International Conference on Hydrogen Safety (ICHS) · Québec · hySafe International Association for Hydrogen Safety · RQEI Réseau québécois sur l'énergie intelligente

Hydrogen Passive Autocatalytic Recombiner (PAR) overcoming CO Poisoning

STACY.

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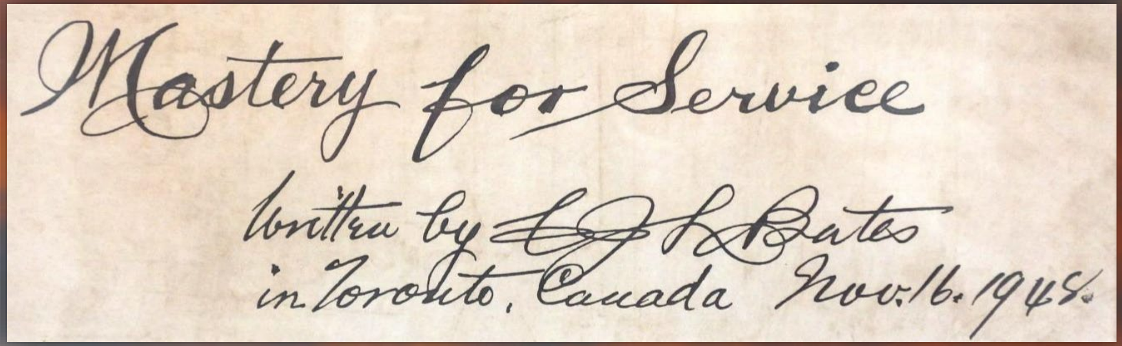
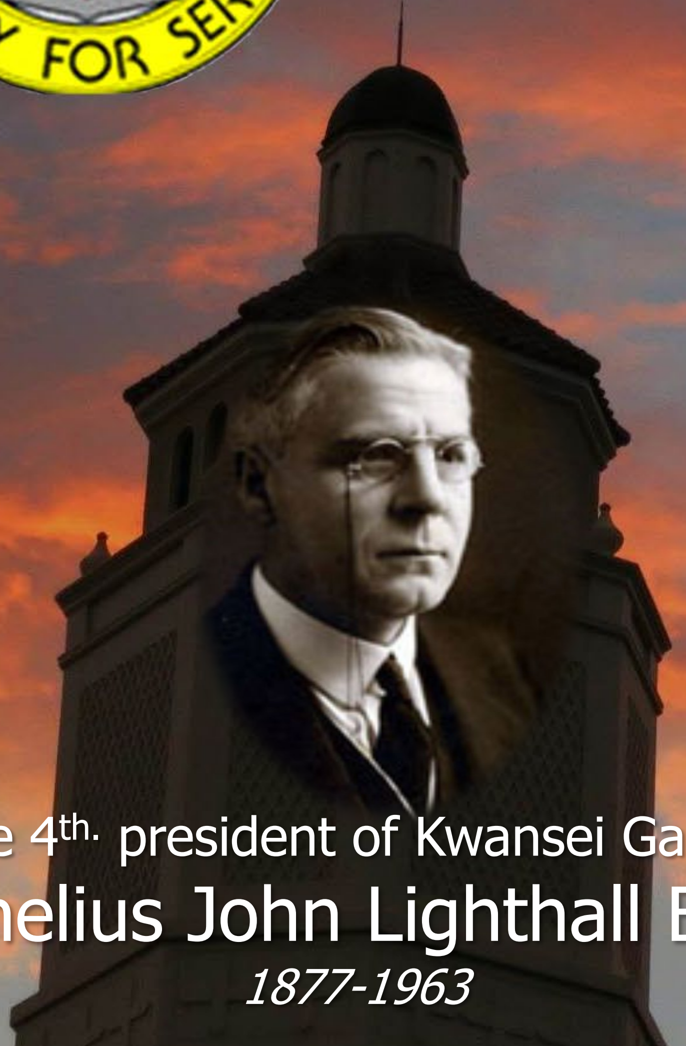
2: Daihatsu Motor Co., Ltd. (DMC), Japan
3: Japan Atomic Energy Agancy (JAEA), Japan
4: Institute de Radioprotection et de Sûreté Nucléaire (IRSN), France
5: Centre National de la Recherche Scientifique (CNRS), France
6: Forschungszentrum Jülich (FZJ), Germany

Kwansei Gakuin University


Mastery for Service
written by C. J. L. Bates
in Toronto, Canada Nov: 16. 1948.

"Mastery for Service"

the school motto of Kwansei Gakuin
reflects the ideal for all its members
to master their abundant God-given gifts
to serve their neighbors, society and the world.



The 4th. president of Kwansei Gakuin
Cornelius John Lighthall Bates
1877-1963

Today's course meal (Agenda)

MENU

1. Appetizer
   - Introduction to STACY Project

2. Soup
   - Passive Autocatalytic Recombiner and Automotive Catalyst
   - PAR for Liquified Hydrogen (LH2)

3. Main Dishes
   - Poisson — Catalytic Performance Evaluation
   - Meat — Synchrotron radiation analysis

4. Café & Dessert
   - Future Aspirations

JÜLICH Forschungszentrum

Centre National de la Recherche Scientifique

IRSN INSTITUT DE RADIOPROTECTION ET DE SÛRETÉ NUCLÉAIRE

KWANSEI GAKUIN UNIVERSITY

STACY

Towards Safe Storage and Transportation of Cryogenic Hydrogen

STACY.

European Interest Group (EIG) CONCERT-Japan

STACY: international collaboration

JÜLICH Forschungszentrum

KWANSEI GAKUIN UNIVERSITY

WP3: Catalytic recombination
WP5: Coordination and Dissemination

Dr. Ernst-Arndt Reinecke
FZJ, Germany

Project management
Hydrogen recombiners,
involved in industrial recombiner development and recombiner qualification

WP3:Catalytic recombination

Prof. Hirohisa Tanaka
KGU, Japan

Design of catalyst, Catalytic cryogenic reaction experiment, Synchrotron radiation analysis
involved in industrial recombiner development

WP1: Critical review & scenario identification
WP4: Application: Safety methodology assessment

Dr. Ahmed Bentaib
IRSN, France

Hydrogen safety assessment in nuclear power plants, involved in development of safety assessment methodologies and risk prevention procedures

WP2: Combustion fundamentals

Dr. Nabiha Chaumeix
CNRS-INSIS, France

Flame and explosion dynamics,
Explosion safety,
involved in industrial projects and research programs

IRSN INSTITUT DE RADIOPROTECTION ET DE SÛRETÉ NUCLÉAIRE

CNRS Centre National de la Recherche Scientifique

Industrial Advisory Board (IAB)

JAPAN

- Kawasaki Heavy Industry
- Daihatsu Motor
- Japan Atomic Energy Agency

GERMANY

- Chemical Consulting Dornseiffer
- EnerSys, Hawker

FRANCE

- Air Liquide/ France

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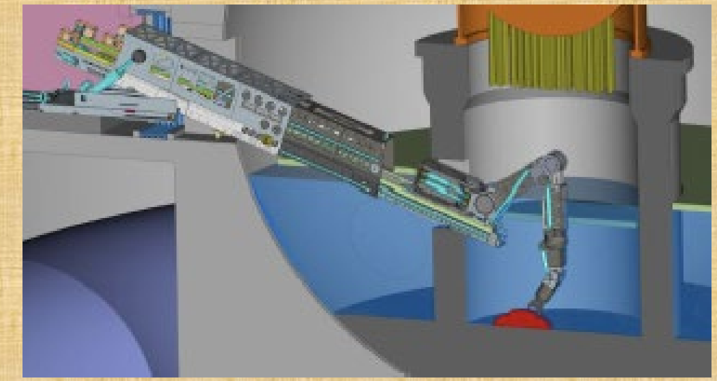
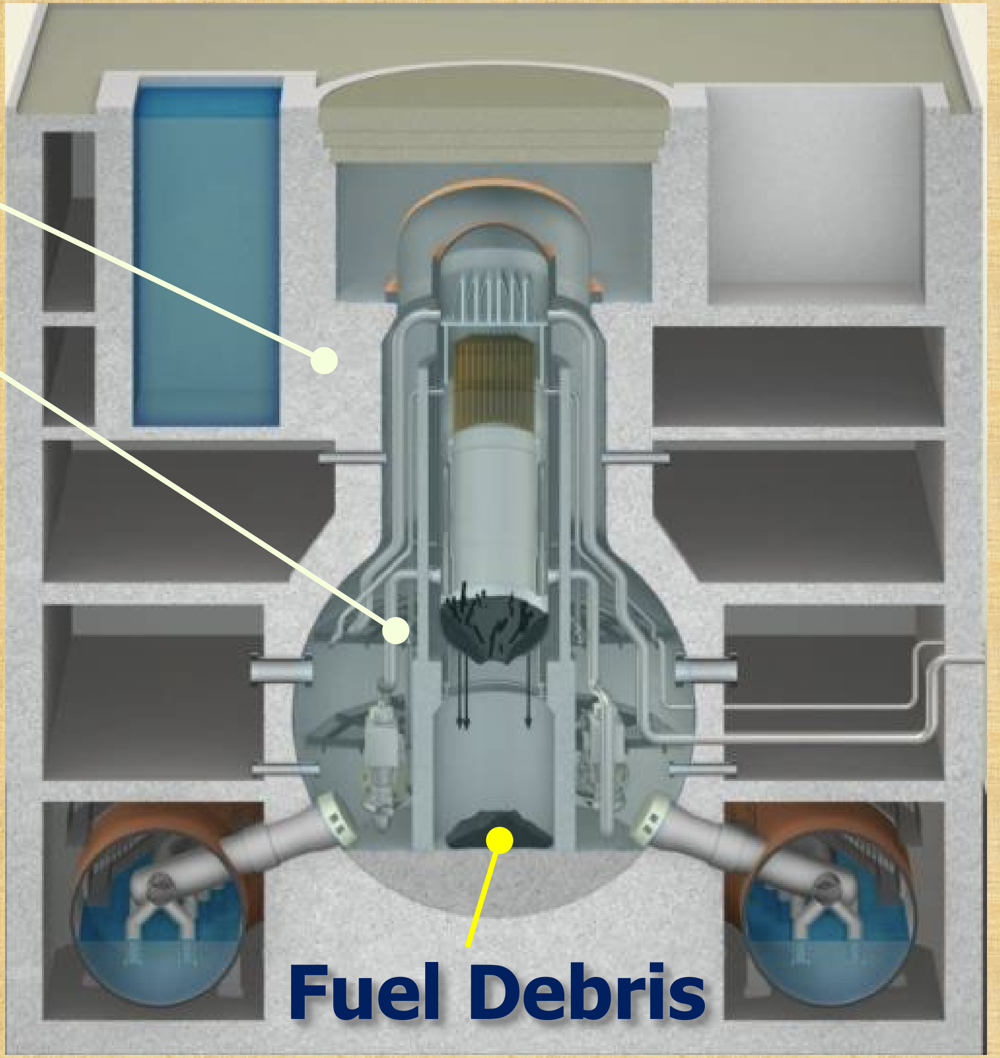
MENU

