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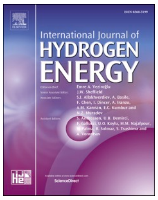

Experimental verification to developing safety technology for liquefied hydrogen in the project "STACY"

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ABSTRACT

Global efforts are being made to decarbonize the energy sector. Liquefied (cryogenic) hydrogen is suitable for large-scale storage and transportation due to its high storage density, so it is likely to play a fundamental role in the future hydrogen economy. The STACY project, “Towards the Safe Storage and Transport of Cryogenic Hydrogen”, is investigating safety aspects of liquid hydrogen in order to overcome potential safety risks. Research is being conducted into passive autocatalytic recombiners using cutting-edge catalyst technology to enable them to be used in conditions where liquid hydrogen escapes, evaporates and forms a cold (<50 °C) explosive gas mixture with the ambient air.

To this end, the crystal structure of the catalyst was designed at the atomic level, an actual catalyst was prototyped, and repeated tests were carried out on a laboratory scale and in a large reaction vessel. Progress has been made in developing catalysts that can oxidize hydrogen even at very low temperatures, high expansion, and low-oxygen environments, are resistant to catalyst poisons, and can prevent spontaneous unintended ignition. The tested catalyst technologies use different carrier materials (alumina and ceria) to control the surface state of precious metals and suppress hydrogen ignition through a multilevel configuration.

1. Introduction

Hydrogen is expected to play a crucial role in the intermediate storage of surplus energy from renewable sources such as solar and wind power. However, the low energy density of hydrogen in gaseous form requires technical solutions to ensure cost-efficient transportation. Existing technical solutions either rely on compressing the gas to pressures of up to 100 MPa or on liquefaction, which increases the density by a factor of approx. 800 [1]. It is generally assumed that, due to its high storage density, the large-scale storage and transport of liquefied (cryogenic) hydrogen (LH2) will play a fundamental role in a potential future hydrogen economy [2].

Handling hydrogen requires fundamental safety measures that result from the specific thermophysical properties of hydrogen. The main points to be considered are the risk of leakage and the large ignition range when mixed with air. The formation of combustible gas mixtures in closed rooms is therefore more easily possible than for other gases used in energy technologies, such as natural gas [3]. Large-scale hydrogen storage and transportation also present additional potential safety risks: large hydrogen inventories, complex geometries with huge confined and semi-confined volumes, congested and hard to ventilate areas, and in the case of maritime transportation long and remote transportation routes that require internal safety measures [4].

The latter aspects in particular are very similar to the conditions under which the safety of nuclear power plants must be ensured in the event of a severe accident. During a nuclear power plant accident, large amounts of hydrogen (in the order of 10,000 m^3) are released, which can form a combustible mixture with the air already present in the

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containment. In this large volume in the order of 60,000 m^3, the formation of combustible gas mixtures is counteracted by the use of so-called passive auto-catalytic recombiners (PARs) [5,6]. The STACY project ("Towards Safe Storage and Transportation of Cryogenic Hydrogen"), an international joint research project between German, French, and Japanese institutions, is therefore investigating whether these measures could also be used in maritime hydrogen transportation. The STACY project is addressing various aspects of the safety of liquid hydrogen transportation [7]. The general idea is that, due to a leak, liquid hydrogen spreads, evaporates and forms a mixture with the surrounding air, the temperature of which is considerably below room temperature [8]. The overall aim of the project is to contribute to the safety of LH2 storage and transportation by.

- experimentally determining fundamental safety-related parameters of hydrogen combustion not yet available for low temperatures,
- developing and qualifying novel catalysts for catalytic recombiners to prevent the formation of flammable gas mixtures in case of LH2 leakages,
- applying advanced numerical tools to study scenarios of potential hydrogen leakages and assessing the efficiency of mitigation measures.

The project work program is divided into five work packages (Fig. 1). The first work package is meant to collect the state of the art at the start of the project and to consider the scenarios to be examined. The experimental work in work packages 2 and 3 is based on this review, and provides the knowledge needed for the final safety assessments (work package 4). The experimental investigations on the combustion behavior of cold hydrogen/air mixtures are carried out in work package 2, while the work on catalytic recombination is located in work package 3. In the following, results achieved in work package 3 are presented and discussed.

