In situ X-ray Absorption Spectroscopy Study on Water Formation Reaction of Palladium Metal Nanoparticle Catalysts

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Background

Hydrogen generation at nuclear power plant

○Radiolytic decomposition of water

○Reduction reaction of water molecules on a surface of zirconium alloy cladding of a fuel rod

Severe accident at Fukushima nuclear power plant: **Hydrogen explosion**

Hydrogen management system using external electric power could not work due to shut down of all outside electric supplies

↓

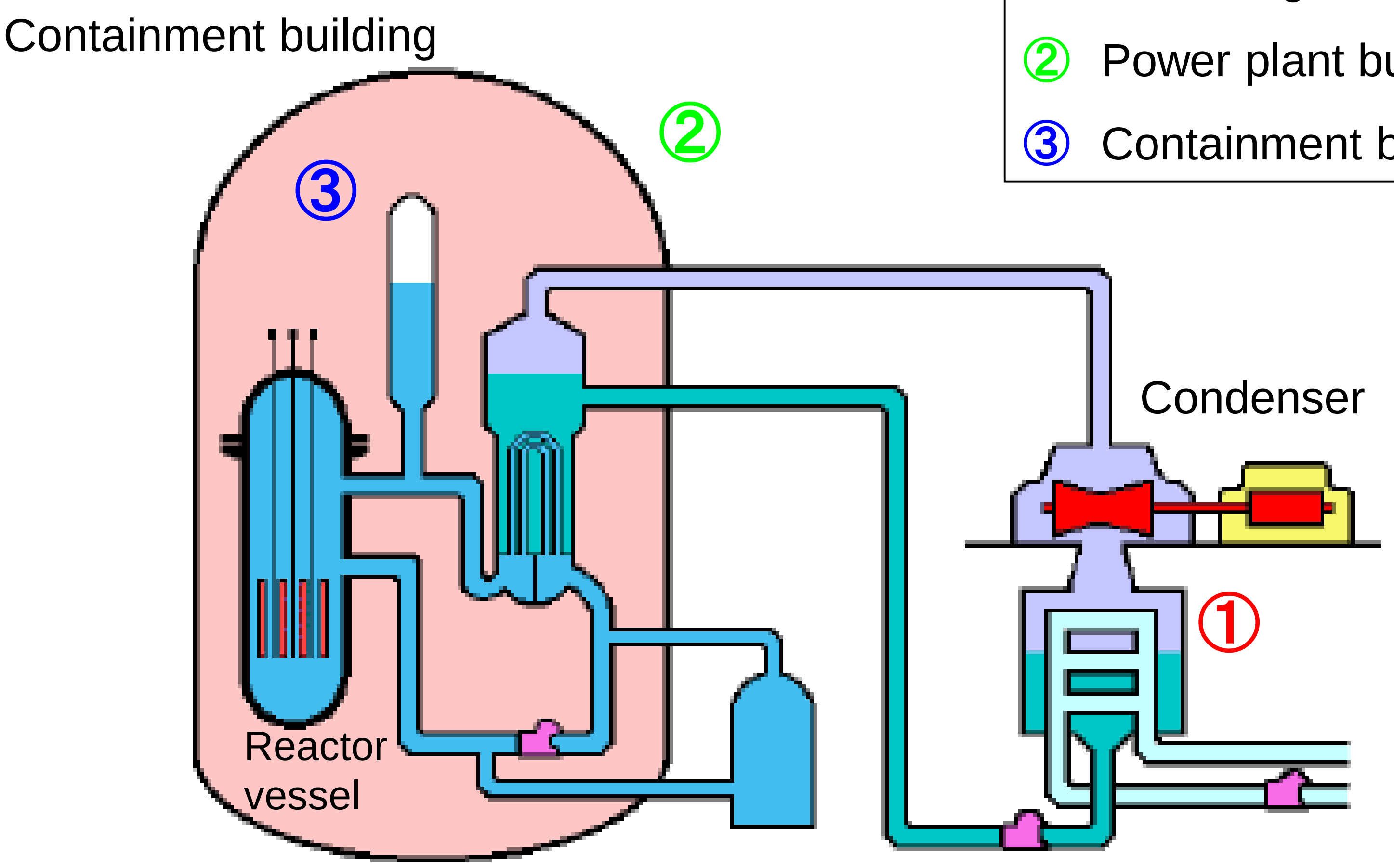
Needs of catalyst without electric power supply for hydrogen management

Passive Autocatalytic Recombiner (PAR)

Hydrogen recombination reaction (water formation reaction) $H_2 + 1/2O_2 = H_2O$

Precious metal nanoparticle such as Pd is used

Water formation catalysts



① Exhaust gas line

② Power plant building

③ Containment building

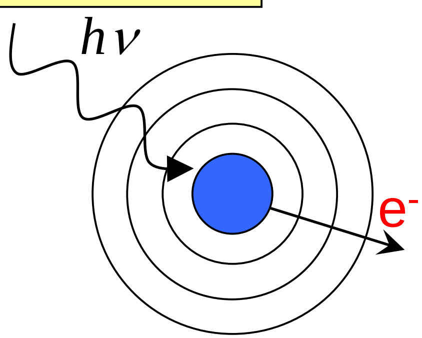
③ In containment building, CO generation is assumed in severe accident