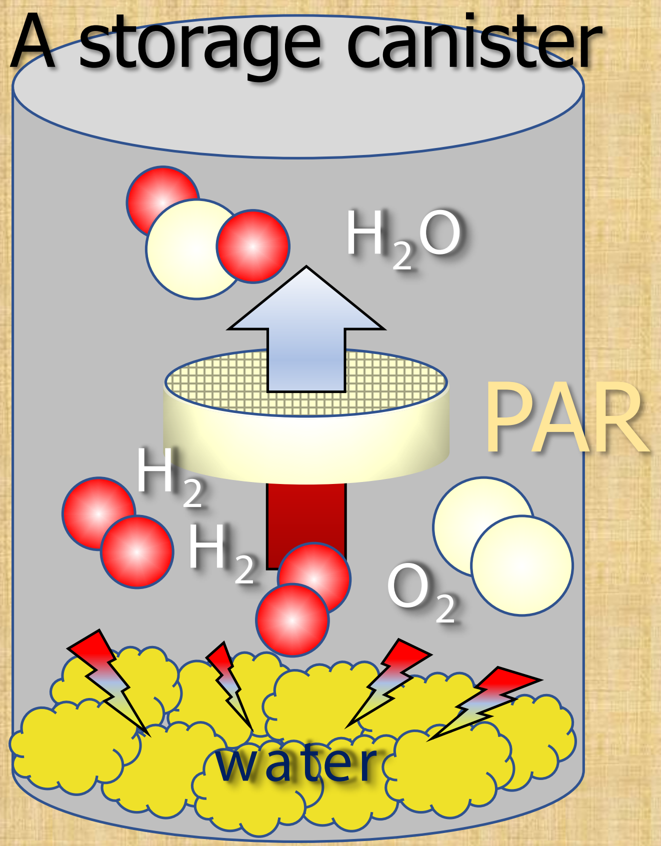
Passive Autocatalytic Recombiner (PAR)

Primary Containment Vessel (PCV)

Reactor Pressure Vessel (RPV)





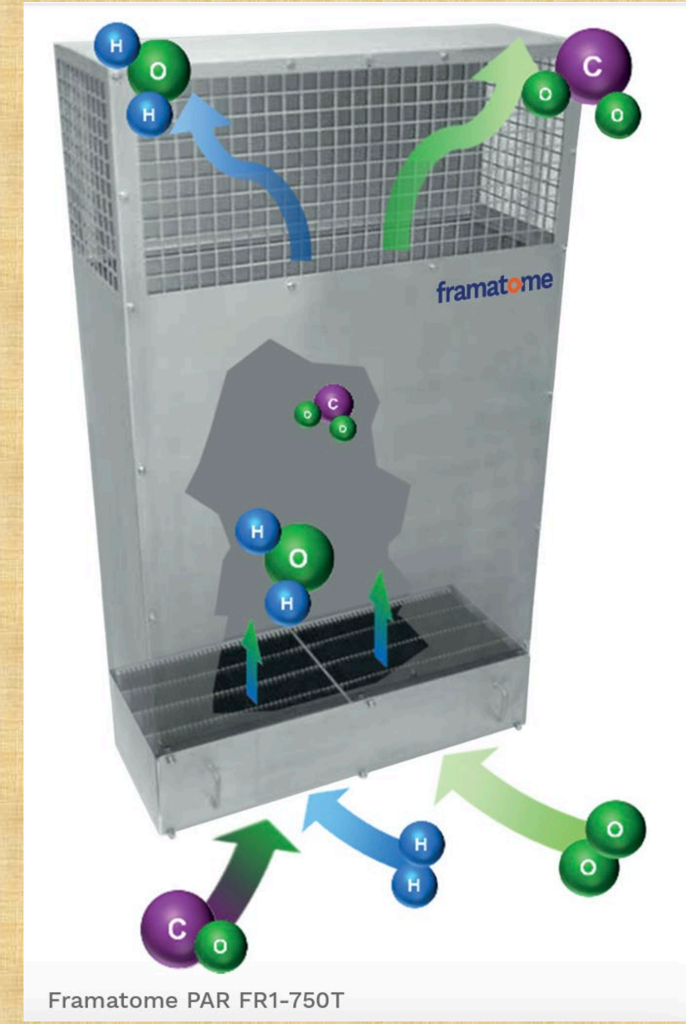


Fuel Debris

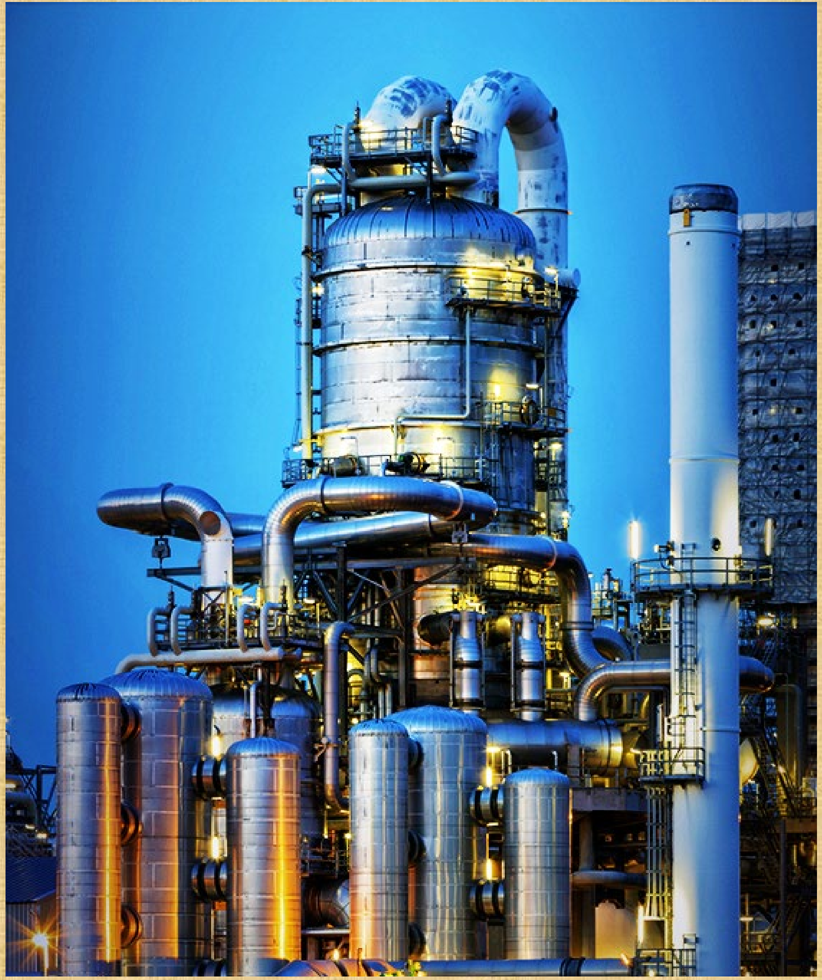
Decommissioning of Fukushima Daiichi (1F)

Fuel debris retrieval / transportation / long-term storage technology

PAR vs Catalysts in Plants



Framatome PAR FR1-750T



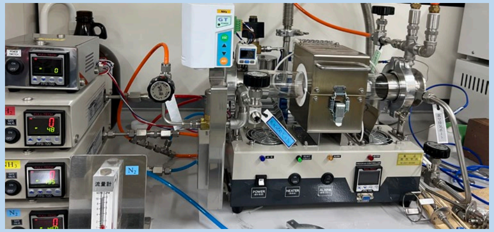
https://appliedcatalysts.com/cat-serv/catalyst-manufacturing/

