HYDROGEN PASSIVE AUTOCATALYTIC RECOMBINER OVERCOMING CO POISONING

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ABSTRACT

Hydrogen is playing a more important role in the transition to clean, safe, and sustainable energy systems towards decarbonization. In order to realize a carbon-neutral hydrogen society, safety technology covering all aspects of hydrogen production, storage, transportation, and utilization is necessary. Hydrogen water formation reactions using passive autocatalytic recombiners (PARs) are one of the candidates for avoiding hydrogen explosions and have been adopted in the nuclear field. For hydrogen to be widely used as a clean energy source in automobiles, industry in general, and in everyday life, PAR should maintain good reactivity in all scenarios, especially must overcome catalyst poisoning, which inhibits the reaction. In this study, we focused on carbon monoxide as the most representative example of catalyst poisoning in hydrogen recombination reactions.

By designing the active site of the catalyst, including the precious metal species, alloying with the transition metals, and the electron donating property of the support materials, it is possible to not only control the adsorption of CO, but also improve the reaction selectivity with hydrogen. Furthermore, it was found that the oxidation reaction can be promoted by introducing oxygen lattice defects into the supporting oxide or by suppressing the specific surface area.

Through international joint research project named STACY, the superiority of the newly designed catalyst was confirmed by reactions in small-scale labs and large-scale reactors. Furthermore, CO poisoning resistance was scientifically proven by X-ray absorption fine structure (XAFS) analysis of the precious metal surface using synchrotron radiation at SPring-8.

Keywords: hydrogen safety, passive autocatalytic recombiner (PAR), CO poisoning, X-ray absorption spectroscopy, safety assessment,

1. INTRODUCTION

Global cooperation has been achieved to establish a sustainable decarbonized society. Hydrogen is playing a more important role in the transition to clean and sustainable energy systems towards decarbonization. In large-scale social implementation of hydrogen, liquefied (cryogenic) hydrogen (LH_2) can be expected to play a fundamental role in the future potential hydrogen economy due to its high energy density. Ensuring safe implementation in all aspects of production, storage, transportation, and utilization of LH_2 is essential for economic benefit and social acceptance. However, the phenomenon at the extremely low temperature of minus 253°C is still not fully understood and is an unexplored frontier.

The STACY project, supported by the European Interest Group (EIG) CONCERT-Japan international joint initiative, brings together experts from internationally recognized institutions in the fields of hydrogen combustion, catalyst design, reaction evaluation, and safety assessment. This interdisciplinary

activity will transfer well-established hydrogen safety knowhow and technologies from the nuclear sector to liquefied hydrogen. The STACY project aims to experimentally determine the basic safety parameters of liquefied hydrogen combustion at cryogenic temperatures and to develop a new passive autocatalytic recombiner (PAR) to prevent hydrogen explosions. For hydrogen to be widely used as a clean energy source in automobiles, industry in general, and in everyday life, PAR should maintain good reactivity in all scenarios, especially must overcome catalyst poisoning, which inhibits the reaction.

One of the most continuously evolving technologies in the last 50 years is catalysts for automotive emissions control. Gasoline vehicle emissions have been reduced to 1/200 of the concentration of pollutants by the automotive catalysts, and the cleanest vehicles have exhaust emissions that are cleaner than the ambient air in big cities. Unlike chemical plant catalysts, the automotive catalysts must be active in a wide range of environments with uncontrolled boundary conditions. By applying the automotive catalyst technology to PARs, highly robust catalysts can be realized. In this study, we focused on carbon monoxide as the most representative example of catalyst poisoning in hydrogen recombination reactions.

2.0. EXPERIMENTAL

2.1. Preparation of Catalysts

2.1.1 Powder catalysts

Platinum, palladium, and rhodium catalysts were prepared by impregnating respective nitric acid aqueous solutions onto γ-Al_2O_3 or $Ce_{0.49}Zr_{0.46}Y_{0.05}O_{2-\delta}$ support materials, respectively. Each catalyst is described as follows: Pt/Al_2O_3, Pd/Al_2O_3, Rh/Al_2O_3, Pt/CZY, Pd/CZY and Rh/CZY. The loading amount of precious metal was standardized at 0.5 wt% with respect to the support material. In addition, an intelligent catalyst (Pt-Pd-Rh) installed in a real automobile was also prepared [1-5]. The total loading amount of precious metals was also standardized at 0.5 wt%.

In addition, a new "anti-CO catalyst" was designed and prepared to overcome CO poisoning. These are catalysts in which Pt is alloyed with Fe and supported on CZY, and their ratios are shown in Table 1.

Table 1. Specifications and codenames of anti-CO catalysts.