→ **CO poisoning effect of water formation** reaction should be studied

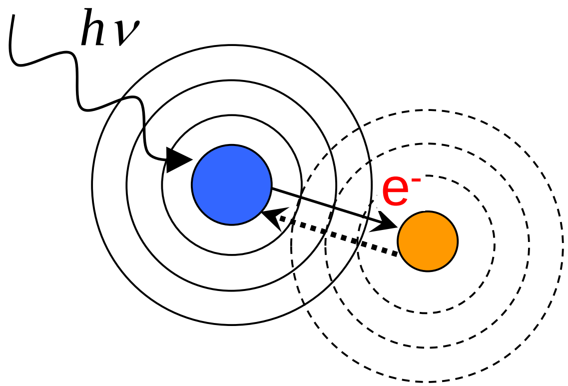
→ Structural change of Pd nanoparticles during catalytic reaction is studied by **in situ and real-time-resolved X-ray Absorption Fine Structure (XAFS)**

Method: XAFS（X-ray Absorption Fine Structure）

Principle



Isolated atom

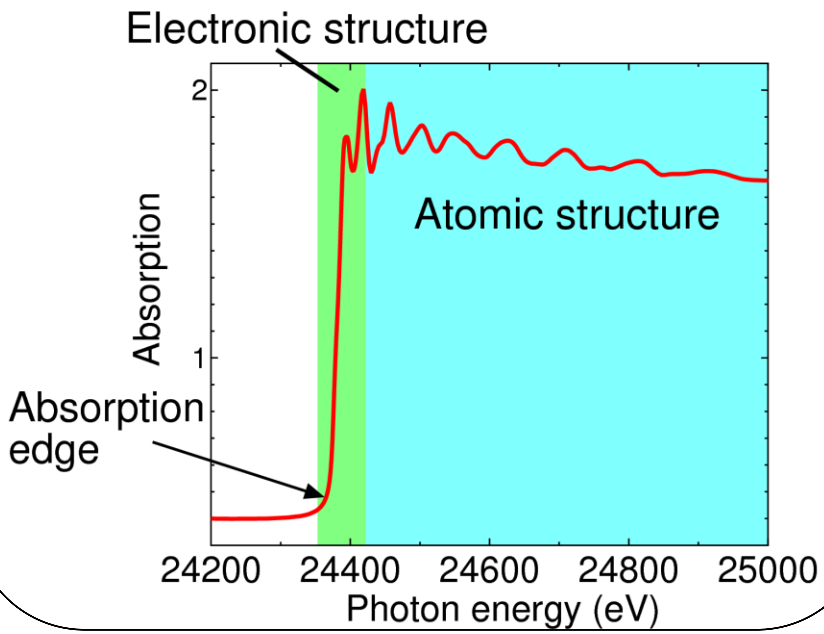


With neighbor atoms

Interference of scattered photoelectron waves from neighbor atoms

Fine structure in absorption spectroscopy

XAFS spectroscopy



Feature

- Element selectivity
- Local sensitivity

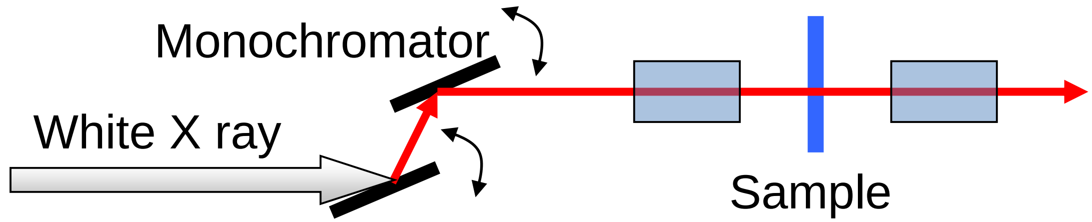
Even under 1% element is selectively observed