Robustness in uncontrolled environments
Performance under the worst conditions

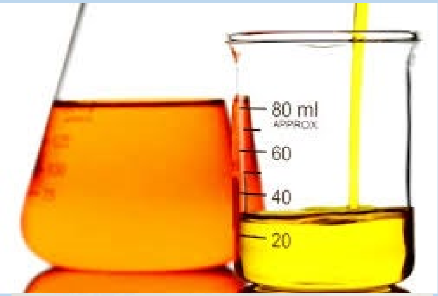
Catalyst Preparation

High Performance PAR

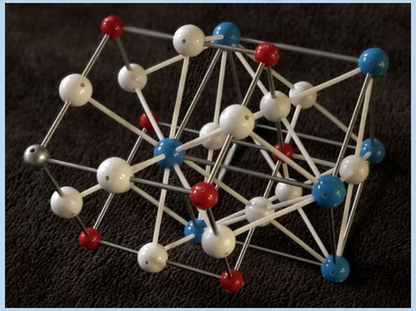
Preparation Method

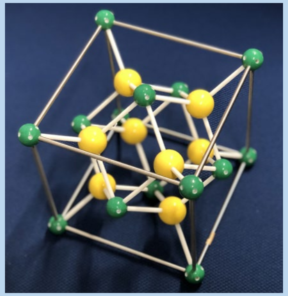


Materials



Crystal Design





Delicious Cakes

Cooking Method

Ingredients

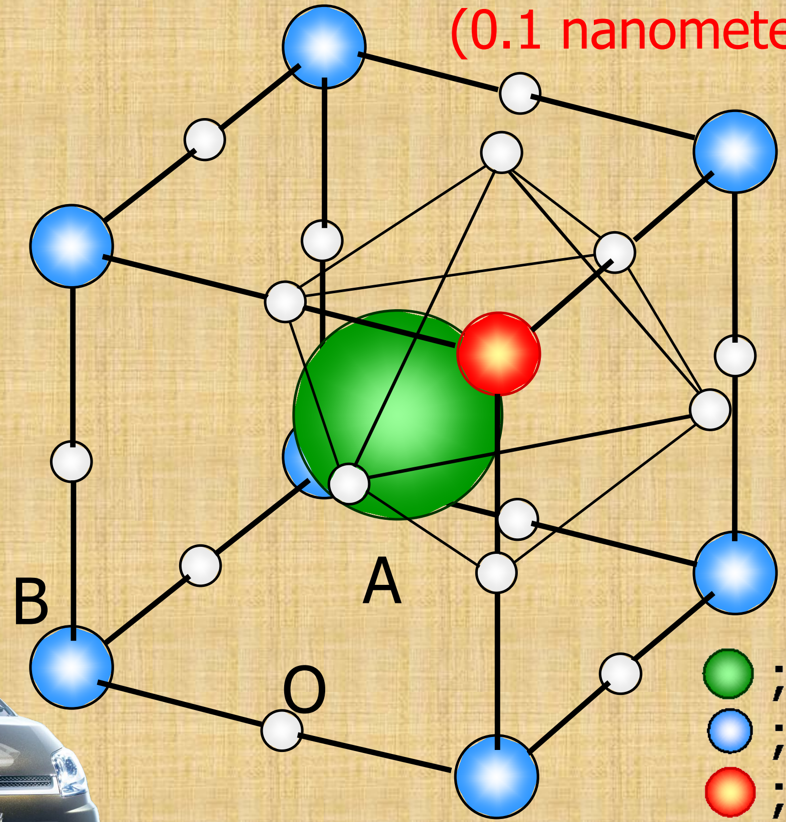
Materials Origin

An Intelligent Catalyst with self-regeneration function

Perovskite-type oxide (ABO_3)

Vol.418, pp.164-167
11 July 2002

Cationic Pd
(0.1 nanometer)



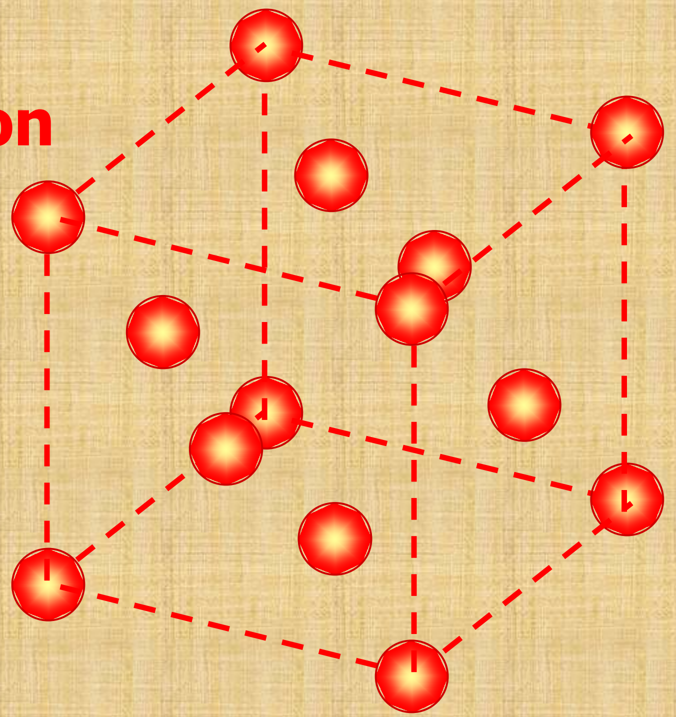
- ; A-site (La)
- ; B-site (Fe)
- ; B-site (Pd)
- ; Oxygen

Self-healing
Solid solution
(Oxidative)

Self-regeneration

Segregation
(reductive)
Self-forming

Metallic Pd
nano-particle
(1 nanometer)



J-SULEV

PGM nano-particles are dispersed as smaller sub-nano cations while in the inherent redox fluctuation of the automotive exhaust.
It has been installed in 6.5 million Toyota and Daihatsu SULEV vehicles.

PAR for Liquified Hydrogen (LH2)

Characteristics of liquid hydrogen		Safety Issues	Requirements for PAR
1	-253 °C = 20 K	Cryogenics	Enhanced catalytic activity
2	High energy density	Ignition	Suppression of catalytic activity
3	High expansion (in case of leakage)	High flow rate	Accelerated catalytic response

Adverse environmental		Safety Issues	Requirements for PAR
1	Long-term exposure (During use)	PGM Surface oxidation	Persistence of anti-oxidation
2	Mounting position (Deck, Engine room)	Sea breeze / Oil mist / Sunlight	Improvement of geometric design, catalyst configuration and materials
3	Fire spread from others	CO poisoning	Resistance to catalyst poisoning Utilizing technology accumulation

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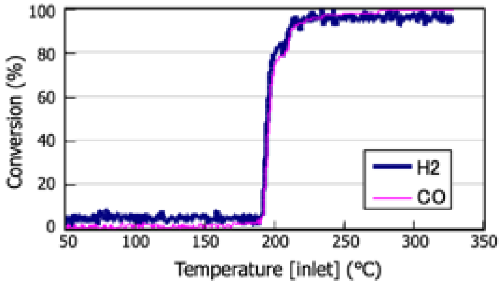
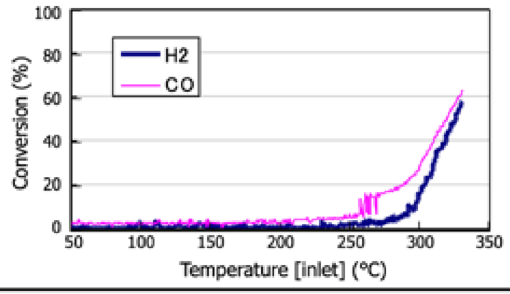
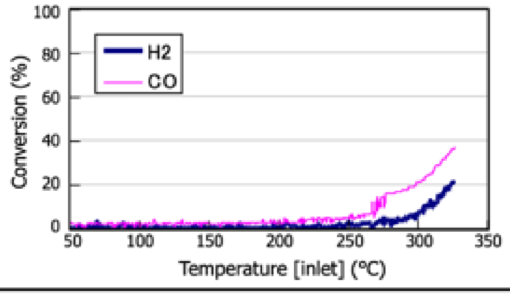
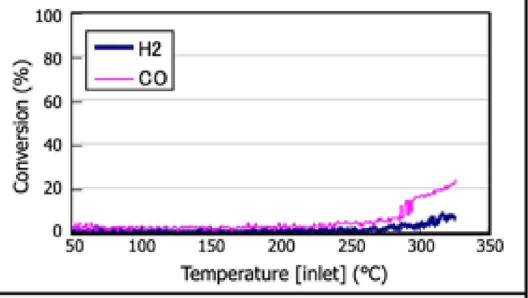
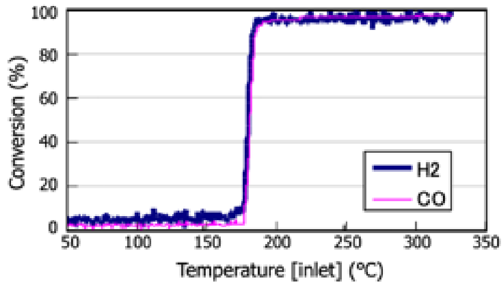
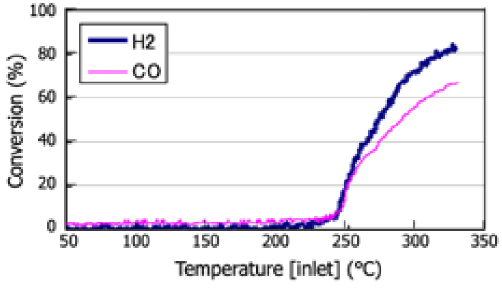
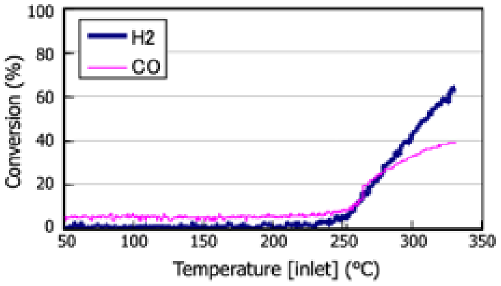
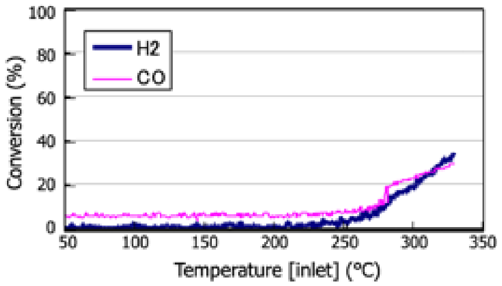
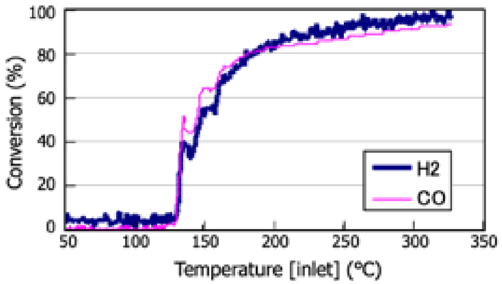
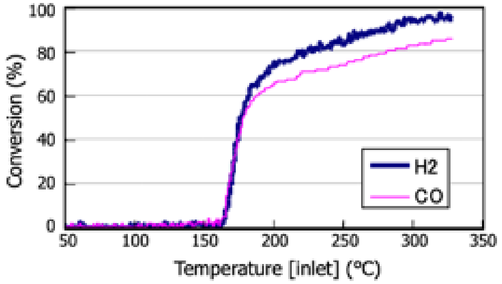
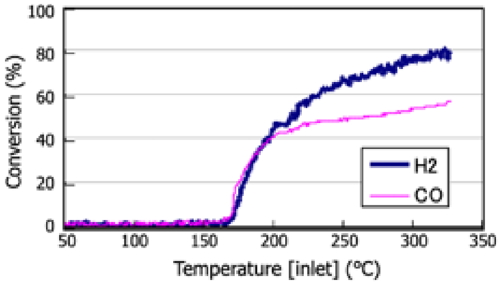
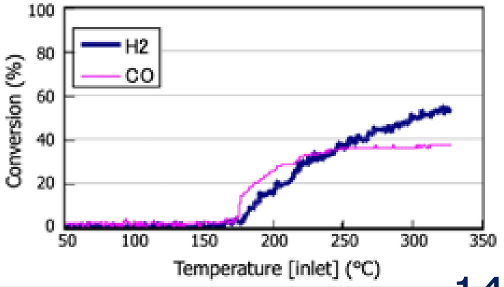
Mixed gas conditions for catalytic activity evaluation

