ➡ Small ΔI



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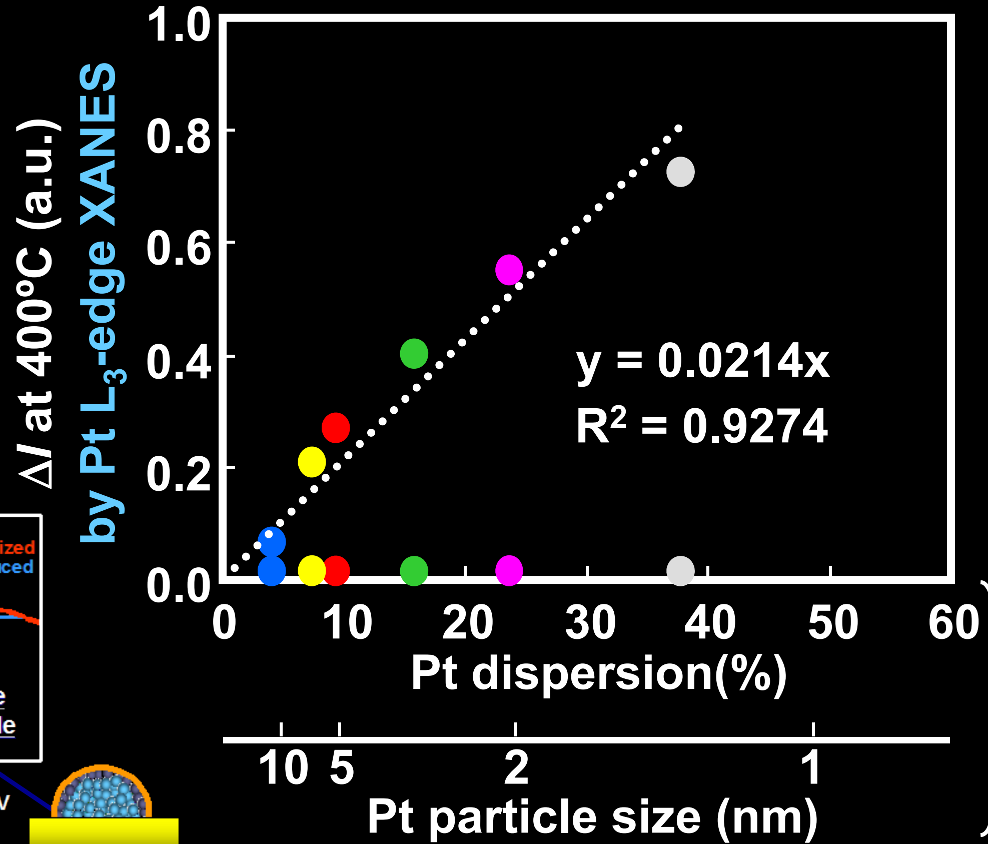
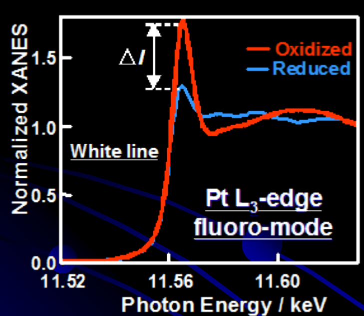
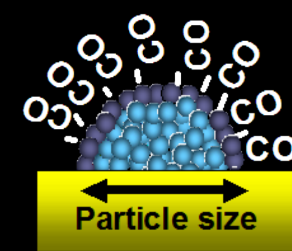
Relationship between Δ*I* and Pt Particle Size



The Pt/CZY catalyst were preliminary aged at various temperature to obtain specific particle size of sintered Pt.



by CO chemisorption method (ex-situ, off-line)



The good linear relationship between Pt dispersion and Δ*I* suggests that the Pt particles are oxidized only on the surface region.

By using fluorescence T-XAS with ~ 1 sec time-resolution (ΔI), it is possible to track the change in Pt particle size under in-situ condition.