→ Good for catalyst

Dispersive optics

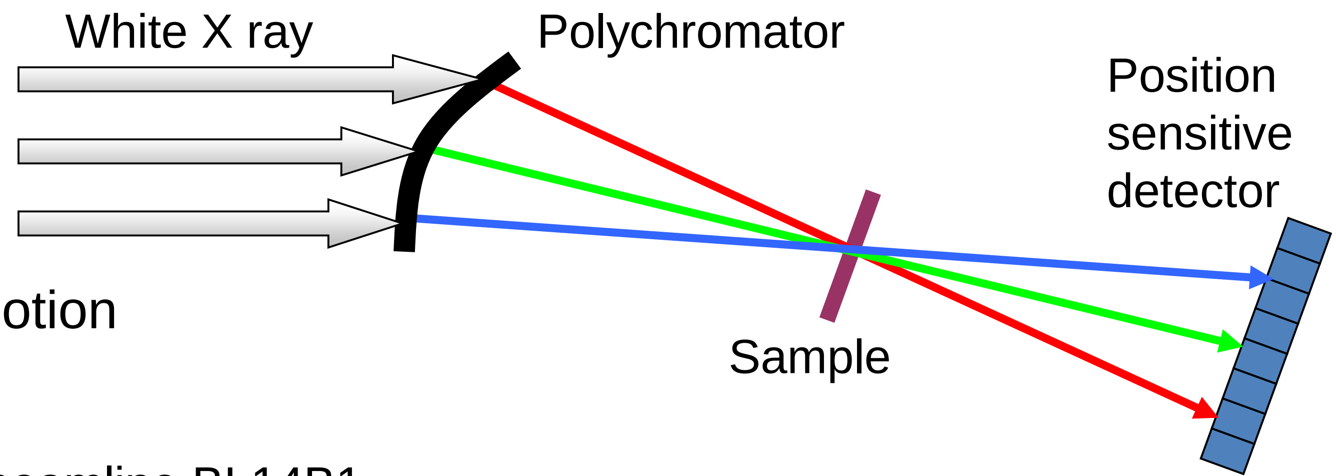
Inner shell spectroscopy

Conventional XAFS



Motion of monochromator

Dispersive XAFS



No mechanical motion

SPring-8 (Japan), beamline BL14B1

Fast and Stable XAFS

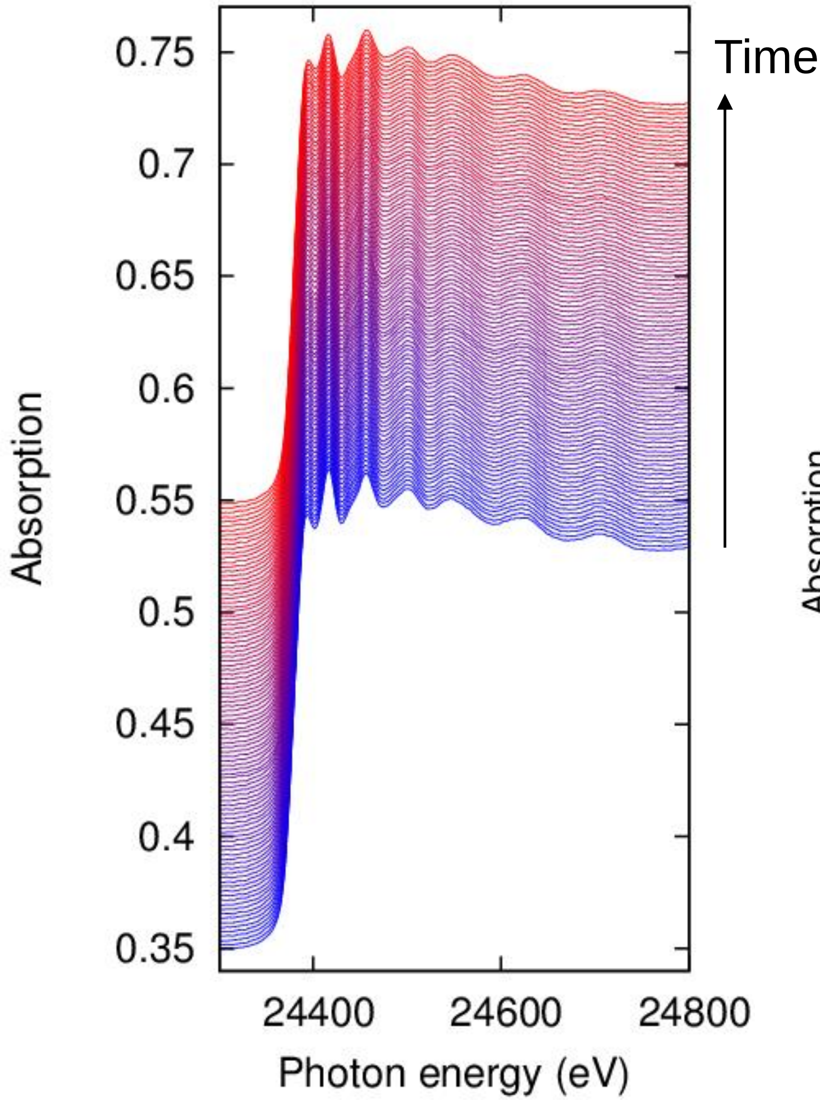
→ In situ and Real-time-resolved XAFS