No	H_2	CO	O_2	oxygen	oxygen ratio
1	1.0	1.0	10.0	excess	x 10 times
2	1.0	1.0	1.0	stoichiometry	100%
3	1.0	1.0	0.75	shortage	75%
4	1.0	1.0	0.5	insufficient	50%

This study focuses on the reaction selectivity to supply oxygen to hydrogen oxidation while minimizing effects of coexisting gases.

PGM on alumina

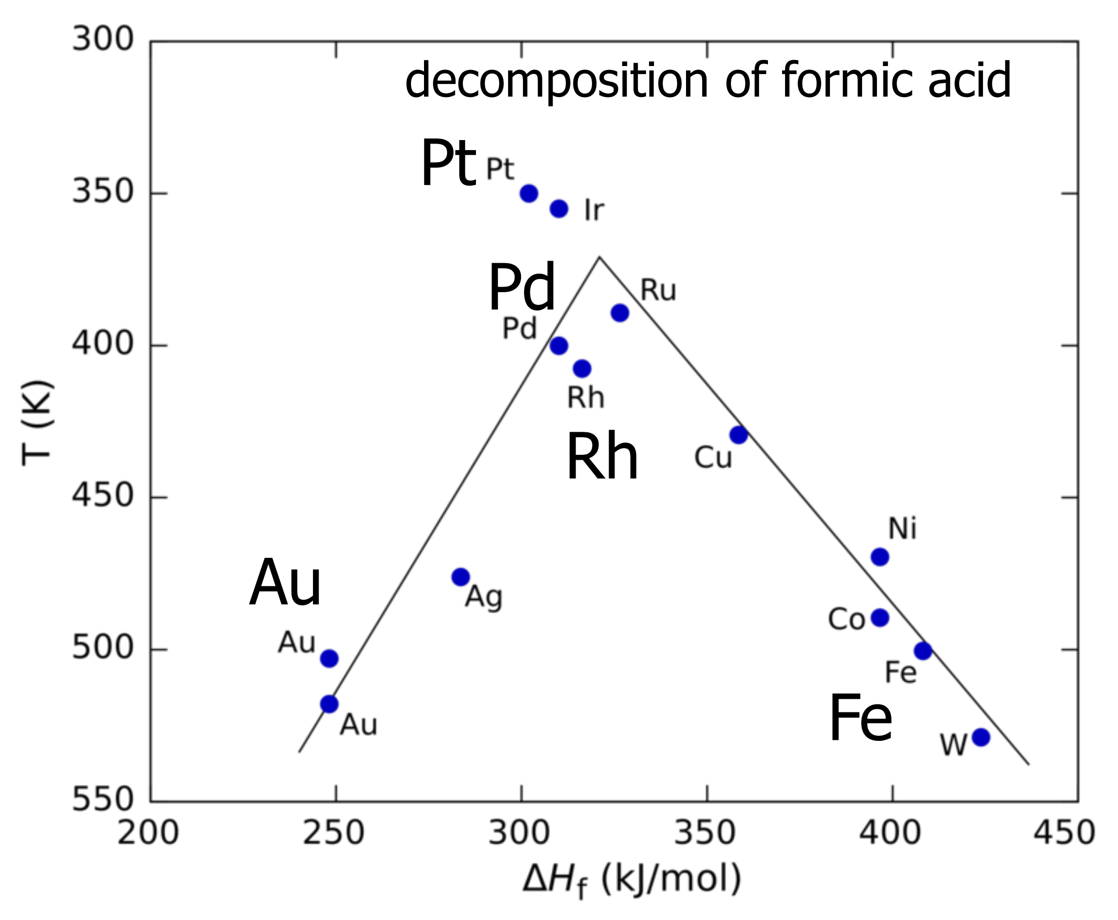
Pre CO poisoning

Gas / Catalyst	H_2: 1,0%, CO: 1.0%			
	O_2: 10% (excess)	O_2: 1.0% (stoichiometry)	O_2: 0.75% (shortage)	O_2: 0.5% (insufficiency)
Pt/Al_2O_3				
Pd/Al_2O_3				
Rh/Al_2O_3				