Code name for Anti-CO catalyst		Fe (wt%)						
		0.0	0.1	0.5	1.0	2.5	4.0	8.0
Pt (wt%)	0.5	Pt (0.5)	Pt-Fe (0.5/0.1)	Pt-Fe (0.5/0.5)	Pt-Fe (0.5/1.0)	Pt-Fe (0.5/2.5)	---	---
	4.0	Pt (4.0)	Pt-Fe (4.0/0.1)	Pt-Fe (4.0/0.5)	Pt-Fe (4.0/1.0)	---	Pt-Fe (4.0/4.0)	Pt-Fe (4.0/8.0)
	8.0	Pt (8.0)	---	---	---	---	---	---

2.1.1 A honeycomb catalyst for REKO-1 evaluation

For the REKO-1 evaluation, the “anti-CO catalyst: Pt-Fe (4.0/1.0)/CZY” was coated on a honeycomb with an outer diameter of 70 mm, a thickness of 5 mm, and a cell density of 900 cpsi (cell per square inch). Reduction pretreatment was performed at 800 °C for 1 h in H_2 (1%) / N_2 (balance) atmosphere (Figure 1).

2.2. Catalytic Activity Evaluation

2.2.1 Pelletized powder catalyst

The catalytic activity was evaluated using a powder catalyst with a fixed-bed flow system. After weighing 0.5 g of each precious metal-supported powder catalyst, compact pellets were prepared by pressing. All catalysts were reduced in H_2 (2%) / N_2 (balance) atmosphere at 400 °C for 10 min. After cooling to room temperature under N_2 flow, H_2 and CO oxidation activities, in the coexistence of CO, were evaluated while increasing the temperature from 50 to 330°C. In particular, in order to investigate the effect of O_2 concentration on catalytic activity, H_2 and CO concentrations were fixed at 1.0%, respectively, and four oxygen concentrations were changed and compared: 10% (excess), 1.0% (stoichiometry), 0.75% (shortage), and 0.5% (insufficiency).

2.2.2. PAR qualification on Honeycomb Catalyst by REKO-1 in FZJ

The activity of the anti-CO poisoning honeycomb catalyst was measured using REKO-1 at the Jülich Institute (Figure 1). A mixed gas of air, CO, and H_2 were injected in parallel toward the catalyst from the bottom in a stainless-steel pipe with an inner diameter of 72 mm. The outlet gas concentrations were measured with analyzers, a thermal conductivity detector (TCD) for H_2, a magnetic pressure detector for O_2, and an infrared absorption (IR) detector for CO, respectively. Inlet gas concentrations were calculated from mass flow values.

The "anti-CO poisoning: Pt-Fe (4.0/1.0)/CZY" honeycomb catalyst with a diameter of 70 mm and a thickness of 5 mm was wrapped with a heat-resistant mat and fixed in a REKO-1 pipe. As shown in Figure 1, the catalyst bed temperature was measured at the center and rim. And the inlet and outlet gas temperatures were measured at the point about 10 mm distance from the surfaces of the catalyst. It is noted that this qualification test is a passive catalytic reaction without any external heating. The bottom temperature approximately 500 mm below the catalyst was also measured to confirm it.

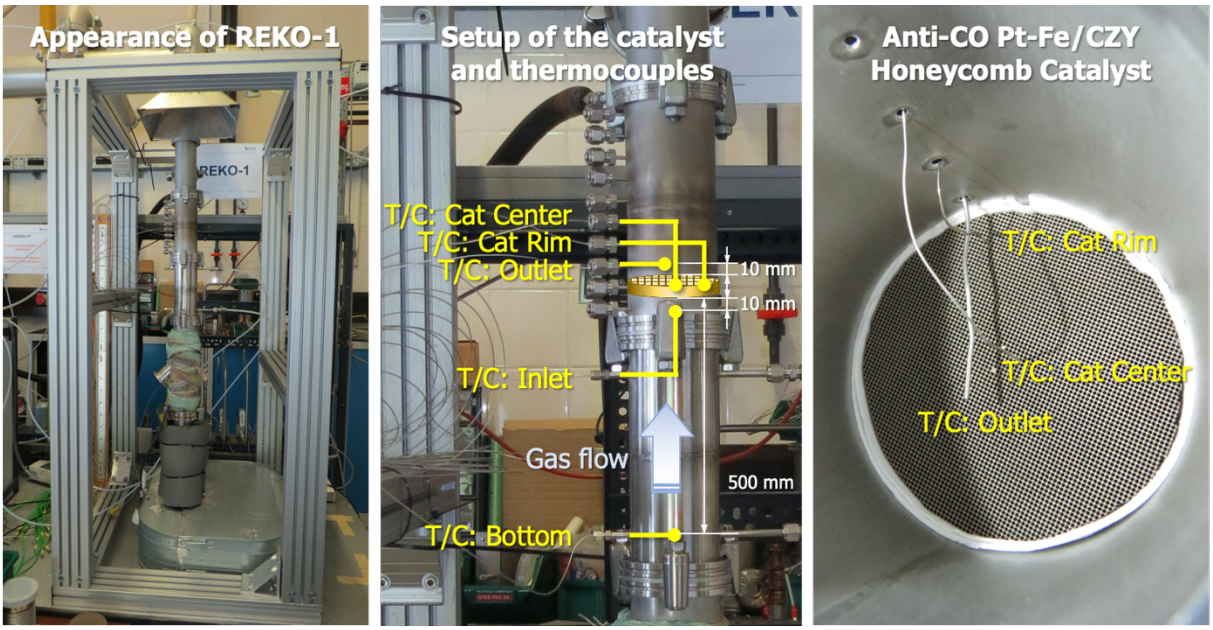

Figure 1. Appearance and setup of the catalyst and thermocouples for the REKO-1 experimental