Work package 3 aims to develop a catalyst to prevent explosions in the event of a liquefied hydrogen leak and to investigate the operating behavior of the corresponding catalytic recombination unit. The research at Kwansei Gakuin University (KGU) focuses on catalytic activity at low temperatures. To ensure reliable catalyst use, it is essential to quantitatively evaluate the catalytic performance under a combination of unfavorable conditions. These effects are therefore quantified in laboratory-scale experiments. For this purpose, KGU works with Daihatsu Motor Co., Ltd. (DMC) to design catalyst materials, prepare catalyst powders, coat catalysts on beads and honeycombs, and evaluate their properties in the laboratory. The team has been successful in the research, development, and commercialization of automotive exhaust purification catalysts [9–14]. Also KGU works with Japan Atomic Energy Agency (JAEA) to perform material analysis using synchrotron radiation at SPring-8 [15,16]. In addition, laboratory experiments are carried out in the REKO-1 experimental facility at the Jülich Research Center (FZJ). This flow tube reactor enables the investigation of different boundary conditions on the operating behavior of small-scale catalyst samples of several square centimeters in size. Finally, the behavior of catalyst assemblies will be investigated under natural flow conditions in the REKO-4 pressure vessel at FZJ [17–19]. The transient behavior (catalyst light-off and recombiners start) as well as the steady-state recombination rates can be determined here for relevant boundary conditions. These data serve to create numerical models that will later be used to simulate the recombiner's behavior in release scenarios.

The objective of the research is to develop technology that can prevent hydrogen explosions in the unlikely event of a leak by oxidizing hydrogen through a catalytic reaction and turning it into water. PARs work autonomously without external heating, ventilation, or stirring [20,21]. New catalysts need to be designed and prototyped to address the individual issues posed by liquefied hydrogen, and PAR's safety achievement have to be improved. Consequently, the crystal structure was designed at the atomic level, and actual catalysts were prototyped and repeatedly tested in the laboratory. While several catalyst developments are known for the nuclear application of PARs, e.g. Refs. [22–24], this is the first study which considers the cold conditions expected after leakage and evaporation of liquid hydrogen.

2. Challenges of LH2 releases for PAR operation

The mitigation of liquefied hydrogen releases is associated with three challenges for the use of PARs. The PAR characteristics required for each challenge are described below as Task 1 to Task 3. Furthermore, robustness (Task 4) is important to ensure the performance of PAR (Table 1).

2.1. (Task 1) cryogenic temperature: improving the low-temperature catalytic activity

Hydrogen needs to be liquefied at extremely low temperatures below −253 °C (20 K). Generally, as shown by the Arrhenius equation, the rate

Table 1
Characteristics of liquefied hydrogen and tasks of PAR.

Task	Characteristics of liquid hydrogen	Safety Issues	Requirements for PAR
1	−253 °C = 20 K	Cryogenics	Enhanced catalytic activity
2	High expansion (in case of leakage)	High flow, low O_2	Accelerated catalytic activity
3	High energy density	Prevent ignition	Suppression of catalytic activity
4	(Long-distance transport)	Robustness	Resistant to surface contamination

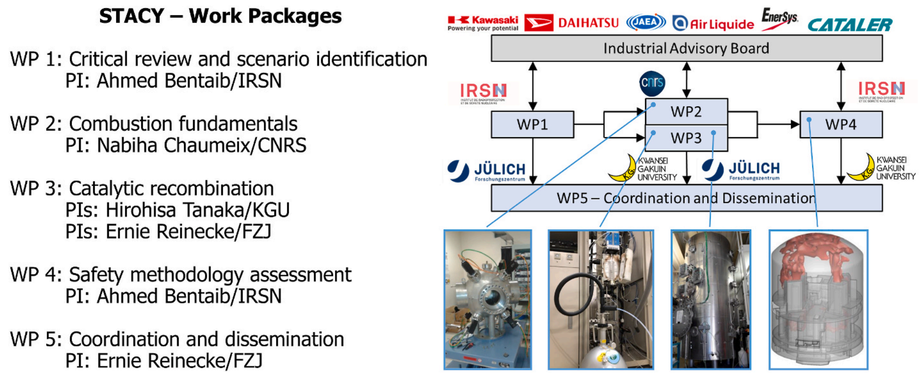

Fig. 1. Work packages of Project "STACY".

of chemical reactions slows down at low temperatures, so using a catalyst to lower the activation energy is an important solution. This problem is mainly aimed at being solved by material development.