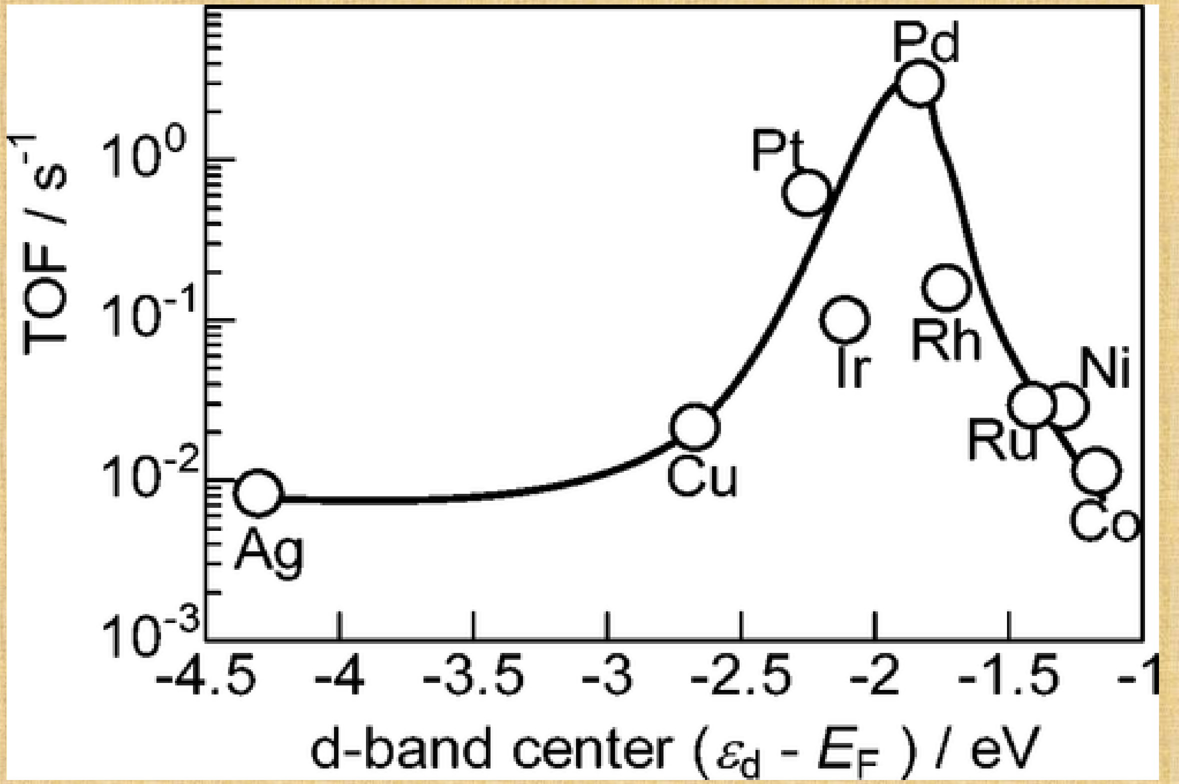
Volcano plot

metallic: Pt > Pd > Rh > oxidative

Stable phase: Pt, (Pd) PdO, Rh_2O_3



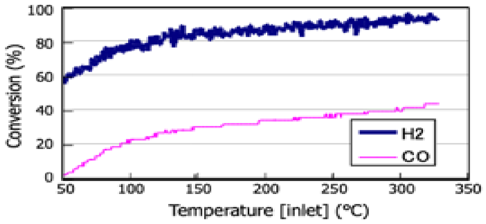
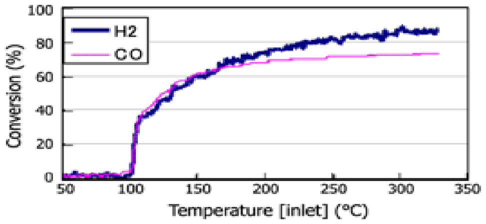
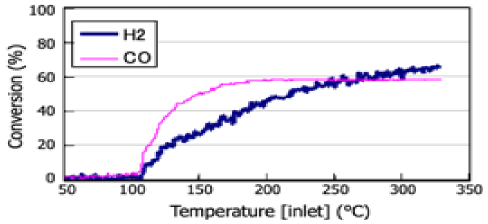
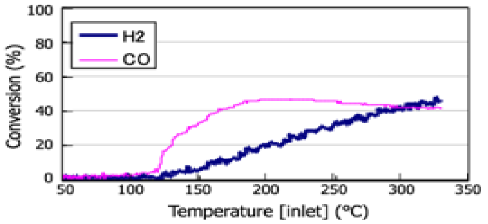
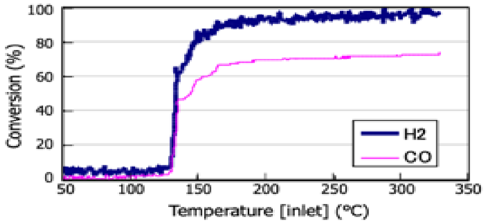
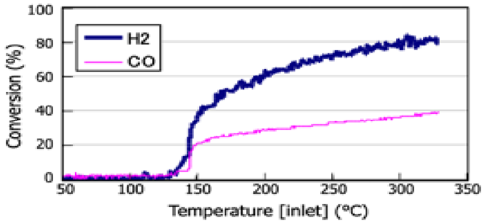
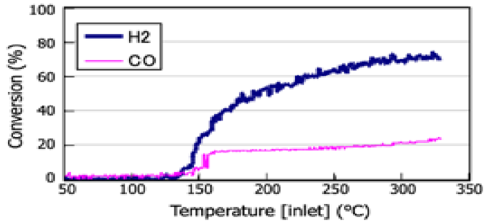
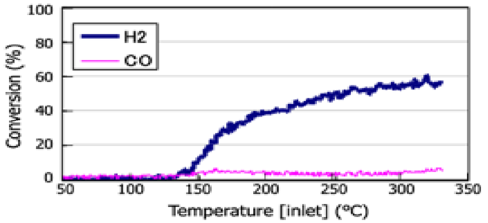
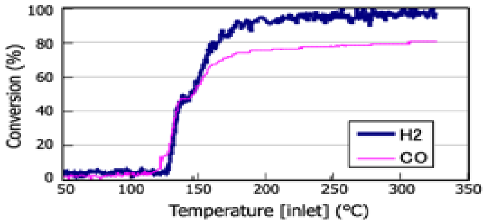
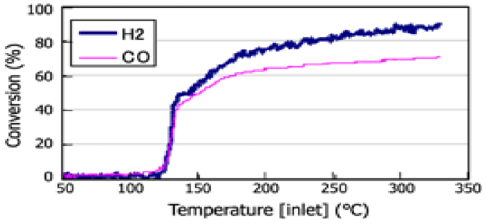
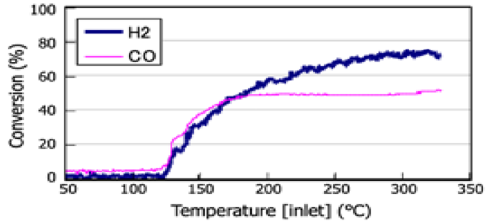
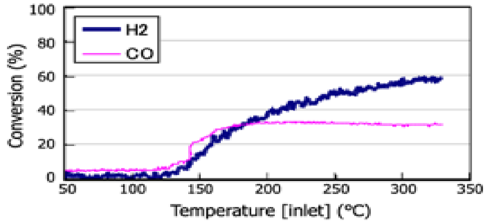
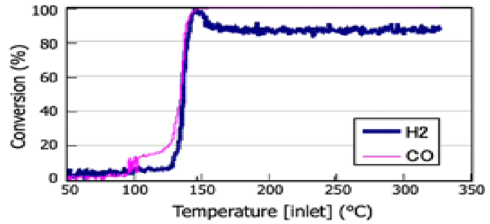
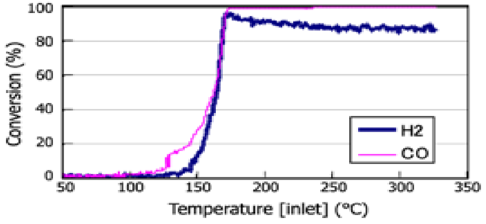
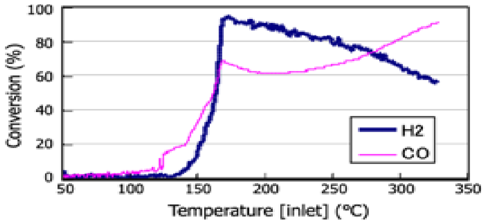
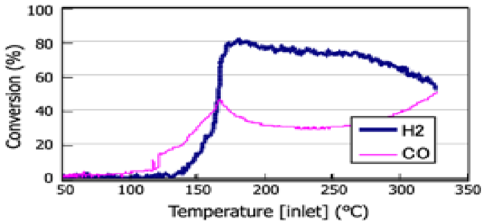
Gadi Rothenberg, *Catalysis: Concepts and Green Applications*. Wiley-VCH (2008) pp. 65



Volcano-Curves for Dehydrogenation of 2-Propanol and Hydrogenation of Nitrobenzene by SiO2-Supported Metal Nanoparticles Catalysts As Described in Terms of a d-Band Model, *ACS Catal.*, 2, 9, (20212) 1904–1909

PGM on CZY oxides

Pre CO poisoning

Gas / Catalyst	H_2: 1,0%, CO: 1.0%			
	O_2: 10% (excess)	O_2: 1.0% (stoichiometry)	O_2: 0.75% (shortage)	O_2: 0.5% (insufficiency)
Pt/CZY				
Pd/CZY				
Rh/CZY				
Intelligent Catalyst				

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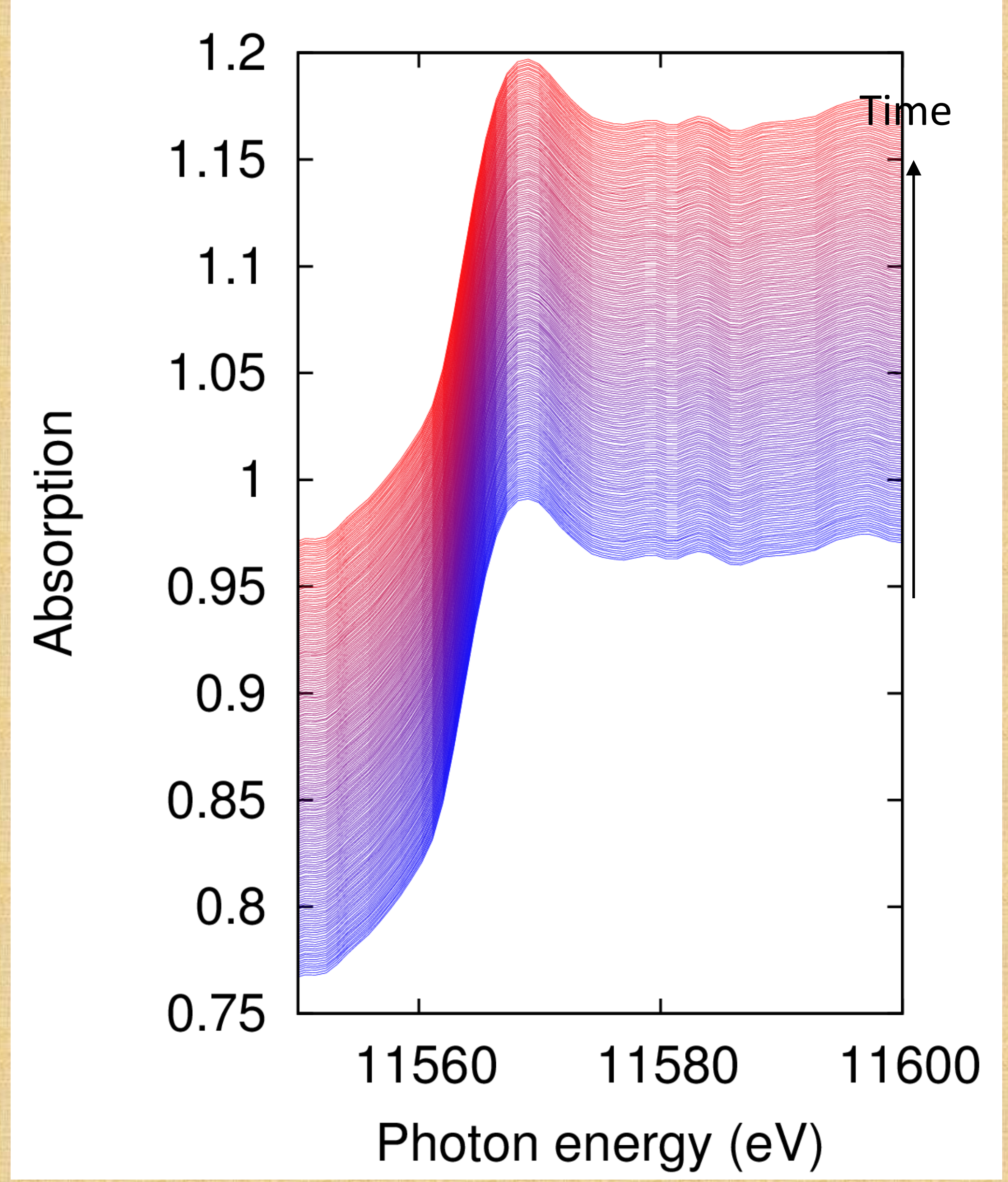
Time-resolved XAFS for Pt