2.3. X-ray Absorption Spectroscopy by Synchrotron Radiation in SPring-8

2.3.1. in-situ observation of adsorbed species on Pt surface

Information of surface structure of precious metal nanoparticles during reaction is important because metal nanoparticles often change their atomic and electronic structures by the fluctuation of surrounding temperature and atmosphere. X-ray absorption fine structure (XAFS) is a unique technique for studying atomic and electronic structures of the target element [6-7].

CO adsorption on Pt surfaces of the powder catalysts, Pt (4.0)/Al_2O_3 and Pt (4.0)/CZY, were observed at BL14B1 in SPring-8 synchrotron radiation facility. Pt L_{III}-edge XAFS spectra were measured using a Si (311) double crystal monochromator. The sample was pre-reduced with 10% hydrogen at 400 °C for 10 min. In the XAFS measurements, He (helium) was used instead of N_2 as the balance gas to suppress X-ray scattering by outer-shell electrons.

3.0. RESULTS AND DISCUSSION

3.1. H_2 Oxidation Activity of Powder Catalysts in CO Coexistence

3.1.1. Examination of precious metal species and oxygen concentration

The H_2 oxidation activity of the pelletized powder catalyst in CO coexistence and low O_2 concentration was measured. The catalytic activities of Pt/Al_2O_3, Pd/Al_2O_3, Rh/Al_2O_3, Pt/CZY, Pd/CZY, Rh/CZY and the intelligent catalysts, all with 0.5 wt% precious metal loading, were compared (Figure 2).