2.2. (Task 2) High expansion and low oxygen concentration: High-speed response and low-oxygen reactivity

In the event of a leak, liquefied hydrogen expands all at once, causing the leaked gas to expand at extremely high speeds. In an enclosed space, it is expected that the oxygen concentration will decrease. In order to deal with high-speed gas expansion, material development and catalyst shape design are important. Additionally, in order to maintain good catalytic reactions in low-oxygen environments, it is important to design the catalyst constituent materials.

2.3. (Task 3) High energy density: Suppression of catalytic activity

Liquefied hydrogen has an energy density approximately 800 times that of gaseous hydrogen. It is also important to note that oxygen also solidifies at temperatures below −218 °C and is present in high concentrations. The flammable mixture range of hydrogen in the atmosphere is extremely wide, ranging from 4 to 75%, and the spontaneous combustion temperature is 572 °C. There is concern that if PAR rapidly oxidizes hydrogen, it will generate excessive heat and become a source of ignition. In order to deal with the leak of liquefied hydrogen, which has a high energy density, a method is required to resolve the contradictory proposition of reducing the hydrogen concentration while suppressing the temperature rise. To solve this problem, it is important not only to design materials but also to design the catalyst structure as a functional component.

2.4. (Task 4) Ensuring robustness: Catalyst poisoning prevention

PAR catalysts are very different from catalysts in chemical plants, and is required to perform under uncontrolled boundary conditions. Specifically, in the emergency situation of a hydrogen leak, all parameters such as hydrogen concentration, oxygen concentration, coexisting gas components, environmental temperature, humidity, and gas flow rate are affected. In addition, for maritime safety, it is necessary to consider that the PAR is exposed to the atmosphere for a long period of time from its manufacture and installation until it is actually in operation. In the worst case, the catalyst is required to maintain catalytic activity even when contaminated with water vapor, oil mist, carbon monoxide, etc. It is particularly emphasized that catalysts that prevent hydrogen explosions must be robust under such uncontrolled environments.

3. Experimental

To evaluate the low-temperature activity of the catalysts, four types of powder catalysts were prepared: Pt(2.0)/Al_2O_3, Pt(4.0)/Al_2O_3, Pd(2.0)/Al_2O_3 and Pd(4.0)/Al_2O_3. The numbers in parentheses indicate the mass percent of the precious metal supported. Pt was prepared using an aqueous dinitro-diamine platinum [$Pt(NO_2)_2(NH_3)_2$] nitrate solution, and Pd was prepared using an aqueous palladium nitrate [$Pd(NO_3)_2$] solution, impragnated onto γ-Al_2O_3 with a specific surface area (SSA) of 138.6 $m^2\ g^{-1}$. The precious metal particle sizes of the Pt(2.0)/Al_2O_3, Pt(4.0)/Al_2O_3, Pd(2.0)/Al_2O_3 and Pd(4.0)/Al_2O_3 catalysts were 2.23, 4.50, 4.46 and 6.00 nm, respectively.

The explosion limit of hydrogen in the atmosphere is a wide range, from 4 to 75%. When liquid hydrogen at −253 °C (20 K) is mixed with air at room temperature of 25 °C (298 K) within this range, the calculated temperature range is 13.9 °C (286.9 K) at 4% to −183.5 °C (89.5 K) at 75%. In this cryogenic test, the measurement range was set from −150 °C (123 K) to room temperature of 25 °C (298 K).

Cryogenic activity was measured using a fixed-bed flow reactor (BELCAT B: Microtrac BEL Corp.) modified in the laboratory. First, pretreatment was performed at a specified temperature using an electric furnace, then cooled to room temperature in a helium stream, and the electric furnace was removed while helium was still flowing. Once at room temperature, a glass wool strip and a foamed polystyrene insulation box were set up in place of the electric furnace, and liquid nitrogen was sprayed on the outside of the glass tube to cool the catalyst sample in the glass tube to −150 °C under a helium stream. −150 °C was maintained for 3 min and then switched to the reaction gas. The reaction gas was hydrogen excess, with 7% hydrogen and 3% oxygen, and the balance helium, flowing at 100 SCCM.

In that state, the hydrogen conversion rate was measured by utilizing the natural rise in temperature in the sample tube to room temperature without using any heater. K-type thermocouple was installed on the inlet gas side, 5 mm upstream of the catalyst, for temperature measurement. A quadrupole mass spectrometer (Q-MASS: JEOL JMS-Q1500) was used as a detector. When the entire amount of oxygen has been consumed, the hydrogen conversion rate reaches 85.7%. A distinctive feature of this modified device is that no external heaters are used to control the catalytic reaction temperature, so that localized heat spots are not generated at all, and gas inlet valves and other parts are kept at room temperature. Without a catalyst, it took 10 min for the temperature to naturally increase from −150 to −50 °C, from −50 to 0 °C, and from 0 to 25 °C, respectively.