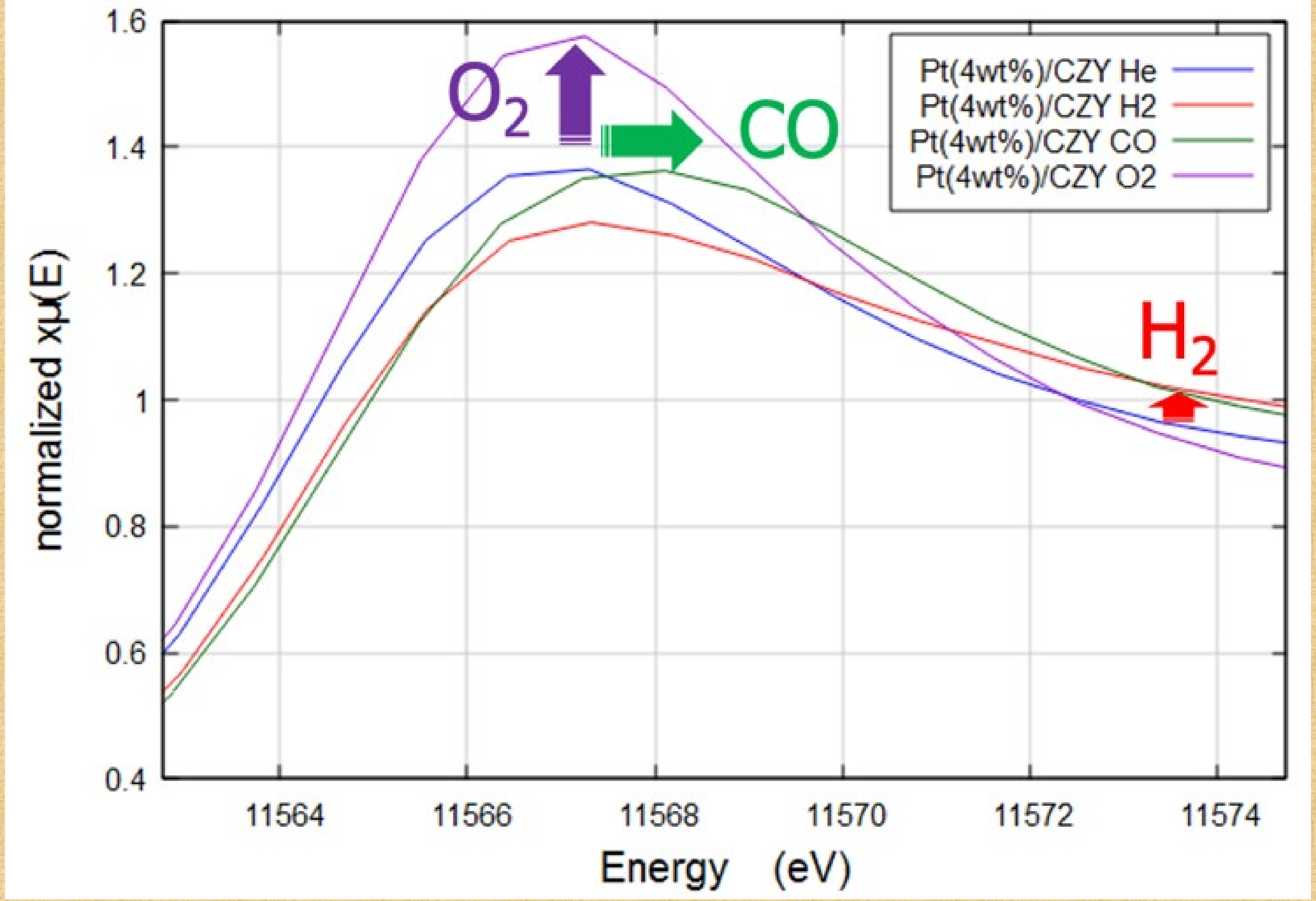
SPring-8 BL14B1

Dispersive optics
Si(111), Bragg configuration
Pt L_3-edge
2 Hz observation
Room temperature

Pt(4 wt%)/Al_2O_3 and Pt(4 wt%)/CZY
For passive autocatalytic recombiner (PAR) catalyst.

Change of spectra during water formation reaction

Preliminary XAFS experiment: Adsorption by single gas



Pt L_{III}-edge XANES spectra of Pt/CZY
under individual gas atmospheres at room temperature

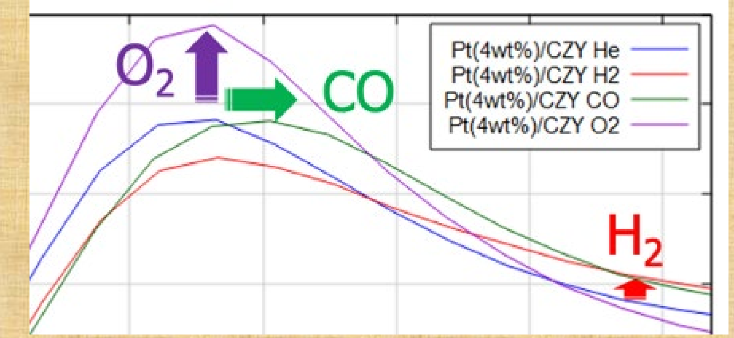
Mixed gas conditions for XAFS experiments

Gas	H_2	CO	O_2	Oxygen ratio
1	4.0	---	10.0	excess
2	4.0	---	2.0	stoichiometry
3	4.0	1.0	10.0	excess
4	4.0	1.0	2.0	insufficient

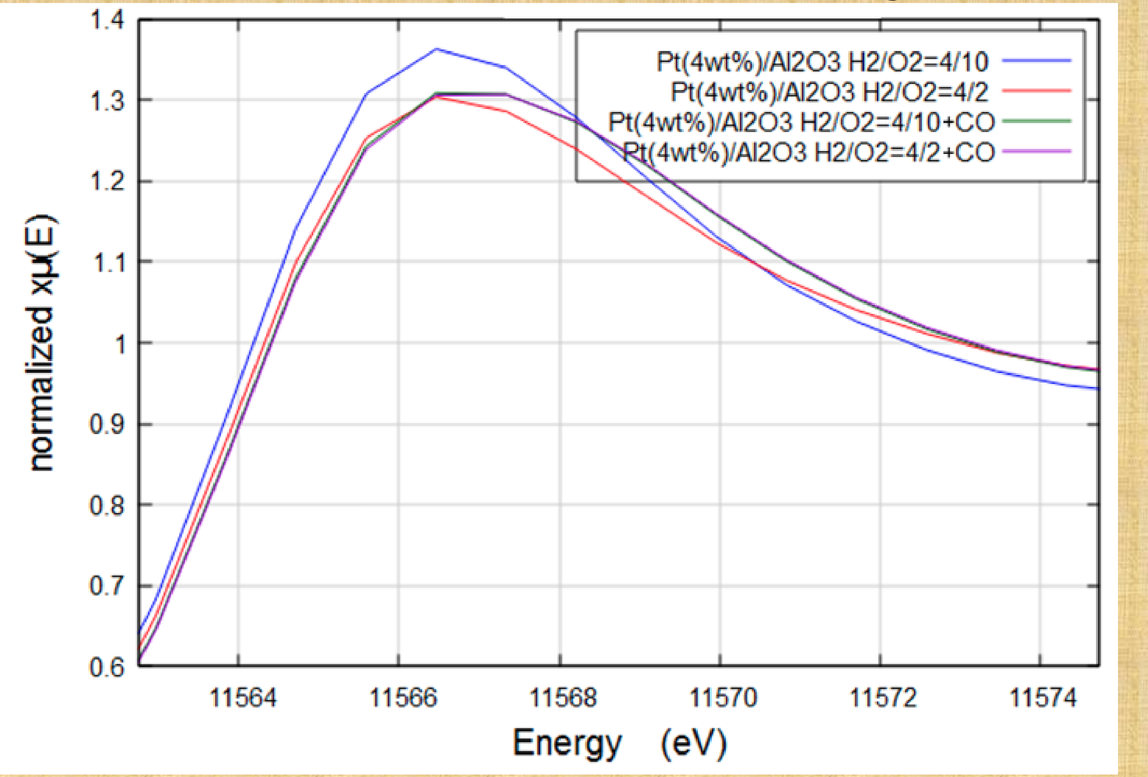
Investigation of competitive gas adsorption onto platinum supported on Al_2O_3 and CZY.