Real-time-resolved XAFS

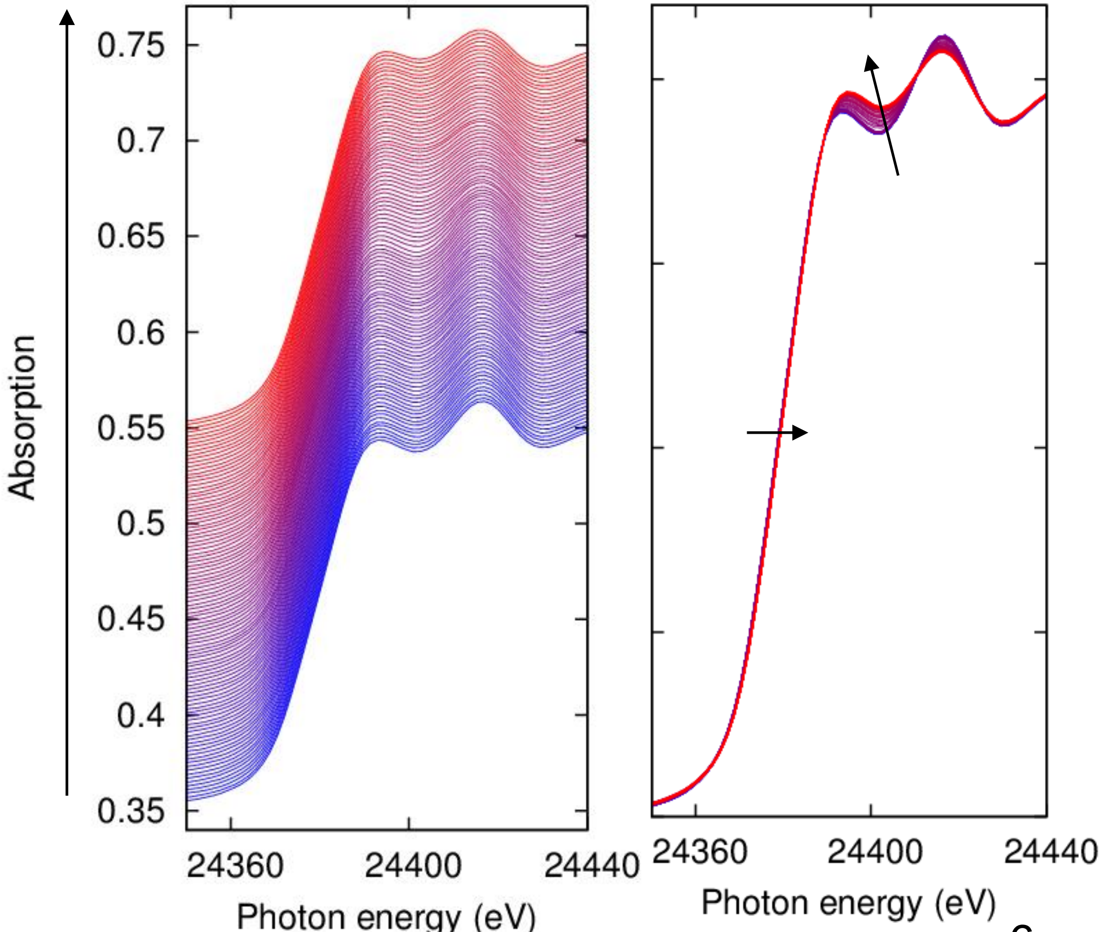
Dispersive optics, Si(422), Pd K-edge

SPring-8 BL14B1, 2 Hz observation

Ex.) Pd(4 wt%)/Al_2O_3

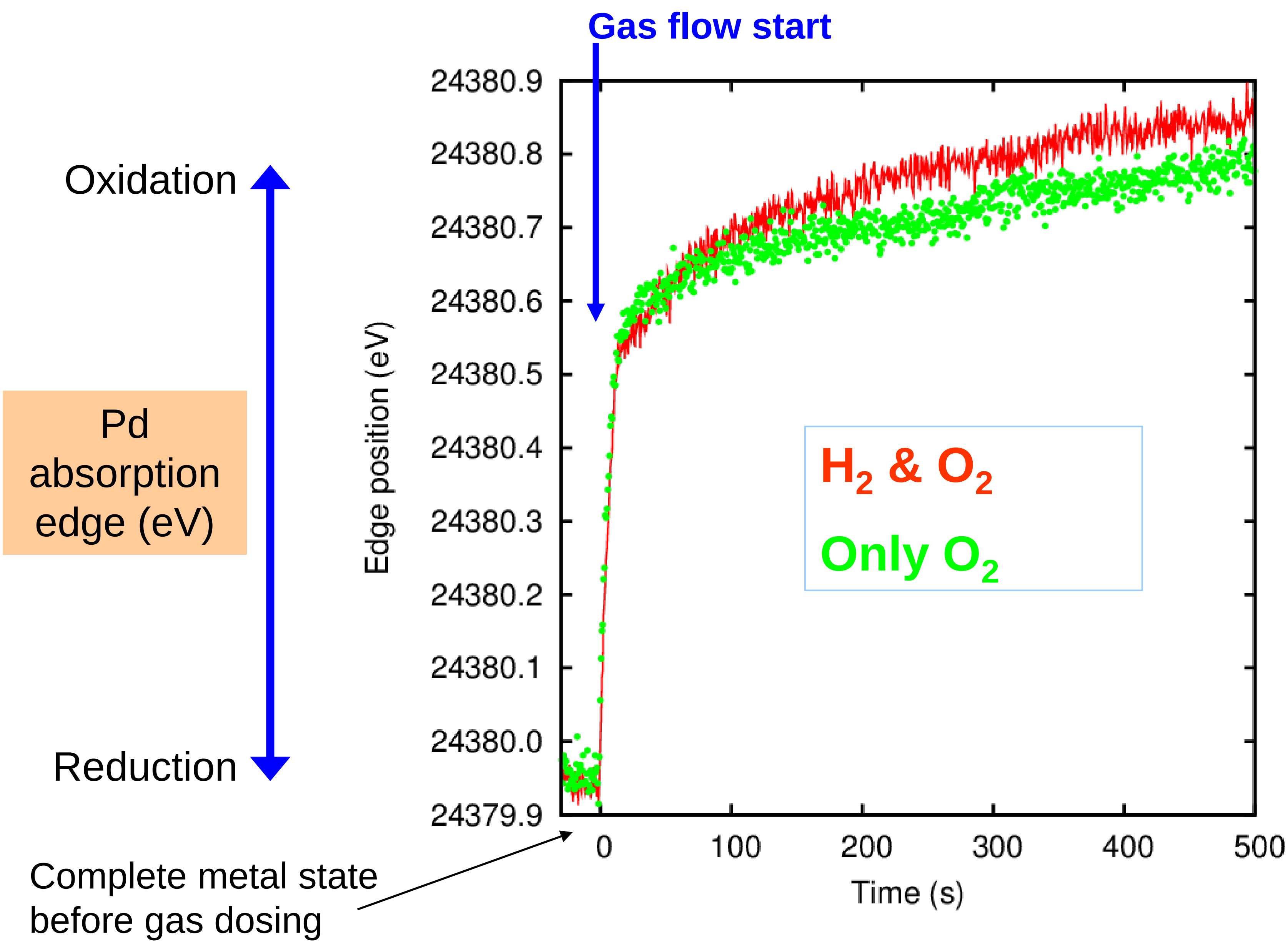


Change of spectra during water formation reaction



Absorption edge change

Sample : $Pd(2wt\%)/Al_2O_3$

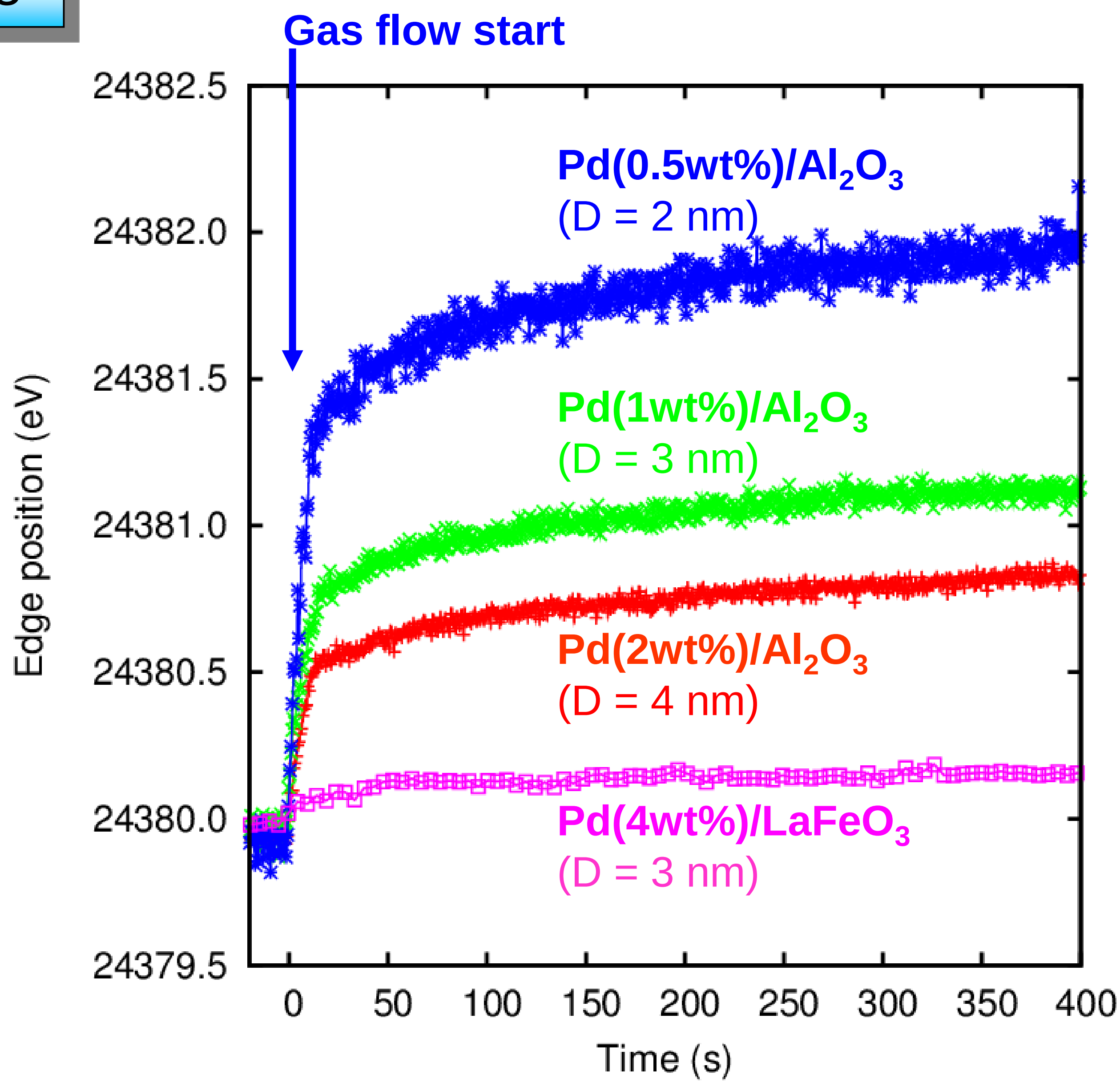