Considering the real-world application of PAR, two types of pretreatment were performed on each catalyst.

- Reduction pretreatment: A model with a clean precious metal surface, reduced with hydrogen at 400 °C and cooled to room temperature with helium.
- Oxidation pretreatment: A model with a precious metal surface contaminated by air. This was assumed to be a long-term standby state in the air after the catalyst was prepared and installed as a safety device until hydrogen leaks. Oxidation was performed at 250 °C with 10% O_2 and then cooled to room temperature with helium.

In this paper, volume percentages of gases are simply expressed as %.

To compare the high-speed response and low-oxygen reactivity of catalytic activity, four types of powder catalysts were prepared: Pt(0.5)/Al_2O_3, Pt(1.0)/Al_2O_3, Pt(4.0)/Al_2O_3 and Pd(4.0)/Al_2O_3. Each powder catalyst was slurried by adding alumina sol (AS-200: Nissan Chemical) to obtain 5% solids content and dispersed in deionized water. Spherical activated alumina beads (KHA-24: Sumitomo Chemical) with a diameter (φ) of 3 mm were coated with 2.5 mass% of each catalyst powder, dried, and calcined at 400 °C for 1 h in air to obtain bead catalysts.

Activity was measured using a homemade fixed-bed flow reactor CATA-5000, and the changes in hydrogen and oxygen concentrations were measured with Q-MASS. Before the start of the measurement, the total gas flow rate was fixed at 4.0 L min^{-1} as a reduction pretreatment, and the mixture was kept at 430 °C for 10 min in a 0.4% hydrogen with nitrogen balance, then cooled to room temperature and the measurement was started.

- High flow rate response: The total gas flow rate was fixed at 4.0 L min^{-1}, and the thickness of the bead catalyst layer was changed to 0.5, 1.0, and 2.0 cm to investigate the response to high flow rates. The volume of each catalyst bed is 3.1, 6.2, and 12.3 cm^3, respectively, and the volume of gas passing through per hour, or Gaseous Hourly Space Velocity (here simply abbreviated as SV), is 78,000, 39,000, and 19,500 h^{-1}, respectively. The changes in hydrogen and oxygen concentrations were measured at room temperature in an oxygen-rich atmosphere of 1.5% H_2 and 15% O_2 with N_2 balance.
- Low oxygen concentration reactivity: Similarly, at room temperature, H_2 concentration was fixed at 1.5% using N_2 balance, and O_2 concentration was changed from 15%, 1.5%, which are oxygen-rich

atmospheres, to 0.75%, which is the stoichiometric mixture ratio, and the change in each gas concentration was measured.

If high-concentration hydrogen is oxidized all at once, a rapid temperature rise occurs, raising concerns that it may exceed the spontaneous combustion temperature. In order to avoid a rapid temperature rise, a concept was investigated in which the catalyst is set in multiple stages, the concentration of precious metals in the upstream front catalyst is kept as low as possible, and the oxidation reaction proceeds gradually. The catalyst was evaluated using REKO-1 at the Jülich Research Center, and the catalyst was installed in three stages. The catalyst specifications are shown in Table 2. The numbers in parentheses indicate the mass percentage of metal supported. The γ-Al_2O_3 used had SSA of 138.6 $m^2\ g^{-1}$, and the CZY ($Ce_{0.49}Zr_{0.46}Y_{0.05}O_{2\text{-}\delta}$), originally developed by Daihatsu for automotive applications, had SSA of 109.1 $m^2\ g^{-1}$. Here CZY was calcined in air at 1000 °C for 5 h, resulting in SSA of 26.3 $m^2\ g^{-1}$. It is denoted as CZY-L.

The multistage catalyst setup is shown in Fig. 2. The size of the honeycomb catalyst is 65 mm in diameter, 5 mm in thickness, and 30 cpsi in cell density. The only exception is Top Cat. #7, which has a thickness of 10 mm. The catalysts were placed at intervals of 20 mm using spacers, and a thermocouple was inserted between them to measure the inter-catalyst temperatures (1) and (2). The temperatures of the front catalyst at the bottom and the rear catalyst at the top were measured by inserting thermocouples into the catalyst beds. Multi-stage catalyst inlet and outlet gas temperatures were also measured. At room temperature, air was passed over the catalyst from below at a flow rate of 0.25 m s^{-1} and the hydrogen concentration was gradually increased to compare the auto-ignition limits depending on the catalyst specifications.