Gas	H_2	CO	O_2	Oxygen ratio
1	4.0	---	10.0	excess
2	4.0	---	2.0	stoichiometry
3	4.0	1.0	10.0	excess
4	4.0	1.0	2.0	insufficient

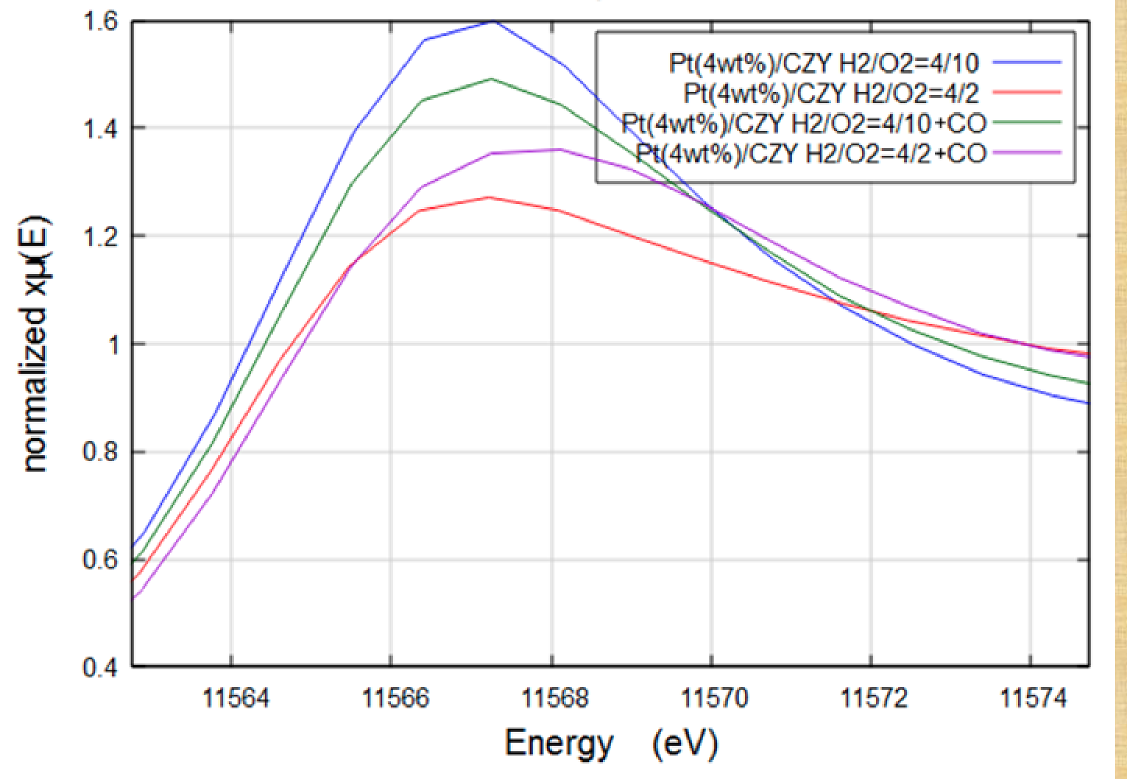
XAFS under mixed gas



XAFS spectra of Pt/Al_2O_3

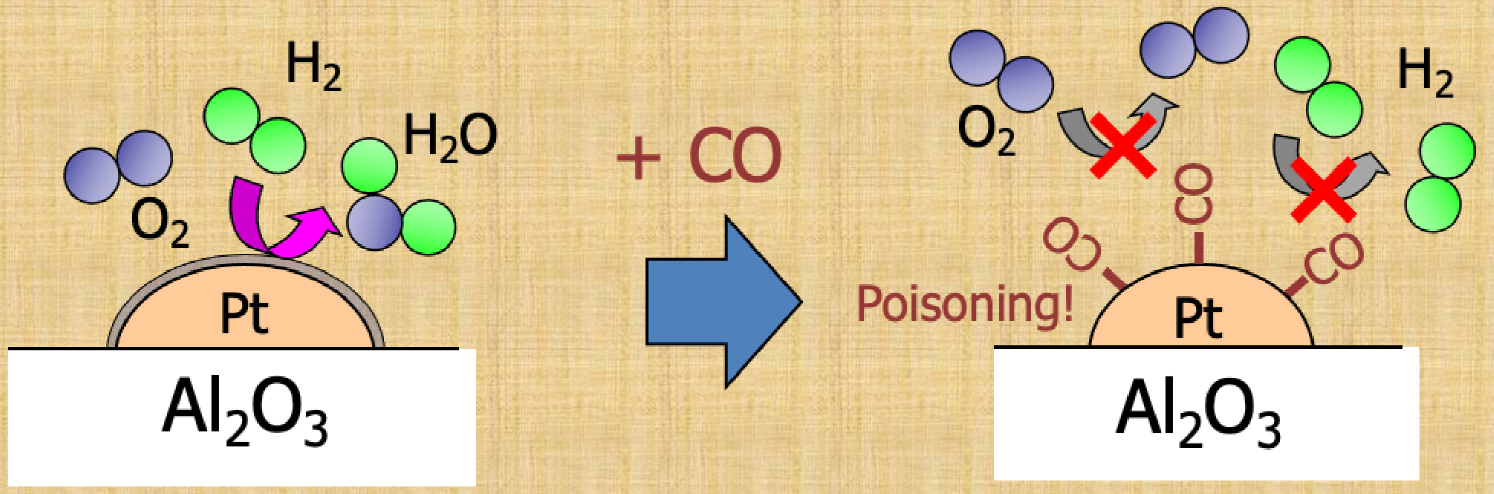


XAFS spectra of Pt/CZY

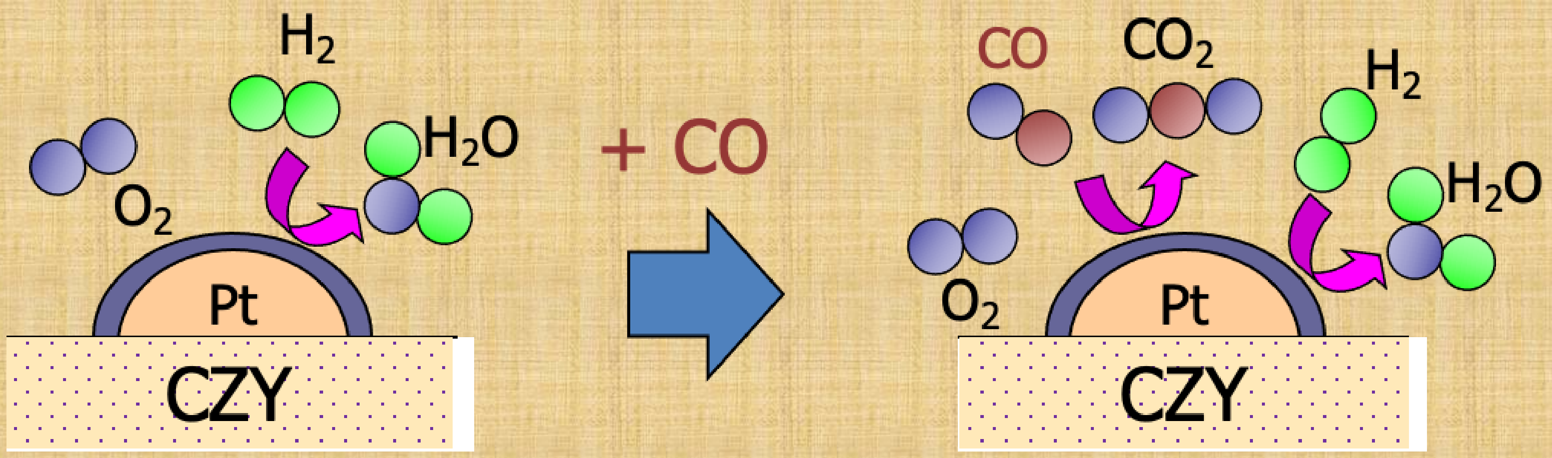


Pt L_{III}-edge XANES spectra of Pt/CZY under mixed gas atmospheres at room temperature

Image diagram



reaction termination due to CO poisoning in Pt/Al_2O_3 catalysts



hydrogen recombination overcoming CO poisoning in Pt/CZY catalysts

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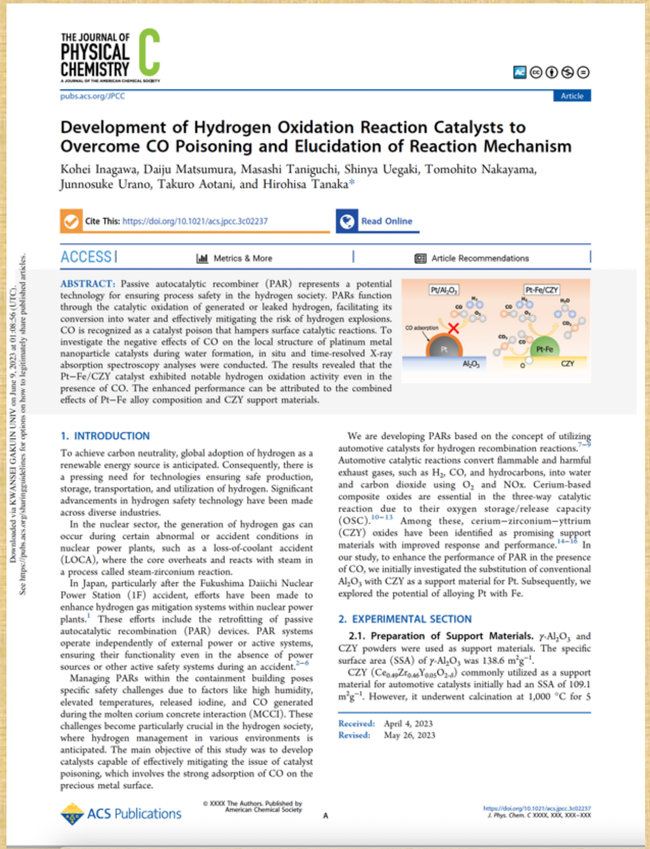
Anti-CO poisoning Pt-Fe/CZY catalyst