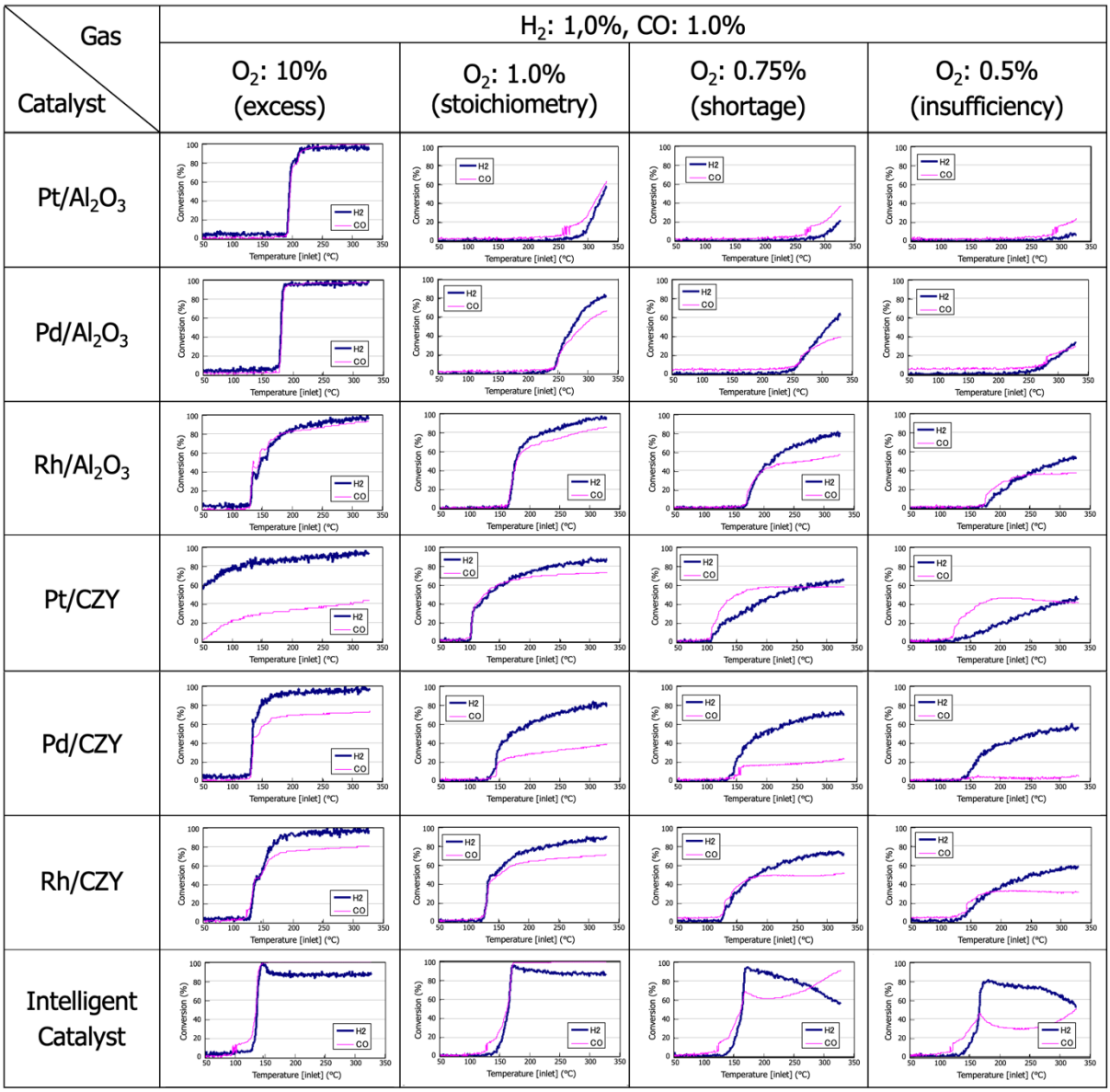

Figure 2. H_2 and CO oxidation activity in CO coexistence and various O_2 concentrations

3.1.2. Excess oxygen conditions

First, the activity when oxygen was sufficiently supplied is discussed. All catalysts showed high hydrogen conversion. Among catalysts using Al_2O_3 support, Rh reacted at the lowest temperature, and the order was Pd and Pt. The oxidation reactions of H_2 and CO occurred almost simultaneously.

Next, catalysts using CZY support are discussed. It is noted that the Pt/CZY already showed a conversion of 60% from the start of the measurement at 50° C. The reactions on Pd and Rh also started

at lower temperatures compared to the Al_2O_3 support. The combination of Pt, Pd, and Rh with the CZY support enhanced the reaction selectivity to hydrogen. An intelligent catalyst for automotive emissions control exhibited dynamic activity from low temperature.

3.1.3. Stoichiometric conditions

The activity is discussed when O_2 was supplied in a stoichiometric ratio to the reducing gases H_2 and CO. Among the alumina-supported catalysts, even under this condition, Rh started to react at the lowest temperature, followed by Pd and Pt, and the difference in activity became more pronounced. In Pt/Al_2O_3, it was clarified that the oxidation of H_2 started after CO, a poisoning substance, was removed by oxidation.

By the combination with CZY support, the low temperature activity, conversion rate, and hydrogen oxidation selectivity of Pt, Pd, and Rh were greatly improved. Intelligent catalysts for automobile exhaust gas control were the only catalysts that could completely oxidize hydrogen below 200 °C.

3.1.4. Short and insufficient oxygen conditions

Activity was discussed when not enough O_2 was supplied to oxidize H_2 and CO, but 75% or 50% was supplied. Pt/Al_2O_3 hardly reacted, but Pd was slightly active, and Rh oxidized H_2 and CO corresponding to the amount of oxygen supplied. All these three catalysts started to oxidize H_2 after CO was removed by oxidation.

On the other hand, Pt/CZY could greatly improve the catalytic performance. It is remarkable that the oxidation of H_2 started after the CO was removed by oxidation. In Pt/CZY, H_2 selectivity appeared in oxygen excess, and CO selectivity appeared in oxygen deficiency.

Compared to Pd/Al_2O_3, Pd/CZY has improved catalytic activity from lower temperatures and hydrogen oxidation selectivity. O_2 was not consumed by CO and the reaction favored H_2 oxidation.

In Rh/CZY, there was a common feature that the oxidation reaction of H_2 and CO started around 125°C, and O_2 reacted more to H_2 in the high temperature range, regardless of the oxygen concentration. Compared to Rh/CZY, Rh/Al_2O_3 had a higher reaction initiation temperature, but Rh with both support materials exhibited stable and good oxidation properties.

Even in an oxygen-deficient environment, the intelligent catalyst started CO oxidation around 125°C, and H_2 followed from 150°C. A phenomenon was observed in which H_2 conversion reached a peak of over 80% and decreased in higher temperatures. It was considered that the water-gas shift reaction occurred in this high temperature region.

3.1.5. Summary of the lab activity measurements

- The oxidation activity of H_2 was good for all catalysts under excess O_2 even in a CO poisoning environment.
- By using CZY support, the oxidation reaction could be accelerated more than Al_2O_3.
- Rh showed good H_2 oxidation activity regardless of support materials.
- The intelligent catalyst showed better properties for both H_2 and CO oxidation in a wide range of boundary conditions.
- Pd/CZY oxidized only H_2 without oxidizing CO in an oxygen-insufficient environment.
- The order of activity was Rh>Pd>Pt and CZY>Al_2O_3, suggesting that the formation of an oxide layer on the precious metal surface is effective for CO tolerance.
- It was considered that the O_2 concentration also contributed greatly to the formation of the oxide layer.
- Even in the presence of CO, Pt/CZY was the only catalyst that showed a high H_2 oxidation activity at a room temperature under excess O_2.