Sample dependence

Room temperature,
H_2 and O_2 reaction

Pd/Al_2O_3:
Surface oxide layer creation for all nanoparticles

$Pd/LaFeO_3$:
Less creation of oxide layer

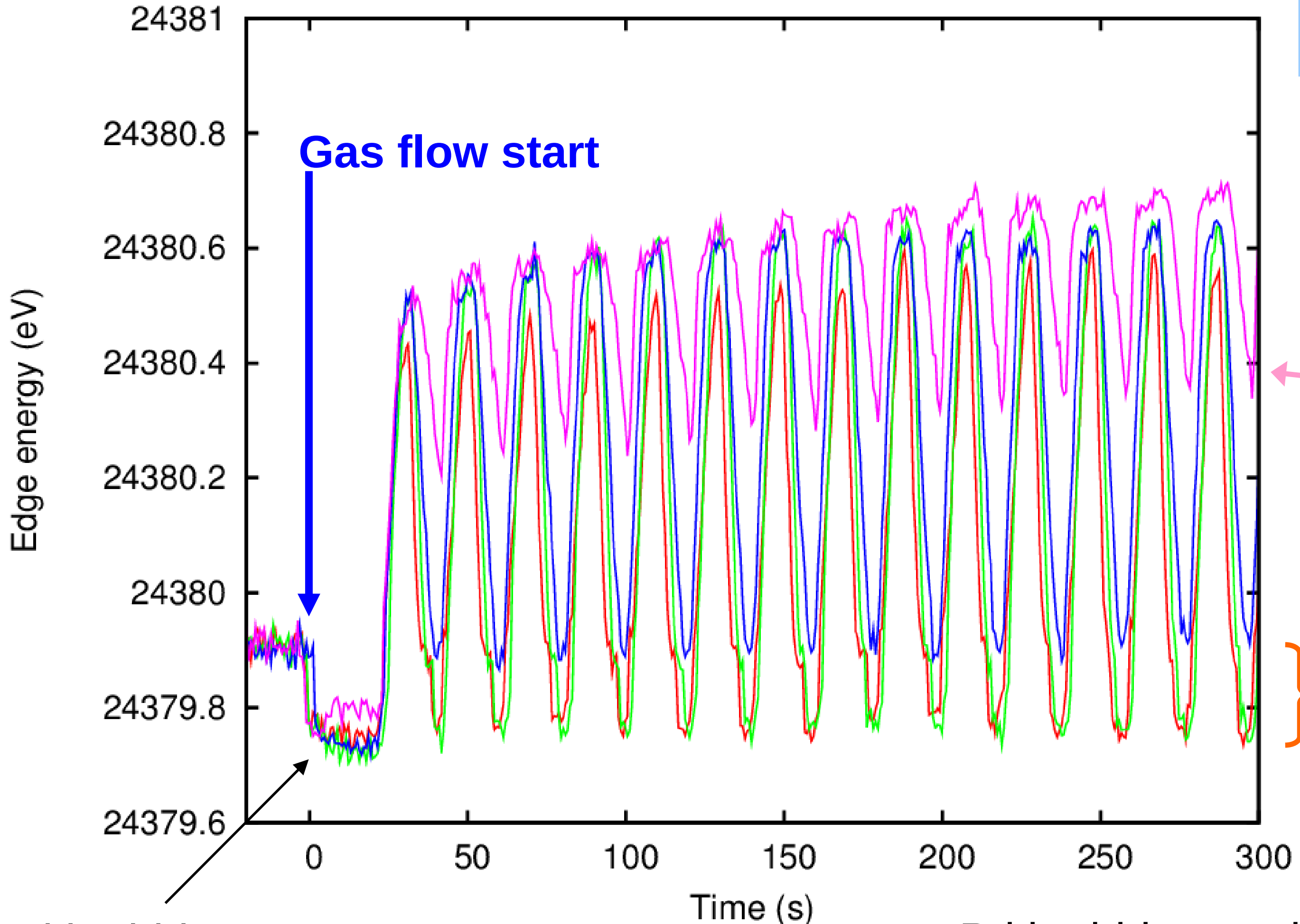


→ <u>Correlation between surface oxide layer and catalysis</u>

Gas switching test: pressure dependence