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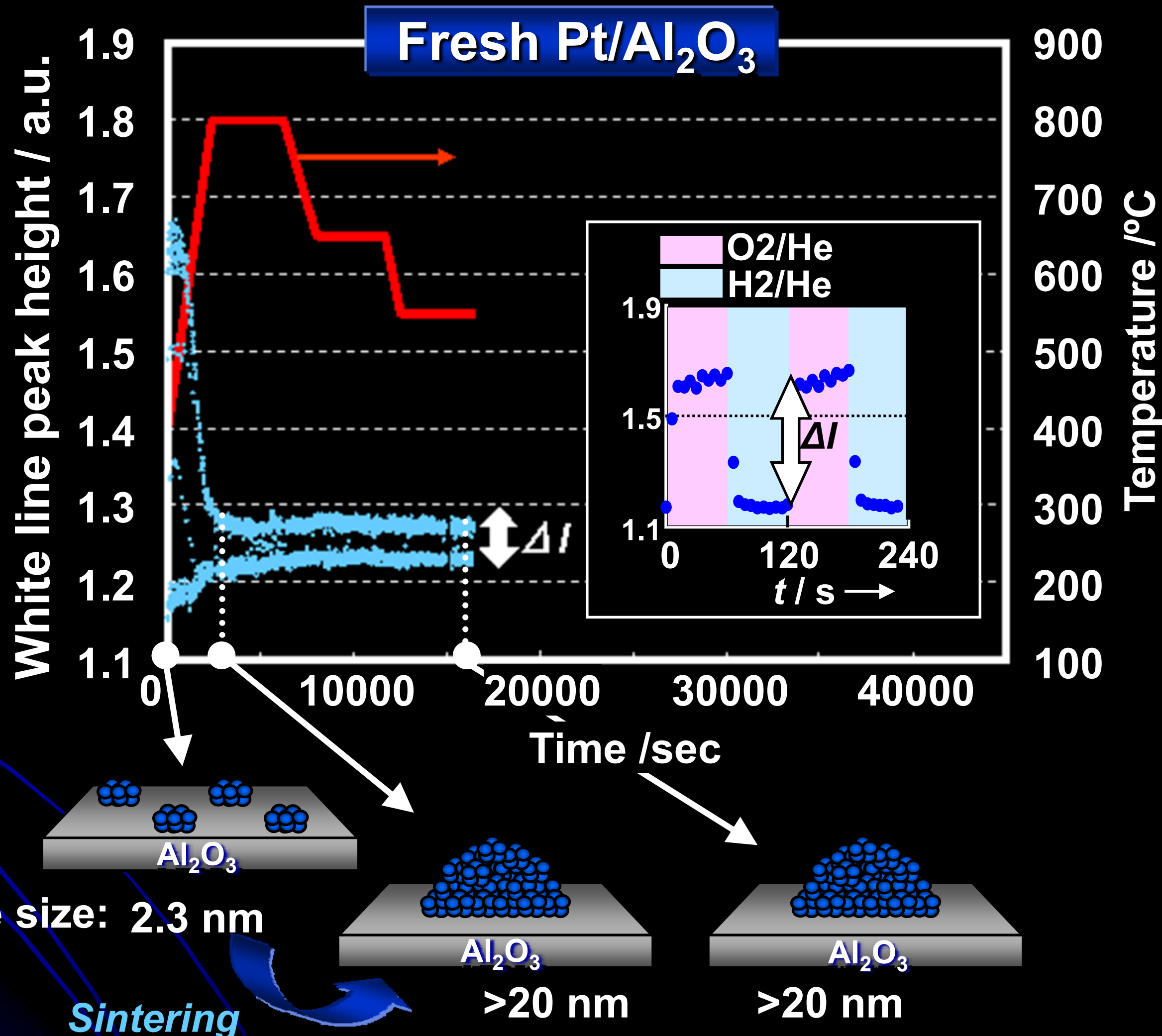
In-situ Dynamic Observation in Pt/Al_2O_3

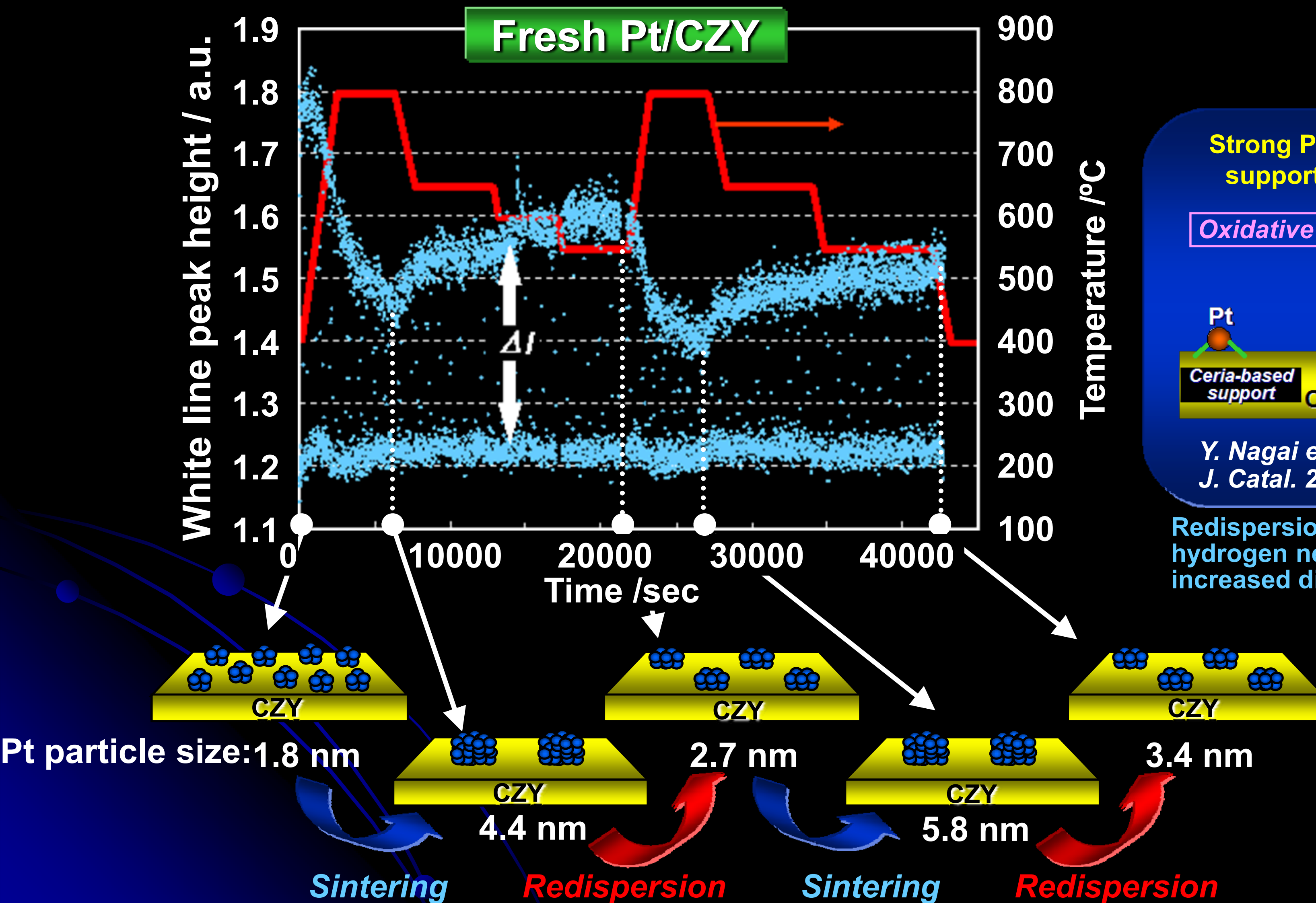
3% H_2/He(60sec) ⟷ 20 or 4 % O_2/He(60sec)