3.2. Design Study of Anti-CO Catalyst

3.2.1. Pt loading concentration

Since Pt/CZY showed hydrogen oxidation activity from room temperature even in the presence of CO, we will further improve the catalyst and design an anti-CO catalyst.

Pt/CZY showed hydrogen oxidation activity from room temperature even in the presence of CO under the condition of excess oxygen. Furthermore, under severe conditions such as coexistence of CO and stoichiometry of O_2 (1.0%), we will design an anti-CO catalyst that exhibits H_2 oxidation activity from room temperature. Three types of catalysts with different Pt loading concentrations, Pt (0.5), Pt (4.0) and Pt (8.0)/CZY, each weighing 0.5 g were prepared (Table 1). The temperature at which H_2 conversion reached 50% (T_{50}) under O_2 (1.0%) conditions was compared (Figure 3).

It was found that even if the Pt concentration was increased 16-fold from 0.5 to 8 wt%, the H_2 50% conversion temperature hardly improved (lowered) under 1.0% oxygen in CO coexistence.

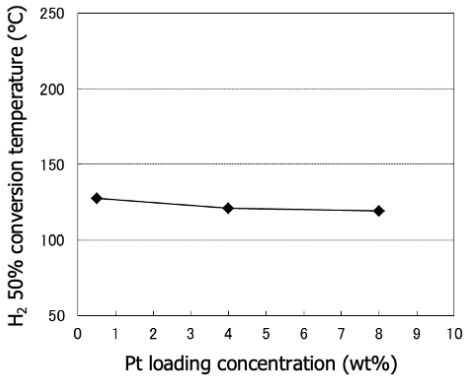

Figure 3. H_2 (T_{50}) vs. Pt loading

3.2.2. Investigation of Pt-Fe alloying

It was suggested that forming an oxide layer on precious metal surface was effective for CO tolerance. This finding is consistent with both the results of H_2-CO-O_2 catalytic reaction experiments in the laboratory, and the analysis results using X-ray Absorption Spectroscopy, which will be detailed later. Therefore, in order to promote the formation of the Pt oxide layer, we investigated whether the activity of Pt/CZY could be improved by adding Fe, which is easily oxidized. The amount of Pt was set to two levels, 0.5 and 4 wt%, and the amount of Fe added to each level was changed to evaluate the effect on the activity (Table 1, Fig. 4). As a result, it was found that both Pt/CZY with a Pt concentration of 0.5 and 4 wt% showed high activity at Fe/Pt = 1/4 to 1/5, and the activity decreased with the addition of Fe in excess. In particular, Pt-Fe (4.0/1.0)/CZY showed high activity from the lowest temperature.

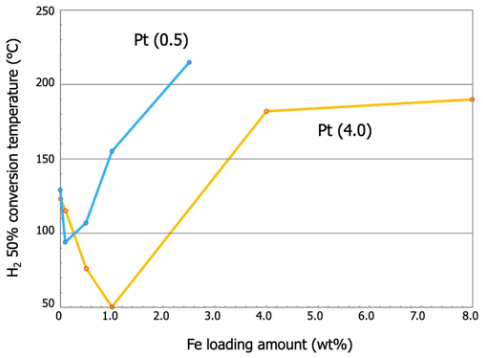

Figure 4. H_2 (T_{50}) vs. Fe loading with Pt

3.3. PAR Qualification by REKO-1

3.3.1. Qualification on anti-CO honeycomb catalyst

It has been reported that the coexistence of CO reduces the H_2 oxidation activity of commercial PAR catalysts [8, 9]. We found the possibility of Pt-Fe (4.0/1.0)/CZY catalyst as an "anti-CO catalyst" to overcome CO poisoning. For PAR qualification, H_2 oxidation activity in the presence of CO was evaluated using REKO-1 from Jülich Institute.

Without using a heating device, the mixed gas was flowed over the catalyst at room temperature while controlling the total gas flow rate to 0.5 m/s. When air mixed with 4% H_2 was flowed, PAR reacted from room temperature and the hydrogen concentration in the outlet gas became 0% (Figure 5). At this time, the temperature in the catalyst bed was approximately 400 °C, and the outlet gas temperature was 300°C. It was confirmed that both H_2 and CO were oxidized and removed when CO was added at every concentration of 1%. At this time, the outlet H_2 concentration did not increase, and it was confirmed that coexistence of CO did not adversely affect the H_2 oxidation activity.

When the H_2 supply was stopped while the CO concentration was maintained at 4%, the catalyst temperature decreased to 170°C as the calorific value decreased, but the CO outlet concentration remained zero, and even CO alone was oxidized by PAR. However, the reaction stopped when the CO concentration was lowered to 3%.