Pd(2wt%)/Al_2O_3, room temperature

$H_2 \rightarrow O_2 \rightarrow H_2 \rightarrow O_2 \rightarrow \ldots$ 10 s gas switching



H_2/O_2=10%/2%
H_2/O_2=10%/4%
H_2/O_2=5%/4%
H_2/O_2=2%/4%

H_2/O_2=2%/4%: Half of oxide layer was removed

Pd hydride creation

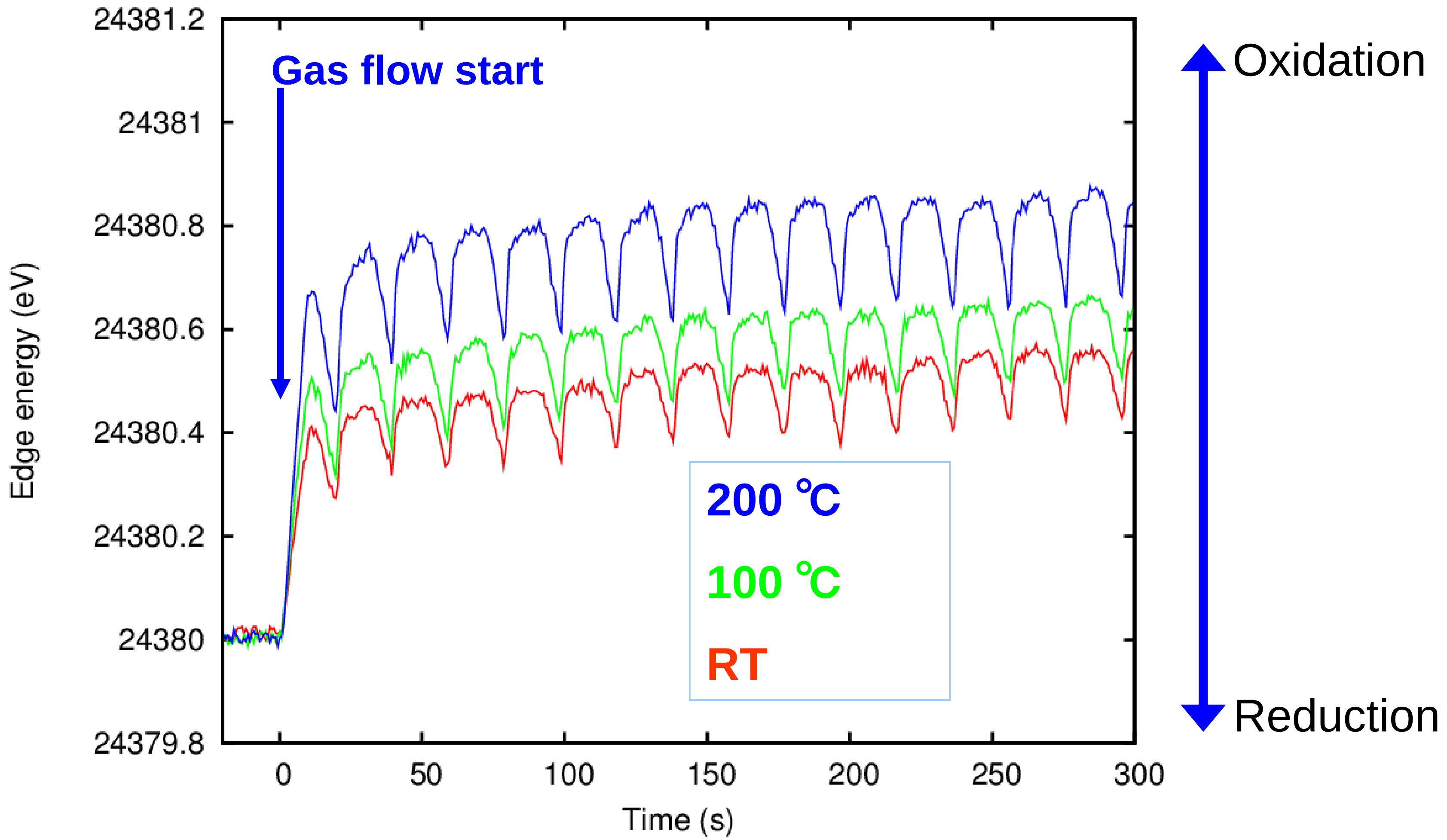
Pd hydride creation in case of hydrogen excess condition