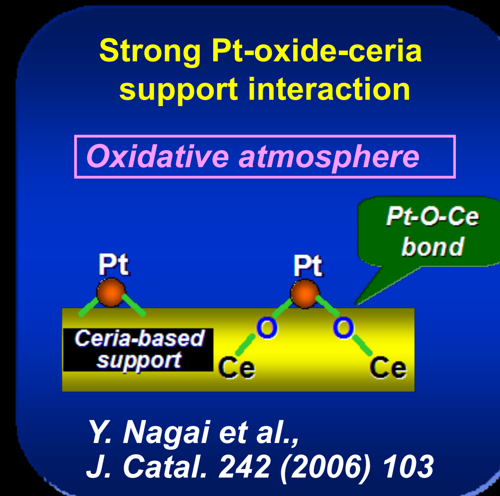


We observed only facile sintering in the Pt/Al_2O_3.

In-situ Dynamic Observation in Pt/CZY

3% H_2/He(60sec) ⟺ 20 or 4 % O_2/He(60sec)





Redispersion experiments in hydrogen never resulted in increased dispersion.

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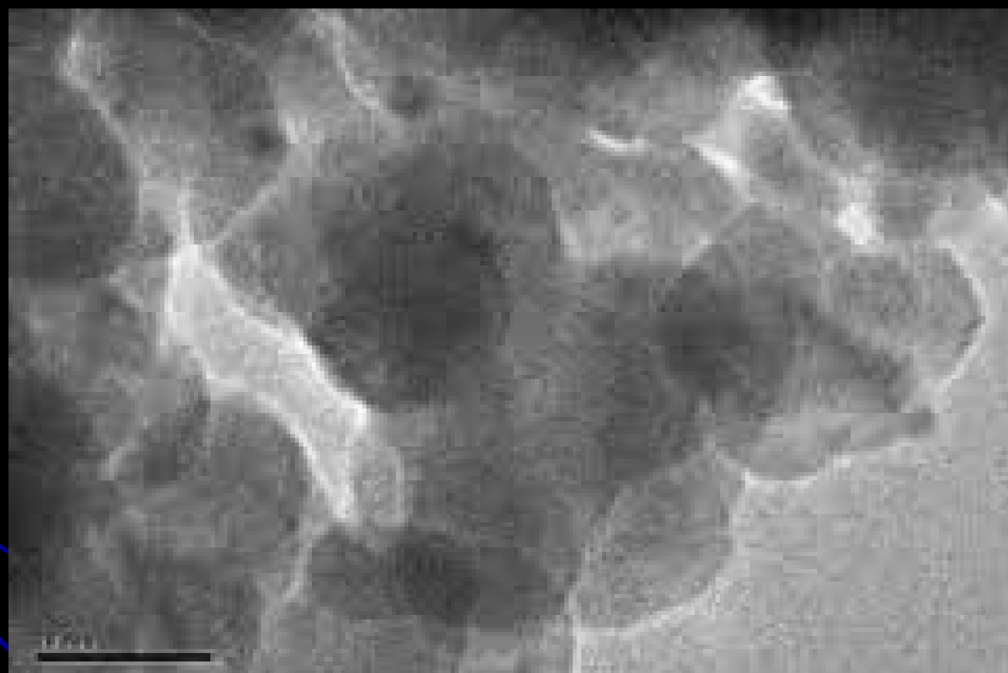
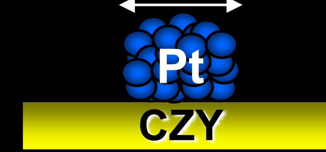
In-situ TEM Observation of Pt Redispersion