Here, the experiment focused on carbon monoxide, which is the most typical substance that poisons catalysts in hydrogen recombination reactions [25–27]. The resistance to CO poisoning varies greatly depending on the type of precious metal, the support material, and even the oxygen concentration.

Platinum, palladium, and rhodium catalysts were prepared by impregnating $[Pt(NO_2)_2(NH_3)_2]$, $[Pd(NO_3)_2]$ and $[Rh(NO_3)_3]$ nitric acid aqueous solutions onto γ-Al_2O_3 (SSA = 138.6 $m^2\ g^{-1}$) or $Ce_{0.49}Zr_{0.46}Y_{0.05}O_{2\text{-}\delta}$ (SSA = 109.1 $m^2\ g^{-1}$) support materials, respectively. Each catalyst is denoted 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% relative to the support material. In addition, the intelligent catalyst (Pt–Pd–Rh) installed in the actual vehicle was also prepared with a total precious metal loading of 0.5 wt% [14].

The catalytic activity was evaluated using the homemade fixed-bed flow reactor CATA-5000 with a powder catalyst. A weight of 0.5 g of each precious metal-supported powder catalyst was measured, and compact pellets were prepared by pressing. All catalysts underwent reduction in an atmosphere of H_2 (2%)/N_2 (balance) at 400 °C for 10 min. After cooling to room temperature under N_2 flow, the H_2 and CO oxidation activities in the presence of CO were evaluated by increasing the temperature from 50 to 330 °C. Specifically, to investigate the effect of O_2 concentration on catalytic activity, fixed concentrations of H_2 and CO at 1.0% were used, while four oxygen concentrations were varied and compared: 10% (excess), 1.0% (stoichiometry), 0.75% (shortage), and 0.5% (insufficiency).

Table 2
Multi-stage catalyst specifications.

No.	#1	#4	#7
Rear Cat. (Top)	Pt (0.5) /Al_2O_3	Pt (0.5) Fe (0.5) /Al_2O_3	Pt (1.0) Fe (0.25) /CZY-L [t = 10 mm]
2nd. Cat. (Middle)	Pt (0.015) /Al_2O_3	Pt (0.015) Fe (0.985) /Al_2O_3	Same as #4
Front cat. (Bottom)	Pt (0.001) /Al_2O_3	Pt (0.001) Fe (0.999) /Al_2O_3	Same as #4

X-ray absorption fine structure (XAFS) analysis of the precious metal surface was performed using synchrotron radiation at BL14B1 in SPring-8 to scientifically confirm the resistance to CO poisoning. Information on the surface structure of precious metal nanoparticles during a reaction is crucial because these nanoparticles often undergo changes in their atomic and electronic structures due to fluctuations in temperature and the surrounding atmosphere. X-ray absorption fine structure (XAFS) is a unique technique used to study the atomic and electronic structures of the target element [15,16].

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 as the balance gas instead of N_2 to minimize X-ray scattering by outer-shell electrons.

4. Results and discussion

The results of cryogenic H_2 conversion activity measurements of pre-reduced and pre-oxidized Pt(2.0)/Al_2O_3, Pt(4.0)/Al_2O_3, Pd(2.0)/Al_2O_3 and Pd(4.0)/Al_2O_3 are shown in Fig. 3. Since the reaction gas has a hydrogen excess of 7% H_2 and 3% O_2, the H_2 conversion ratio of 85.7% indicates that all O_2 has been consumed. All of the catalysts pretreated for reduction showed good hydrogen oxidation ractivity from cryogenic temperatures, and Pt/Al_2O_3 catalysts show activity at minus 90 °C, while Pd/Al_2O_3 catalysts show activity from around minus 80 °C. On the other hand, there was a marked difference in activity for each of the catalysts that had been pretreated for oxidation. In particular, Pd(4.0)/Al_2O_3 showed no activity even at room temperature, while Pd(2.0)/Al_2O_3 showed activity at around 18 °C, suggesting that the grain-grown PdO is not easily reduced. Pt(2.0)/Al_2O_3 exhibited activity from around minus 55 °C, while Pt(4.0)/Al_2O_3 exhibited activity from around minus 85 °C, indicating that increasing the loading amount is effective in the platinum system. When hydrogen oxidation activity from cryogenic temperatures is emphasized, platinum-based systems are also promising in terms of robustness after long-term atmospheric exposure.