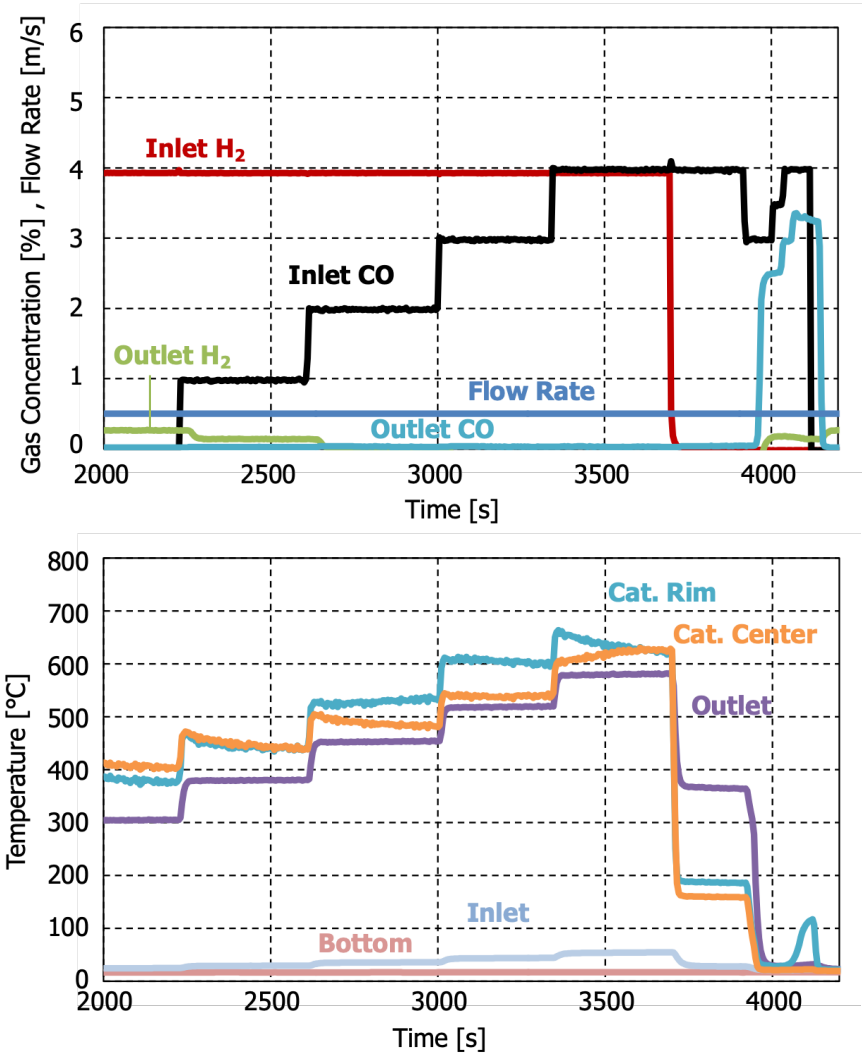

Figure 5. Qualification on anti-CO PAR

3.4. X-ray Absorption Spectroscopy in SPring-8

3.4.1. XANES spectra of adsorbed species on Pt surface

The local structure of Pt catalysts was analyzed by XAFS measurements. The valence state of Pt can be estimated from X-ray absorption near edge structure (XANES) spectrum at Pt L_{III}-edge. The profile of Pt/CZY in He atmosphere after reduction treatment shows clean metallic platinum, which is the standard state (Figure 6). Adsorption structures of Pt nanoparticles can be analyzed from the spectral changes in an atmosphere in which O_2, CO, and H_2 are separately added to He. The increase in white-line intensity in an oxidizing atmosphere indicates that Pt is in a highly oxidized state, that is, the average valence is increased [10]. Furthermore, when CO is adsorbed, an overhang to the high energy side of the peak is observed. It is sometimes expressed as a peak shift, but it is characterized by being broad [11]. When H_2 is adsorbed, the tail around 11,572-11,575 eV is lifted.

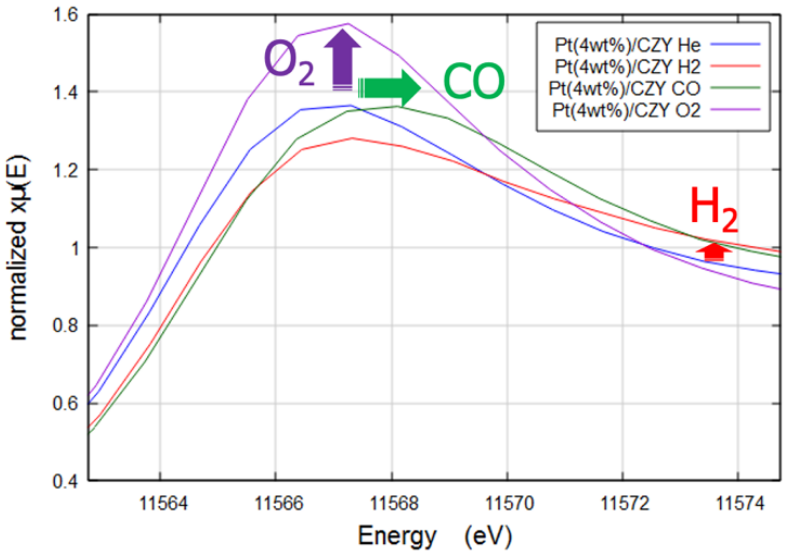

Figure 6. Pt L_{III}-edge XANES spectra of Pt/CZY under individual gas atmospheres at room temperature.