Pt redispersion process on CZY



6.7 nm



average starting size 6.7nm

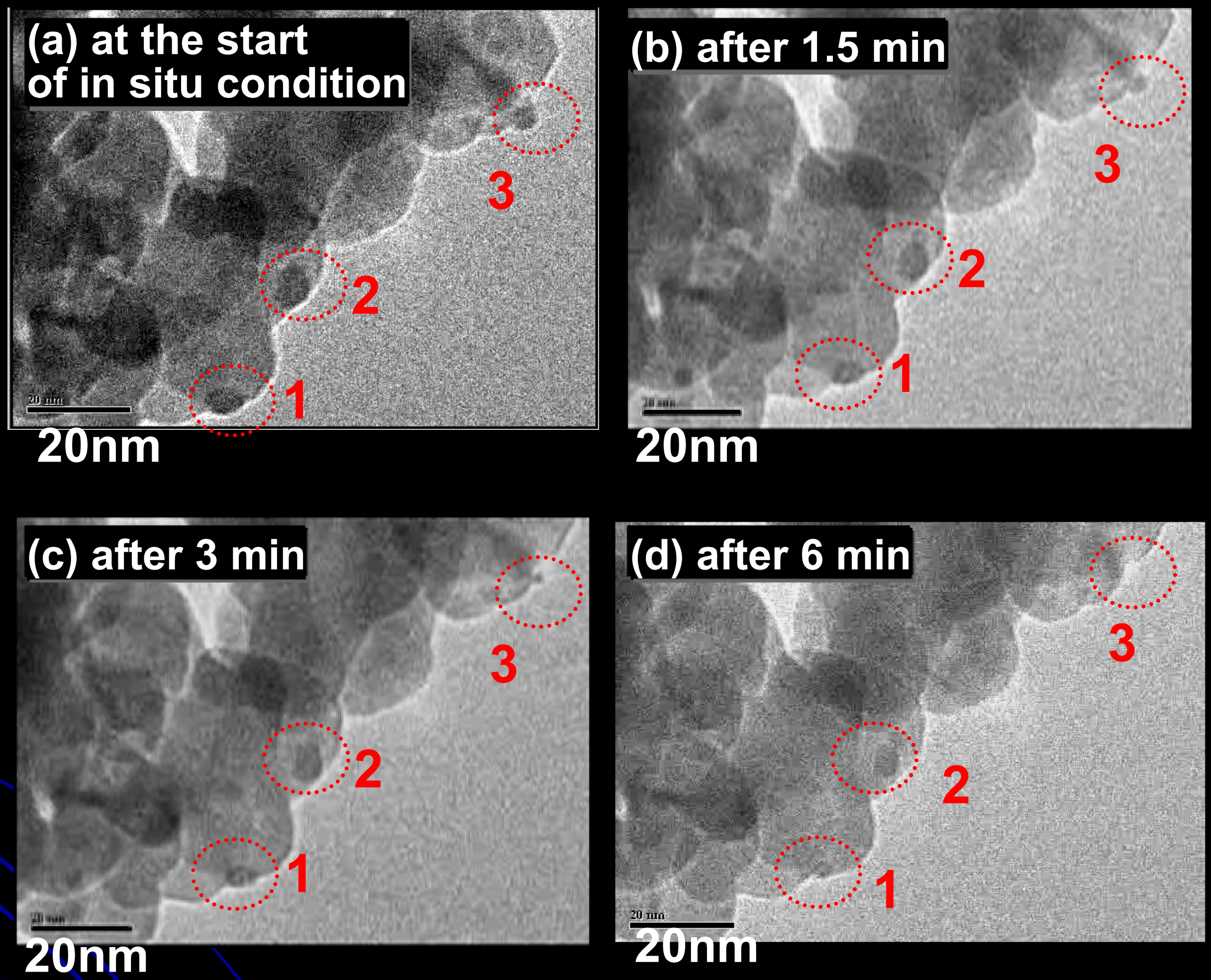
10 torr O_2 at 820ºC

Oxidative redispersion

7 fold speed play (7sec → 1sec)