The high-speed response of four types of catalysts, Pt(4.0)/Al_2O_3, Pt (1.0)/Al_2O_3, Pt(0.5)/Al_2O_3 and Pd(4.0)/Al_2O_3, is shown in Fig. 4, and their low-oxygen reactivity is shown in Fig. 5. These tests assume that liquid hydrogen will expand rapidly when it leaks, resulting in high velocity and low oxygen in the gas flow reaching the PAR. Both Pt and Pd catalysts with higher loadings maintained activity up to high SV, while those with lower loadings showed a decrease in addition rate at high SV. Thus, increasing the amount of precious metals is considered to be an effective way to keep up with high SV. Furthermore, the technology used in automobile catalysts can also be applied to this field in terms of shape. In this case, bead catalysts were used, but further improvement can be achieved by using honeycomb catalysts. These catalysts were confirmed to achieve complete reaction when an amount of oxygen equivalent to the stoichiometric amount of hydrogen oxidation is present. Oxygen storage materials can also be used to deal with momentary oxygen shortages.

The results of addressing the contradictory challenge of being active at extremely low temperatures while allowing the reaction to proceed slowly to suppress heat generation will be presented using the design concept of a multi-stage catalyst.

Results of Set #1: First, the experimental results of catalyst set #1 with three stages of Pt/Al_2O_3 are shown in Fig. 6. The platinum loading relative to the mass of the alumina coating was 0.001%, 0.015%, and 0.5%, respectively, from the upstream of the gas. The concept of this multi-stage catalyst set #1 is to gradually oxidize hydrogen and slow the

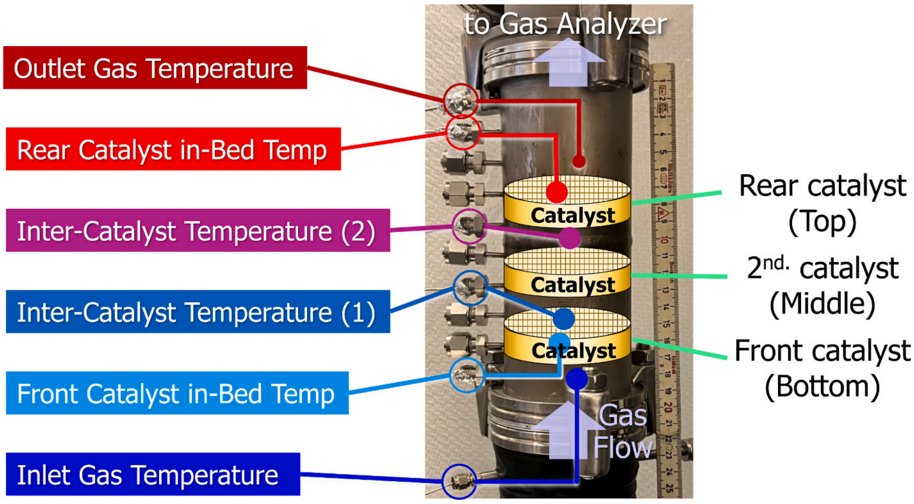

Fig. 2. Multi-stage catalyst setup using REKO1 at the Jülich Research Center.

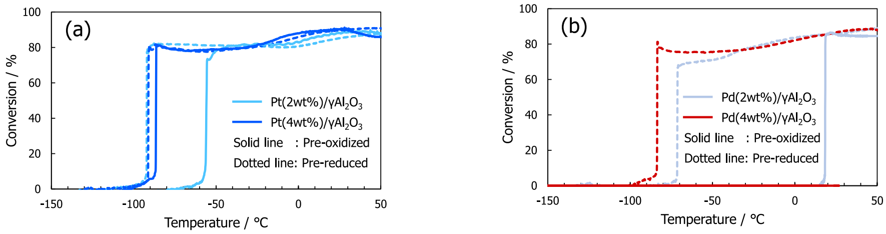

Fig. 3. Cryogenic activity of pre-reduced and pre-oxidized catalysts, (a) Pd/Al_2O_3 and (b) Pt/Al_2O_3.