Development of hydrogen oxidation reaction catalysts
to overcome CO poisoning and elucidation of reaction mechanism,
J. Phys. Chem. C 127, (2023) 11542−11549



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Development of Hydrogen Oxidation Reaction Catalysts to Overcome CO Poisoning and Elucidation of Reaction Mechanism

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ABSTRACT: Passive autocatalytic recombiner (PAR) represents a potential technology for ensuring process safety in the hydrogen society. PARs function through the catalytic oxidation of generated or leaked hydrogen, facilitating its conversion into water and effectively mitigating the risk of hydrogen explosions. CO is recognized as a catalyst poison that hampers surface catalytic reactions. To investigate the negative effects of CO on the local structure of platinum metal nanoparticle catalysts during water formation, in situ and time-resolved X-ray absorption spectroscopy analyses were conducted. The results revealed that the Pt−Fe/CZY catalyst exhibited notable hydrogen oxidation activity even in the presence of CO. The enhanced performance can be attributed to the combined effects of Pt−Fe alloy composition and CZY support materials.

1. INTRODUCTION

To achieve carbon neutrality, global adoption of hydrogen as a renewable energy source is anticipated. Consequently, there is a pressing need for technologies ensuring safe production, storage, transportation, and utilization of hydrogen. Significant advancements in hydrogen safety technology have been made across diverse industries.

In the nuclear sector, the generation of hydrogen gas can occur during certain abnormal or accident conditions in nuclear power plants, such as a loss-of-coolant accident (LOCA), where the core overheats and reacts with steam in a process called steam-zirconium reaction.

In Japan, particularly after the Fukushima Daiichi Nuclear Power Station (1F) accident, efforts have been made to enhance hydrogen gas mitigation systems within nuclear power plants.[1] These efforts include the retrofitting of passive autocatalytic recombination (PAR) devices. PAR systems operate independently of external power or active systems, ensuring their functionality even in the absence of power sources or other active safety systems during an accident.[2−6]

Managing PARs within the containment building poses specific safety challenges due to factors like high humidity, elevated temperatures, released iodine, and CO generated during the molten corium concrete interaction (MCCI). These challenges become particularly crucial in the hydrogen society, where hydrogen management in various environments is anticipated. The main objective of this study was to develop catalysts capable of effectively mitigating the issue of catalyst poisoning, which involves the strong adsorption of CO on the precious metal surface.

We are developing PARs based on the concept of utilizing automotive catalysts for hydrogen recombination reactions.[7−9] Automotive catalytic reactions convert flammable and harmful exhaust gases, such as H_2, CO, and hydrocarbons, into water and carbon dioxide using O_2 and NOx. Cerium-based composite oxides are essential in the three-way catalytic reaction due to their oxygen storage/release capacity (OSC).[10−13] Among these, cerium−zirconium−yttrium (CZY) oxides have been identified as promising support materials with improved response and performance.[14−16] In our study, to enhance the performance of PAR in the presence of CO, we initially investigated the substitution of conventional Al_2O_3 with CZY as a support material for Pt. Subsequently, we explored the potential of alloying Pt with Fe.

2. EXPERIMENTAL SECTION

2.1. Preparation of Support Materials. γ-Al_2O_3 and CZY powders were used as support materials. The specific surface area (SSA) of γ-Al_2O_3 was 138.6 m^2g^{-1}.

CZY ($Ce_{0.49}Zr_{0.46}Y_{0.05}O_{2-\delta}$) commonly utilized as a support material for automotive catalysts initially had an SSA of 109.1 m^2g^{-1}. However, it underwent calcination at 1,000 °C for 5

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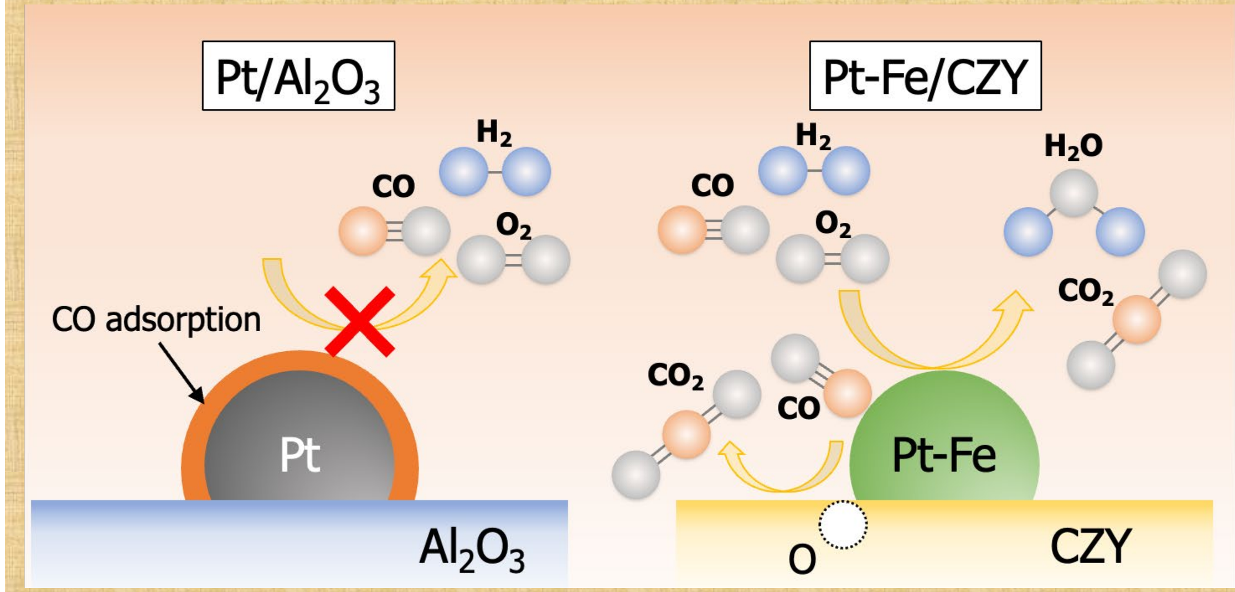

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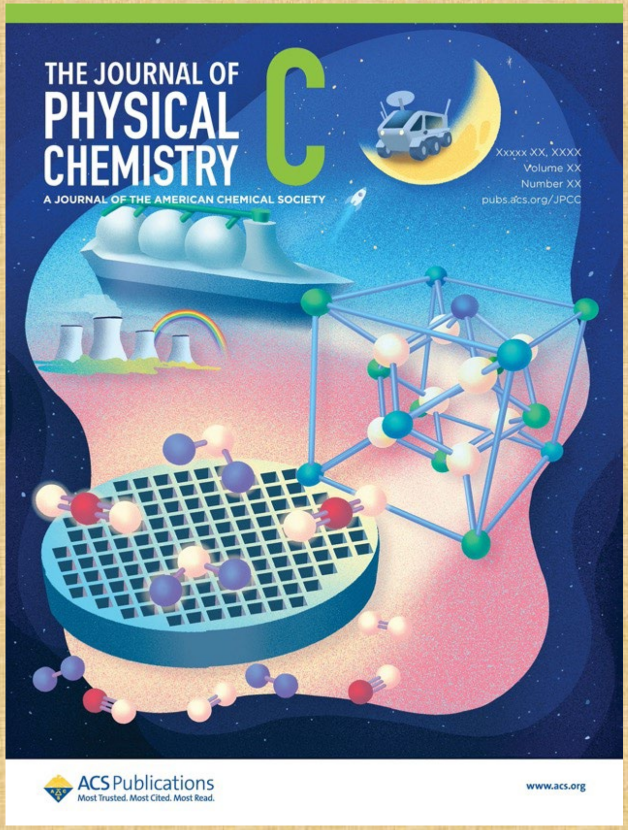

Illustrated by
Remi Tanaka (my daughter)

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Summary

- In the presence of excess O_2, all Pt, Pd and Rh catalysts exhibited good oxidation activity for H_2 even in a CO-poisoned environment.
- The activity order was Rh > Pd > Pt for the precious metal species, and CZY > Al_2O_3 for the support materials, suggesting that the formation of an oxide layer on the precious metal surface is effective for CO tolerance.
- Even in the presence of CO, Pt/CZY was the only catalyst that showed a high H_2 oxidation activity at lower temperature under excess O_2.
- Pd/CZY selectively oxidized H_2 without oxidizing CO in an oxygen-insufficient environment.
- The intelligent catalyst displayed superior properties for both H_2 and CO oxidation across a wide range of boundary conditions.
- Oxygen affinity is critical to catalyst design, and control at the atomic level is key to achieving desired performance under adverse conditions such as CO poisoning.

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