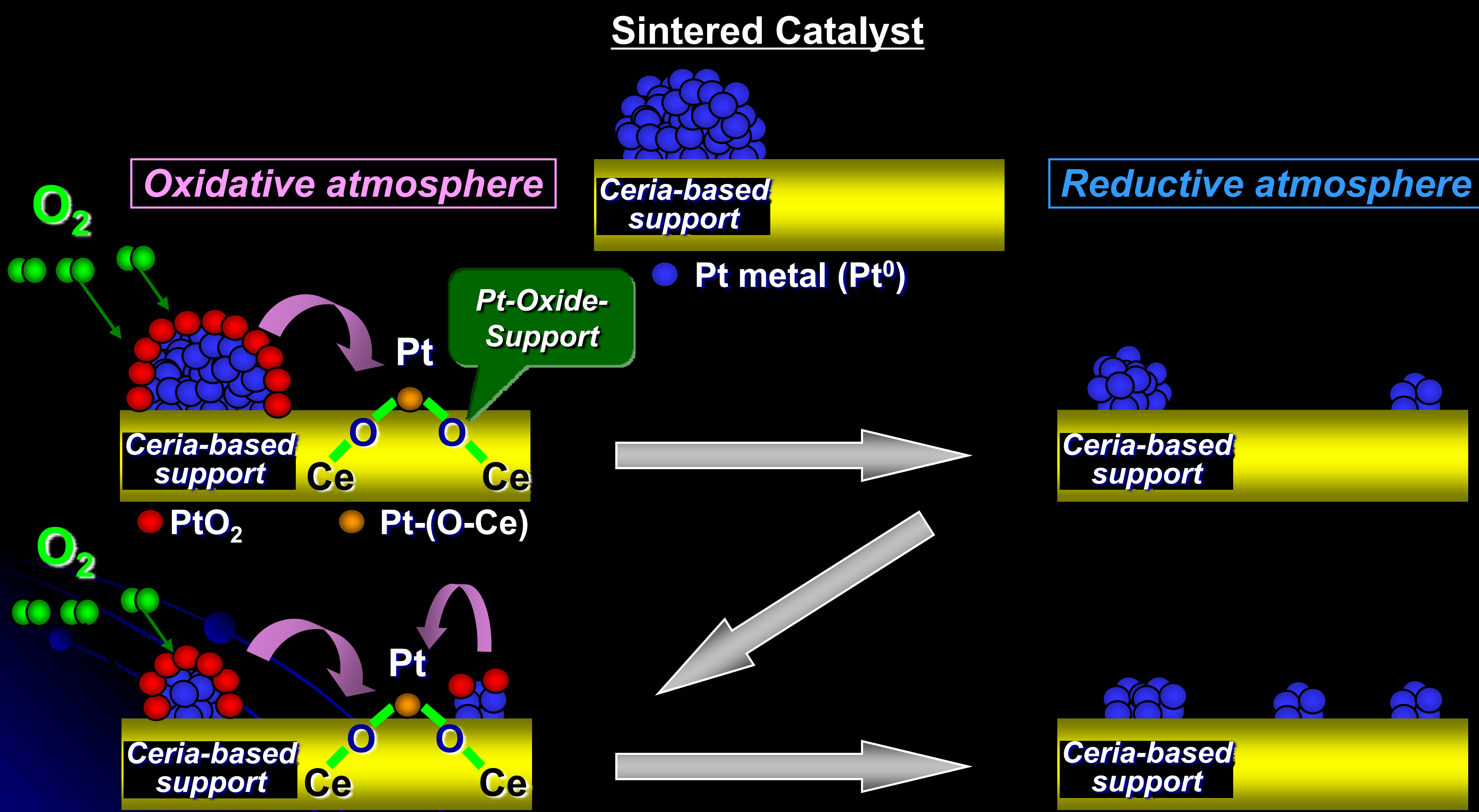
Pt sintering could not be observed in this field of view, this movie captured the Pt redispersion process.

Snapshots of Pt Redispersion



Pt particle size in the circle 1 and 2 decreased remarkably, and the Pt particle in the circle 3 disappeared. Crystallites migration and splitting was not observed.

Proposed mechanism of Pt redispersion



The Pt redispersion process proceeds by the repetition of the atomic migration of Pt oxide from the surface of large metal particles and the reduction of Pt-O-support species. (Not Pt crystallites migration)

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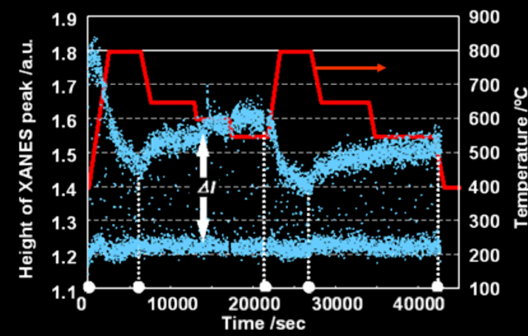
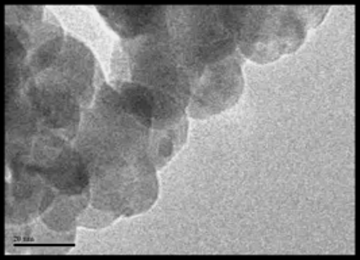
Significance