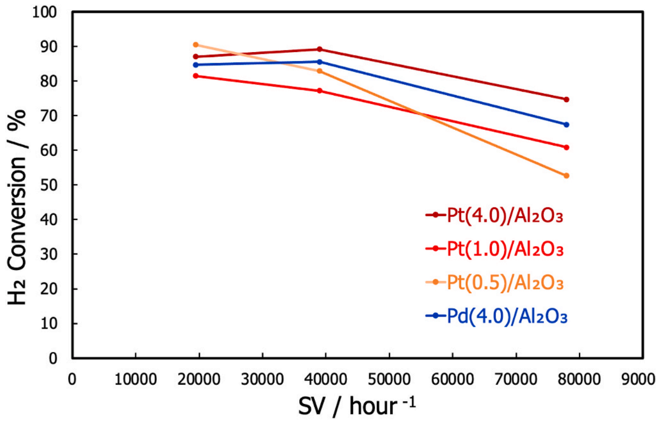

Fig. 4. High-speed response.

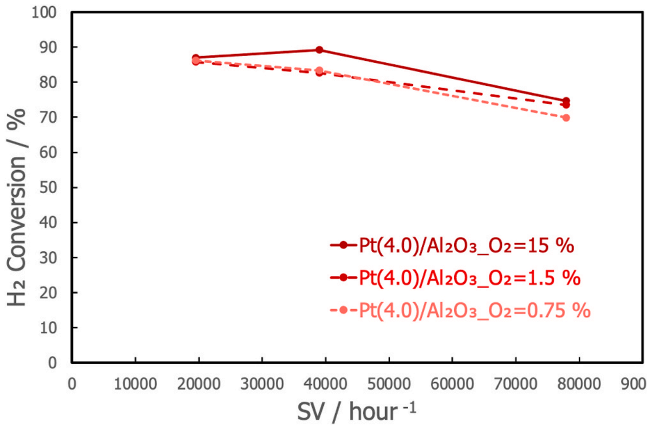

Fig. 5. Low-oxygen reactivity.

temperature rise by significantly reducing the precious metal usage of the front and second stage catalysts. Room temperature air was injected from below at a rate of 0.25 m s^{-1}, and the hydrogen concentration was gradually increased. Focusing on the outlet H_2 concentration, it can be seen that the hydrogen concentration dropped rapidly after 600 s had passed since the start of the test, when the inlet H_2 reached 6.0%. At this time, the outlet gas temperature also rose sharply, but the temperature of neither the Front-Cat-Bed nor the Inter-Cat (1) had risen, indicating that the Front catalyst had not yet been activated. The temperature rise of Inter-Cat (2) was slightly delayed, which is thought to be due to the effect of radiant heat caused by the activation of the Rear Catalyst. It is believed that 800 s after the start of the test, the 2nd catalyst was activated when the inlet H_2 concentration was 6.5%, and 1100 s later, the rear catalyst was activated when the hydrogen concentration was 8.0%. After 1500 s, the inlet hydrogen concentration was increased to 9.5%, causing both Inter-Cat (2) and Inter-Cat (1) to exceed 570 °C, and as soon as the inlet hydrogen concentration was increased to 10.0%, ignition occurred and the inlet gas temperature also rose sharply, so the hydrogen supply was stopped and the experiment was completed. Since the catalyst is hardly activated until the inlet hydrogen concentration reaches 6% and the outlet hydrogen concentration exceeds 4%, it can be said that the safety device has not achieved its purpose.

Results of Set #4: Next, the experimental results for catalyst set #4, which is a triple-stage Pt–Fe/Al_2O_3 catalyst set, are shown in Fig. 7. The amount of platinum loaded is the same as #1, but Fe is added as a post-loading, and the total amount of metal loaded is adjusted to 1.0 mass%

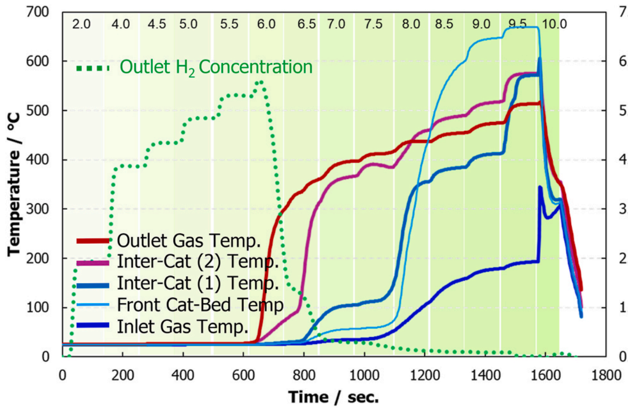

Fig. 6. Multi-stage catalyst set #01 (Pt/Al_2O_3 x3).