3.4.2. in-situ observation of adsorbed species on Pt surface

XAFS spectra were measured in a mixed gas flow close to the real environment, and surface adsorbed species of platinum were observed. There are four types of mixed gas in total, two types of conditions without CO and two types of conditions with CO added (Table 2).

Table 2. Mixed gas conditions for XAFS experiments

Condition	H2	O2	CO	atomosphere
1	4.0	10.0		excess oxygen
2	4.0	2.0		stoichiometry
3	4.0	10.0	1.0	excess oxygen
4	4.0	2.0	1.0	insufficient oxygen

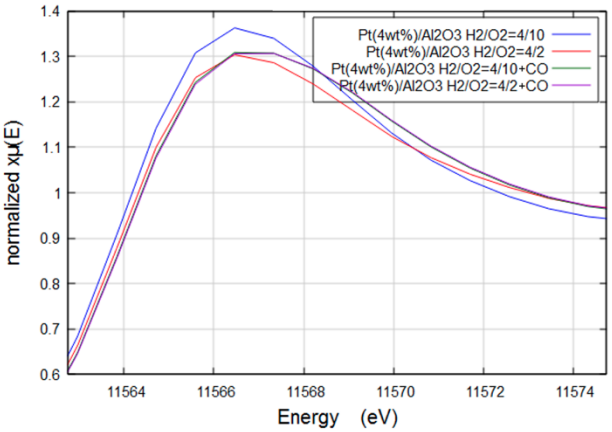

Figure 7. XAFS spectra of Pt/Al_2O_3.

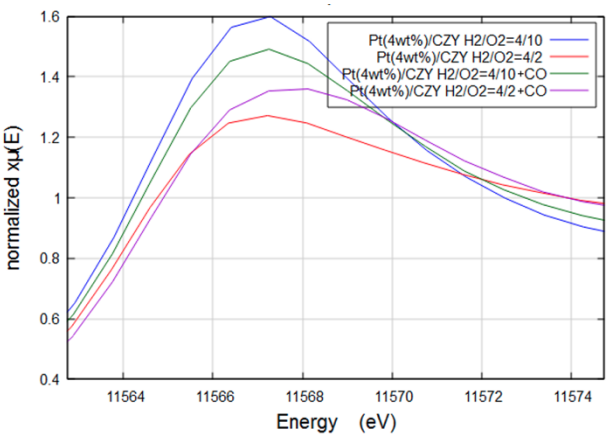

Figure 8. XAFS spectra of Pt/CZY.

XAFS spectra of Pt/Al_2O_3 with four gas conditions are shown in figure 7. In condition 1 (excess oxygen), the white line intensity increases, indicating that Pt is in an oxidized state. In condition 2 (stoichiometry), Pt is almost in a metallic state, and hydrogen oxidation occurs even at room temperature, and the Pt surface is clean. Since the absorption intensity increases slightly in the region of 11,572-11,575 eV, hydrogen adsorption is observed, and it is speculated that the settings of the experimental equipment such as the mass flow controller are slightly on the oxygen-deficient side. The profile of conditions 3 (excess oxygen) and 4 (insufficient oxygen) with CO coexistence almost overlapped, and it was clarified that CO was adsorbed from the overhang to the high energy side. Even in excess oxygen (condition 3), Since the entire Pt surface was covered with the CO adsorption layer, the Pt surface was not oxidized, and the reaction was inhibited.

XAFS spectra of Pt/CZY with four gas conditions are shown in figure 8. In condition 1 (excess oxygen), the intensity of the white line increases more, indicating that Pt is in a highly oxidized state. In condition 2 (stoichiometry), similar to Pt on Al_2O_3, Pt on CZY was almost in the metallic state and hydrogen adsorption was observed. From the overhang of the profile of condition 4 (oxygen deficiency) where CO coexists, it was confirmed that CO was adsorbed on the Pt surface, as with Pt/Al_2O_3. Characteristic is condition 3 (excess oxygen) with CO coexistence, and it was clearly observed that Pt on CZY was oxidized. In other words, it was found that surface of Pt on CZY was not poisoned even in the presence of CO at room temperature if enough oxygen was supplied. An image of changes in the surface of Pt metal nanoparticles and overcoming CO poisoning is shown in Figure 9.