a. Advanced technique for dynamic observation

in-situ time-resolved Turbo-XAS

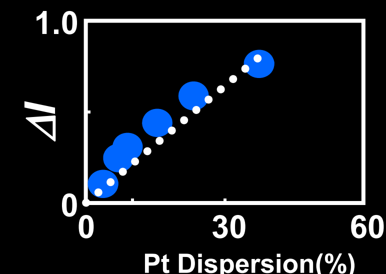
in-situ TEM





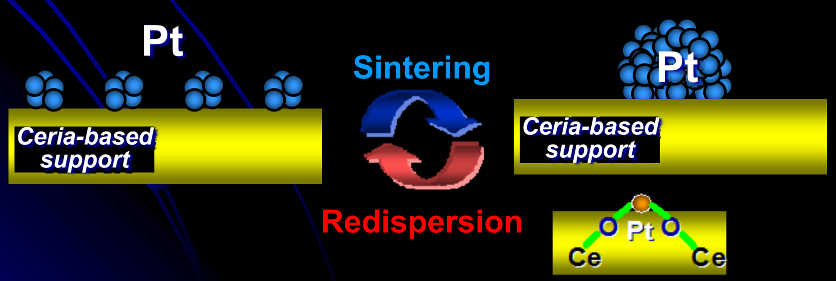
b. Novel method

in-situ dynamic measurement of Pt particle size using Pt L_3-edge XANES



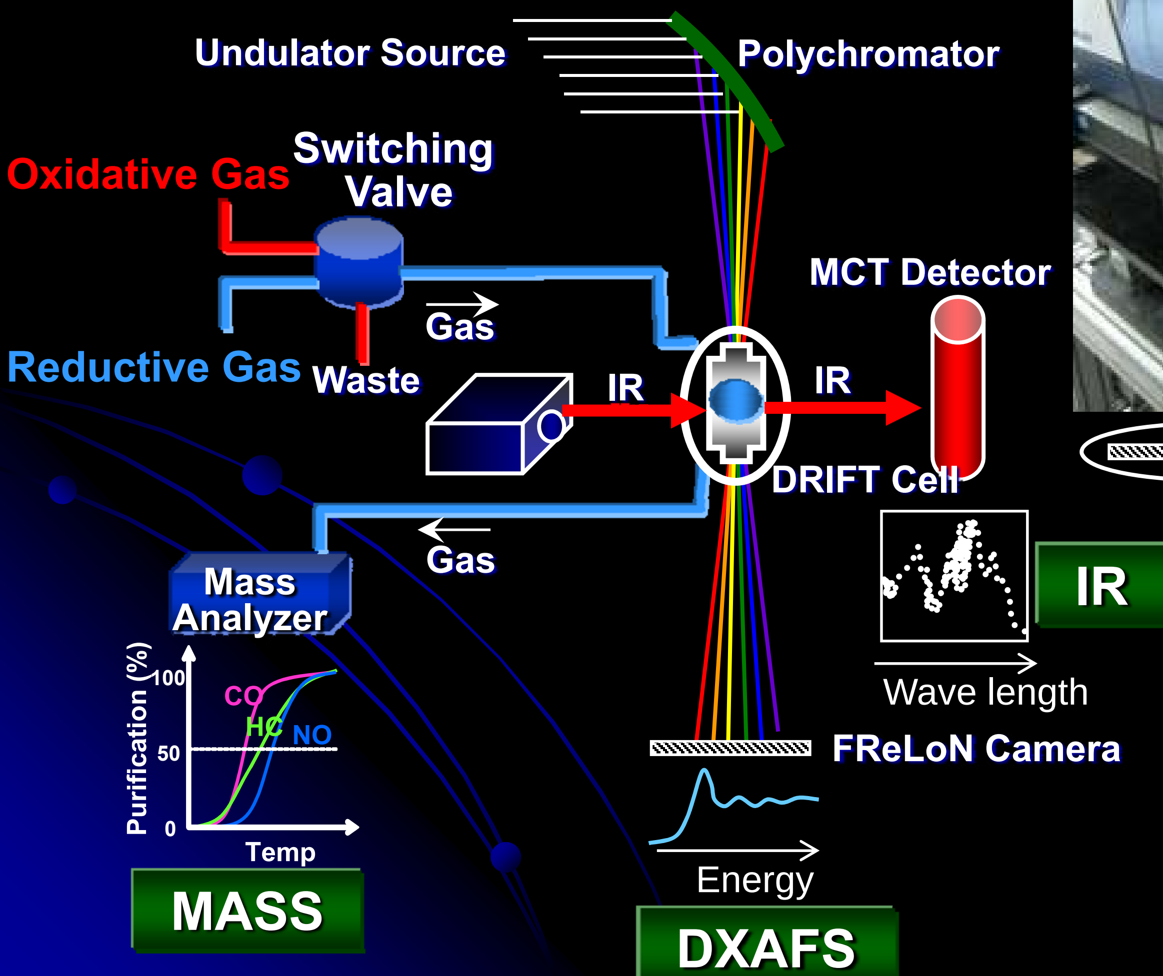
c. New discovery

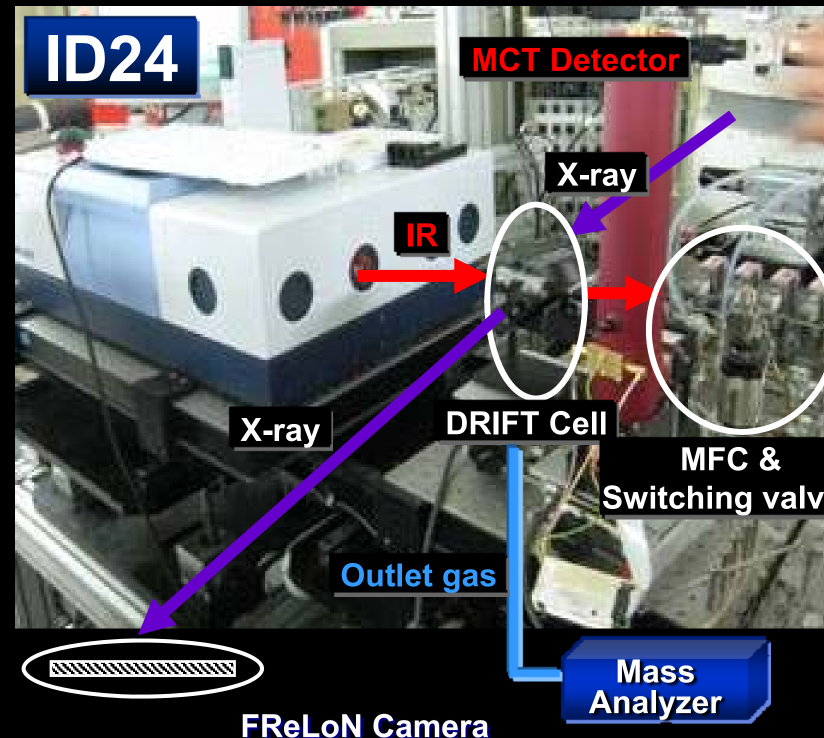
- Reversible sintering/redispersion in simulated exhaust flowing (effective Pt redispersion in the absence of Cl)
- An atomic migration model accounts for the observed redispersion through the strong Pt-oxide-support interaction.