Gas switching test: temperature dependence

$Pd(2wt\%)/Al_2O_3$

$H_2/O_2=2\%/4\%$

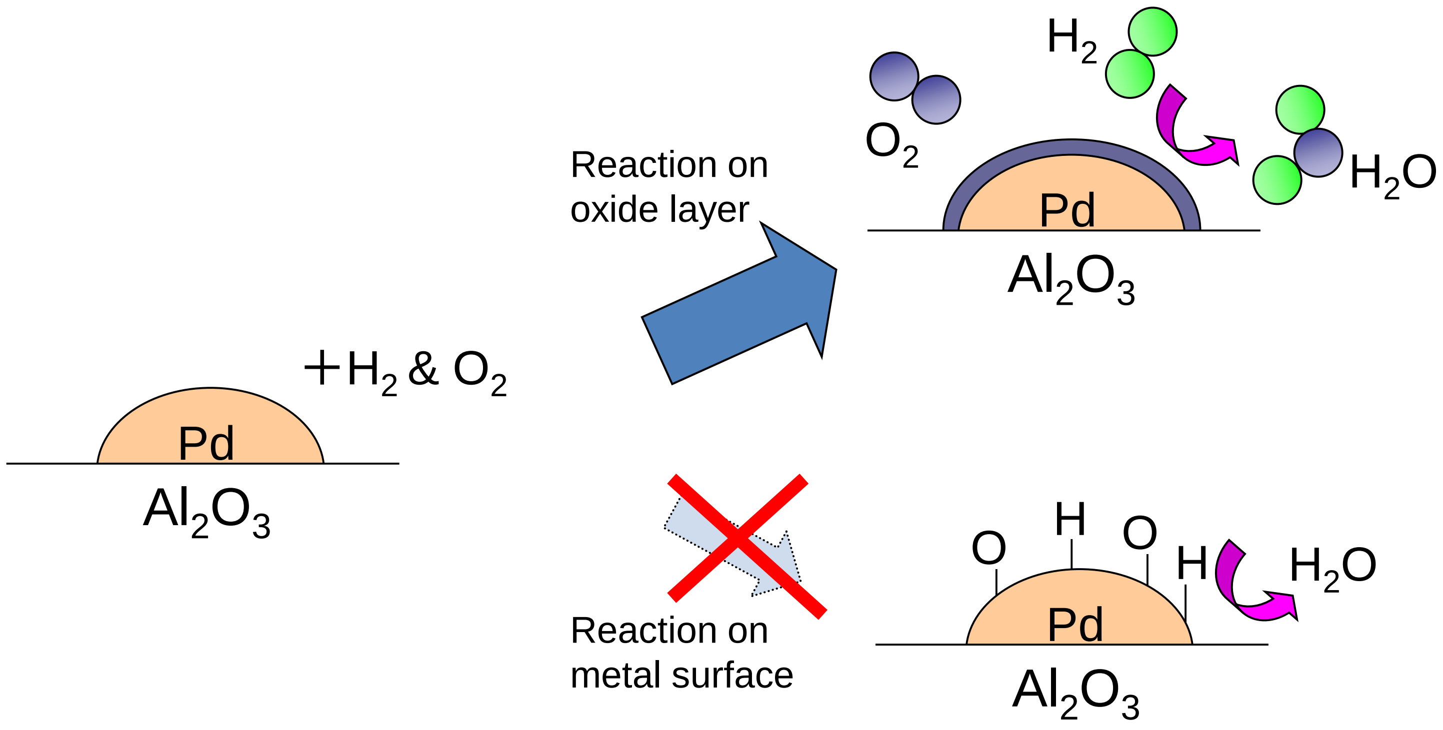
$O_2 \rightarrow H_2 \rightarrow O_2 \rightarrow \ldots$ 10 s gas switching



Temperature increase (Catalysis increase) → Oxide layer growth

Reaction model

Oxide layer is created in both cases of “H_2 and O_2” and “Only O_2”
→
After creation of surface oxide layer, water formation reaction proceeds