A great suggestion was given here for designing an "anti-CO catalyst" to overcome CO poisoning. The XAFS results show that CO poisoning can be prevented by forming oxygen and/or oxide layer on the Pt surface. CZY, a cerium-based composite oxide support material with oxygen storage capacity, promotes the formation of oxygen and/or oxide layer on Pt. Furthermore, in laboratory tests, it is considered that the order of Pt<Pd<Rh under CO coexistence conditions improved the H_2 oxidation activity and the formation of an oxygen/oxidized layer on the surface of precious metals. The reason why intelligent catalysts for automotive emissions control can demonstrate H_2 oxidation performance in a wide range of environments is that they are designed to exhibit performance in environments with varying redox conditions.

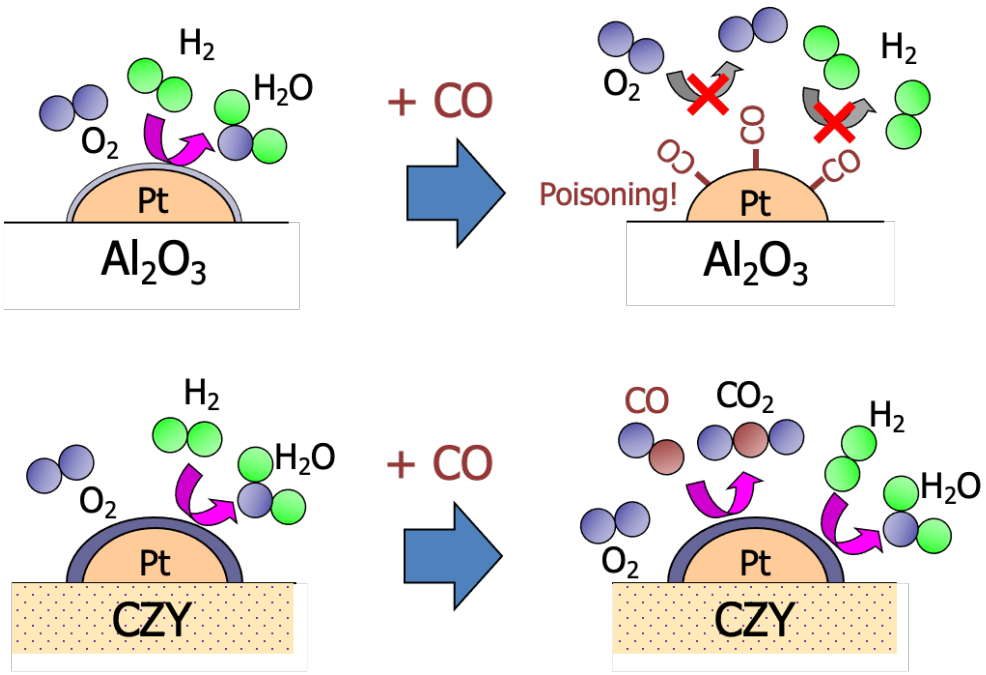

Figure 9. Image diagram of reaction termination due to CO poisoning in Pt/Al_2O_3 catalysts, and hydrogen recombination overcoming CO poisoning in Pt/CZY catalysts.

4. FUTURE OUTLOOK

So far, passive autocatalytic recombiners (PARs) have been required and put into practical use in the nuclear industry and have been widely put into practical use as devices that can prevent hydrogen explosions. However, it has not yet been used in other industries [12-13].

Hydrogen is expected more than ever as a clean and sustainable energy in the global movement toward carbon-neutral society. In particular, liquefied hydrogen is expected to be a favorite next-generation energy because it can be produced, stored, transported, and used with high energy density. Establishment of safety technology using PAR is essential for the realization of the looming hydrogen society [14-16].

In this research, we aimed to develop catalyst materials that overcome CO poisoning, which is one of the weak points of PAR, and clarified the direction of the solution. However, there are still many new challenges before cryogenic PAR is put into practical use. We will promote further research and development through international research cooperation.

5. CONCLUSIONS

- The effect of CO poisoning on the hydrogen oxidation catalytic reaction was investigated in detail by combining three kinds of precious metals and two kinds of support materials.
- In an environment with sufficient oxygen and high temperature, the effects of CO poisoning were eliminated.
- The effects of CO poisoning were more severe at low oxygen and low temperatures.
- CO poisoning resistance was observed in the order of Rh>Pd>Pt for precious metal species and CZY>Al_2O_3 for support material.

・X-ray absorption spectroscopy revealed that the formation of an oxygen/oxidized layer on the surface of precious metal is effective for the hydrogen oxidation reaction, and that CO poisoning inhibits the formation of this layer.

・The order of resistance to CO poisoning coincided with the ease of forming an oxygen/oxidation layer on the surface of the precious metal.

・"Anti-CO poisoning catalyst" in which Pt-Fe alloy is supported on a cerium-based composite oxide started the hydrogen-oxygen recombination reaction at room temperature even in the coexistence of CO.

・The PAR qualification of practical honeycomb coated with "anti-CO poisoning catalyst" was verified.

・These findings will be utilized in the design of even higher performance "anti-CO poisoning catalysts"

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