Future View

DXAFS - IR - Mass





Designed by M. A. Newton at ID24.

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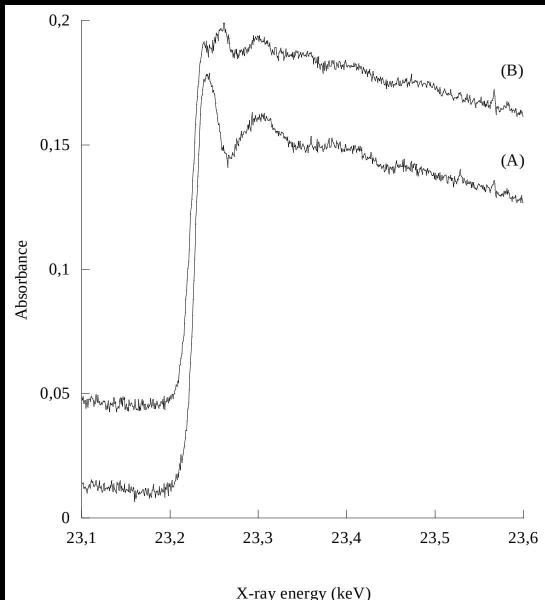
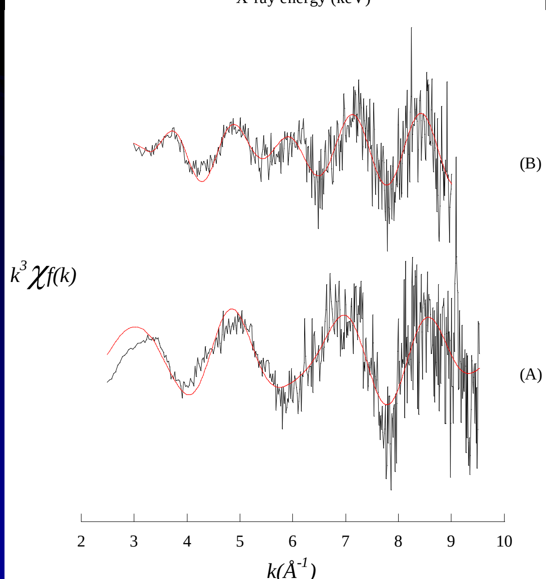
Now at 1wt% Rh…..





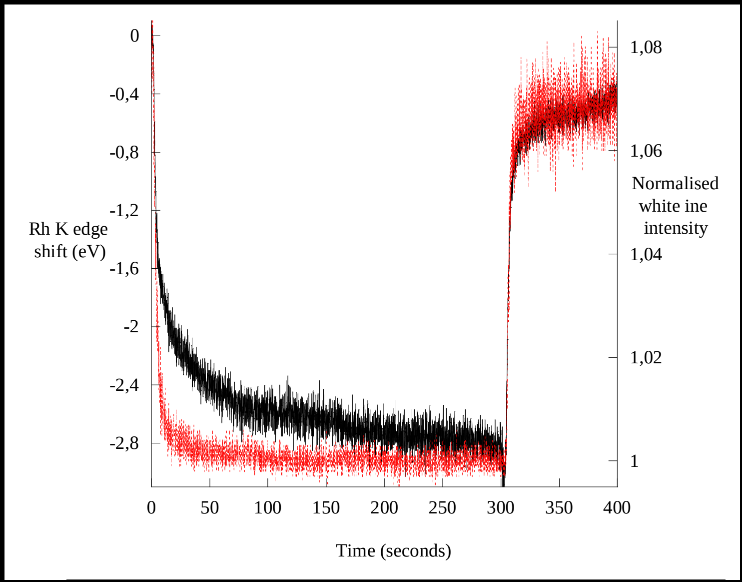
T = 573K

Reducing feed =
300ppm NO + 300ppm CO
78msecs/per spectrum

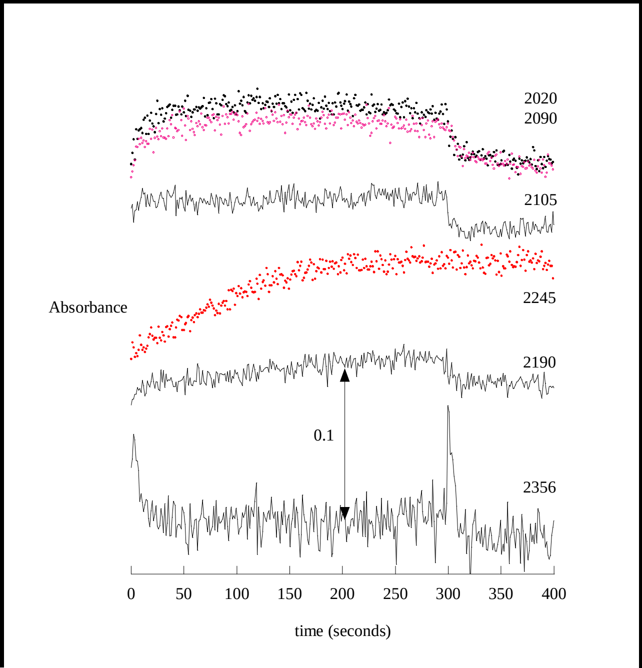
A *big improvement on previous achievements* at Rh

