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

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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)  \[ H_2 + \frac{1}{2}O_2 = H_2O \]

Precious metal nanoparticle such as Pd is used
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**
- Interference of scattered photoelectron waves from neighbor atoms
- Fine structure in absorption spectroscopy

**XAFS spectroscopy**
- Electronic structure
- Atomic structure

**Feature**
- Element selectivity
- Local sensitivity

Even under 1% element is selectively observed
→ Good for catalyst
Dispersive optics

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

Ex.) Pd(4 wt%)/Al₂O₃

Dispersive optics, Si(422), Pd K-edge
SPring-8 BL14B1, 2 Hz observation

Change of spectra during water formation reaction
Absorption edge change

Sample: Pd(2wt%)/Al₂O₃

Oxidation

Pd absorption edge (eV)

Gas flow start

Reduction

Complete metal state before gas dosing

H₂ & O₂

Only O₂
Room temperature, $\text{H}_2$ and $\text{O}_2$ reaction

**Pd/Al$_2$O$_3$:** Surface oxide layer creation for all nanoparticles

**Pd/LaFeO$_3$:** Less creation of oxide layer

→ Correlation between surface oxide layer and catalysis
Gas switching test: pressure dependence

\[ \text{Pd(2wt\%)/Al}_2\text{O}_3, \text{ room temperature} \]

H\(_2\) → O\(_2\) → H\(_2\) → O\(_2\) → … 10 s gas switching

**Pd hydride creation**

**Pd hydride creation in case of hydrogen excess condition**

- \(\text{H}_2/\text{O}_2=10\%/2\%\)
- \(\text{H}_2/\text{O}_2=10\%/4\%\)
- \(\text{H}_2/\text{O}_2=5\%/4\%\)
- \(\text{H}_2/\text{O}_2=2\%/4\%\)

**Gas flow start**

- \(\text{H}_2/\text{O}_2=2\%/4\%:\)
  - Half of oxide layer was removed
Gas switching test: temperature dependence

Pd(2wt%)/Al₂O₃

H₂/O₂=2%/4%

O₂→H₂→O₂→… 10 s gas switching

Temperature increase (Catalysis increase) → Oxide layer growth

Oxidation
Reduction
Oxide layer is created in both cases of “H₂ and O₂” and “Only O₂”

→

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

Severe accident → High temperature → CO generation

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

Gas flow start

RT without CO

RT with CO

200 °C with CO

CO effect

Thermal effect

Pd(2wt%)/Al$_2$O$_3$

$H_2/O_2=2\%/4\%$
CO poisoning for Pd

Over 200 °C, 
CO + 1/2O₂ = CO₂
reaction starts.

Stop of water formation reaction

Reaction proceeds on oxide layer

Water formation reaction also starts.

Competition of oxidation reactions of H₂ and CO is now being examined
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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