Surface oxide layer creation of Pd nanoparticles
should be studied

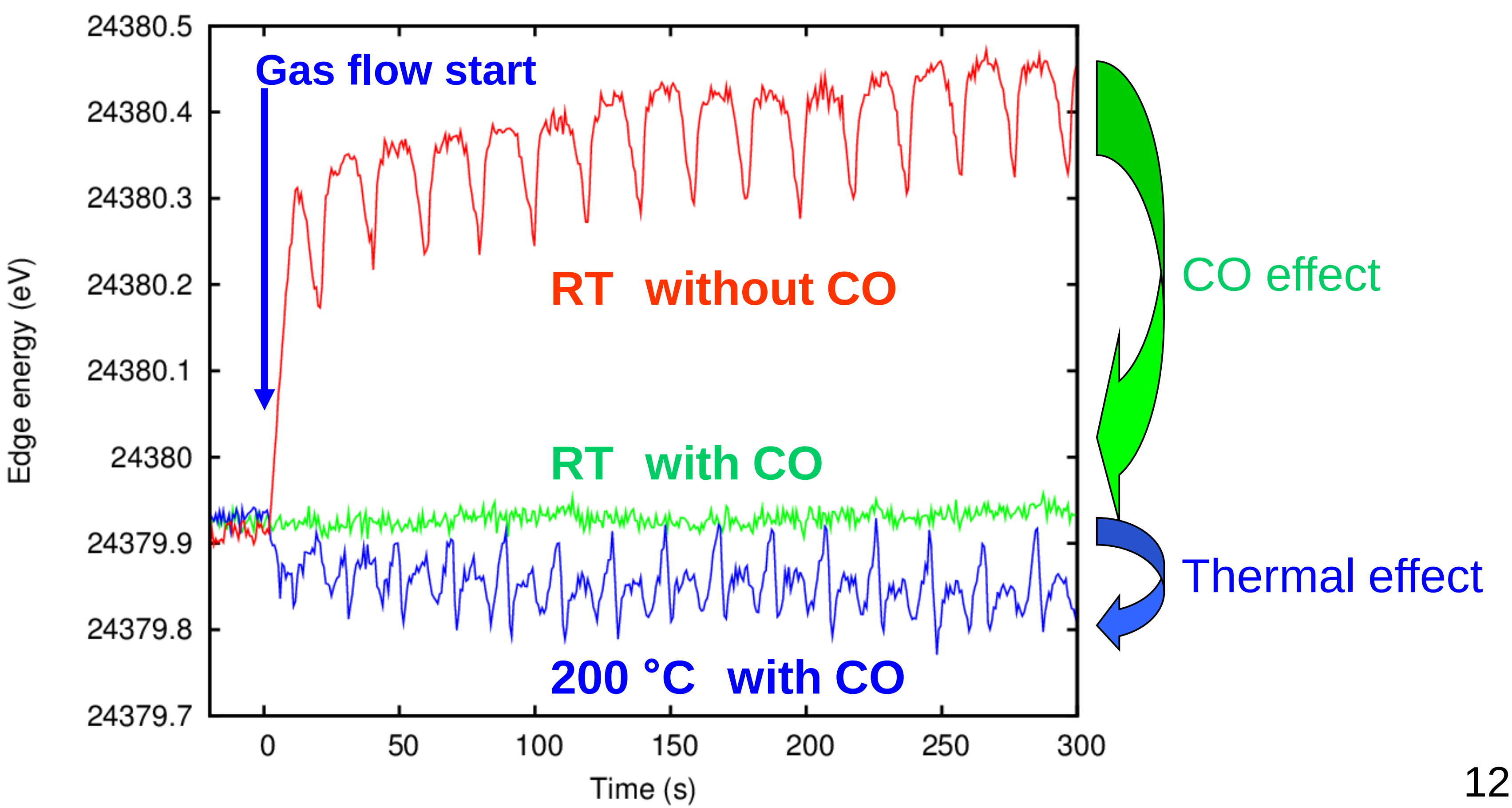
Gas switching test: CO effect

$Pd(2wt\%)/Al_2O_3$

H_2/O_2=2%/4%

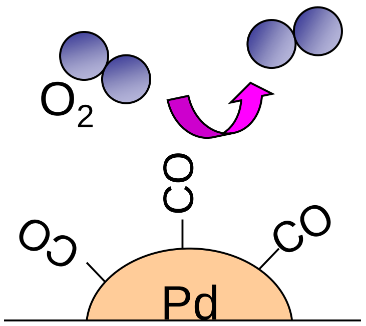
Severe accident → High temperature → <u>CO generation</u>

$O_2 \rightarrow H_2 \rightarrow O_2 \rightarrow \ldots$ 10 s gas switching

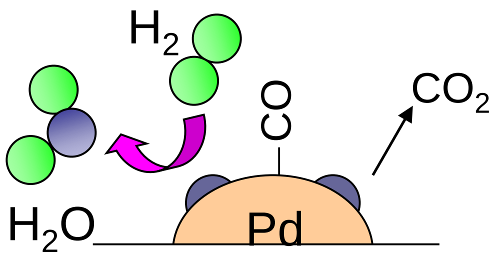


CO poisoning for Pd

Reaction proceeds on oxide layer



CO adsorption blocks O_2 adsorption → Stop of water formation reaction



Over 200 °C,

$CO + 1/2O_2 = CO_2$

reaction starts. → Water formation reaction also starts.

→ Competition of oxidation reactions of H_2 and CO is now being examined

Summary

Structure of Pd nanoparticle during water formation reaction was studied by in situ and real-time-resolved XAFS

・Creation of surface oxide layer of Pd nanoparticle is important for water formation catalytic reaction

・Reaction mechanism of water formation reaction and CO poisoning effect were revealed.

Further experiment will assist the development of passive autocatalytic recombiner for nuclear plant.

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