A direct result of a better understanding of the Tolerances w.r.t instability the beamline optics have to work within for these systems

Rh K edge position and white line intensity

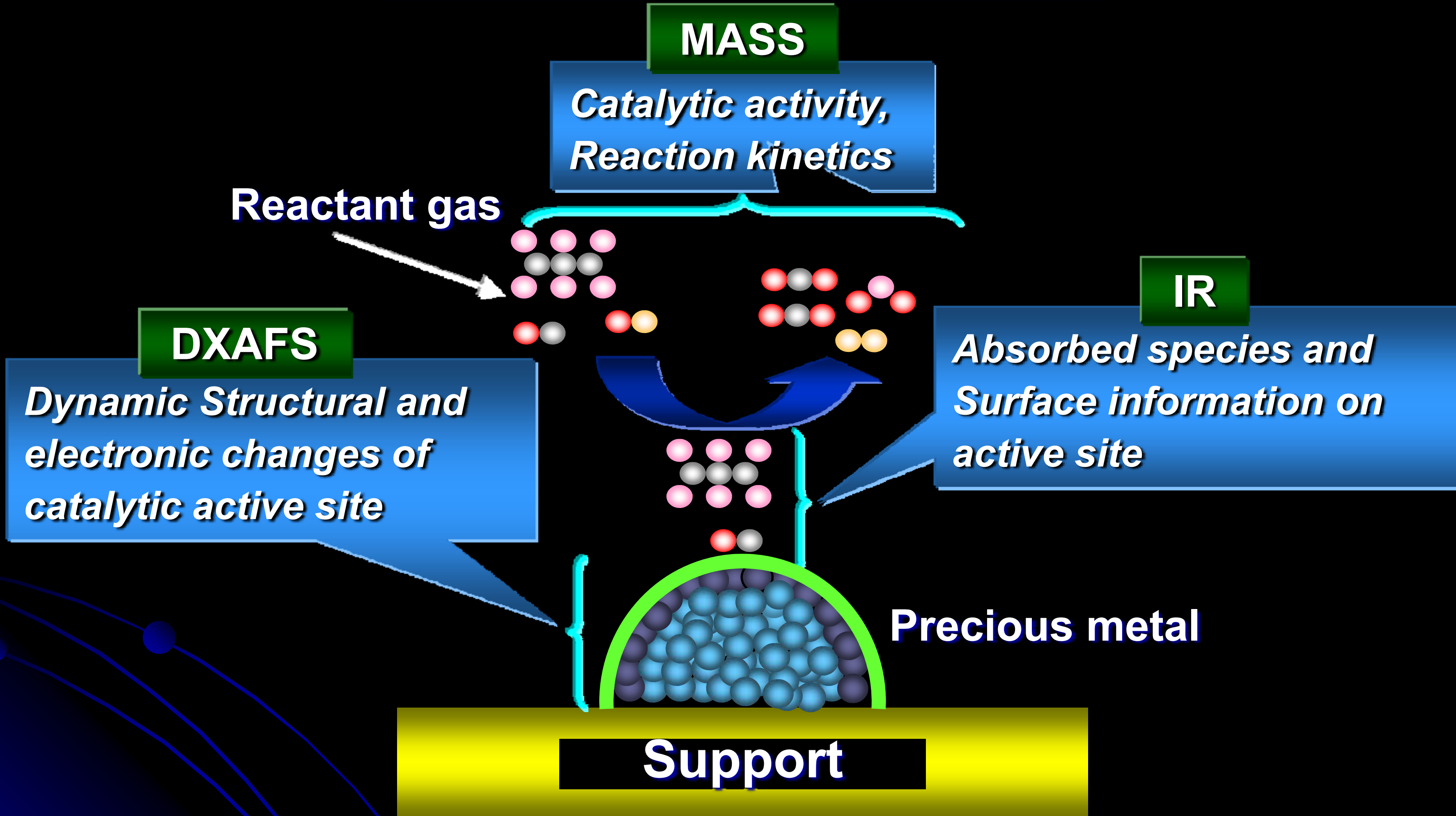


Adsorbate behaviour (DRIFTS)



M. A. Newton, Topics in Catal, 2009, in press

Obtainable Information



Synchronised DXAFS-IR-Mass system is an "Ultimate Operando System" for heterogeneous catalysis.

Acknowledgments

ESRF

Bernard Gorges, Olivier Mathon, Sebastien Pasternak, Florian Perrin, Steven Fiddy

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TOYOTA Motor North America

Paul Fanson

TOYOTA Motor Corp.

Takeshi Hirabayashi, Masahide Miura, Keisuke Kishita

TOYOTA Central R&D

Takamasa Nonaka, Satoshi Yamaguchi, Naoki Takahashi, Yoshiki Seno

~Towards a clean future~