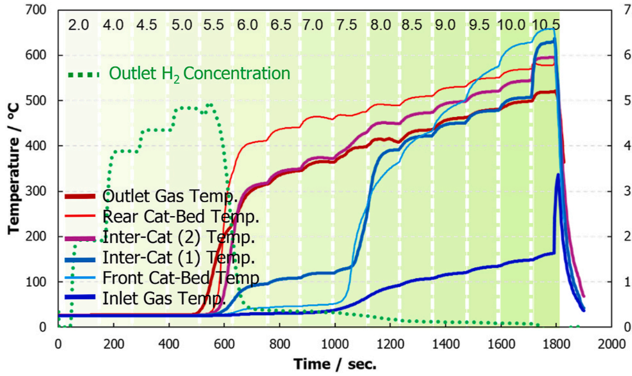

Fig. 7. Multi-stage catalyst set #04 (Pt–Fe/Al_2O_3 x3).

relative to the alumina coat. The concept of this multi-stage catalyst set #4 is to compensate for the lack of activity in set #1 and to prevent rapid oxidation reactions, the greatly reduced platinum usage is supplemented by iron to slowly oxidize hydrogen. As in the previous experiment #1, room temperature air was injected from below at a rate of 0.25 m s^{-1} while gradually increasing the hydrogen concentration. It can be seen that the hydrogen concentration dropped rapidly after 500 s from the start of the test when the inlet H_2 reached 5.5%. At this time, the outlet gas and rear Cat-Bed temperatures also rose sharply, but the Inter-Cat (2) temperature also rose, so it is assumed that the 2nd catalyst was also activated. It can be seen that the front catalyst was activated after 1000 s when the hydrogen concentration reached 7.5%. After that, even when the hydrogen concentration was gradually increased, the temperature increase was relatively gradual. After 1700 s, the inlet hydrogen concentration was increased to 10.5%, causing the Rear Cat-Bed, Inter-Cat (2), and Inter-Cat (1) to all exceed 570 °C. 1800 s after the start of the test, ignition occurred. As the inlet gas temperature also rose sharply, the hydrogen supply was stopped and the experiment was completed. By compensating for the shortage of Pt with Fe, hydrogen oxidation activity started at H_2 concentration of 5% at the inlet, and a slow temperature rise was observed. However, H_2 concentration cannot be kept below 4%, and further improvement is needed.

Results of Set #7: Furthermore, the experimental results for catalyst set #7, which was constructed in three stages with the rear catalyst changed to Pt(1.0)Fe(0.25)/CZY-L, are shown in Fig. 8. The concept of this multi-stage catalyst set #7 was to enhance the oxidation activity of the Rear (Top) layer catalyst to compensate for the lack of activity at low H_2 concentrations in sets #1 and #4. In #1 and #4, none of the three catalysts were activated even when the inlet H_2 fraction exceeded the lower flammability limit of 4%, but in set #7, a significant improvement was observed. The rear catalyst was activated from the inlet hydrogen concentration of 2% immediately after the start of the test, and the outlet hydrogen concentration was reduced to almost 0%, which was an extremely good performance. After 200 s, the temperature of Inter-Cat (2) rose at an inlet hydrogen concentration of 4%, indicating that the 2nd catalyst was also activated. After that, as the inlet hydrogen concentration increased, the temperatures of the outlet gas, rear Cat-Bed, and Inter-Cat (2) gradually rose. After 900 s, the front catalyst was activated at a hydrogen concentration of 7.0%, and the temperatures of the Front Cat-Bed and Inter-Cat (1) rose sharply. After 1700 s had passed and the hydrogen concentration was set to 10.5%, the temperatures of both Inter-Cat (2) and Inter-Cat (1) exceeded 600 °C, and 1800 s after the start of the test, ignition occurred and the inlet gas temperature also rose sharply, so the hydrogen supply was stopped and the experiment was completed. At this point, the outlet gas temperature had not reached 500 °C, and a sudden rise in temperature was successfully prevented over a wide range of inlet H_2 concentrations from 2.0% to 10.0%, confirming a certain degree of effectiveness of the multi-stage catalyst design concept. Further research developments are expected in the future.

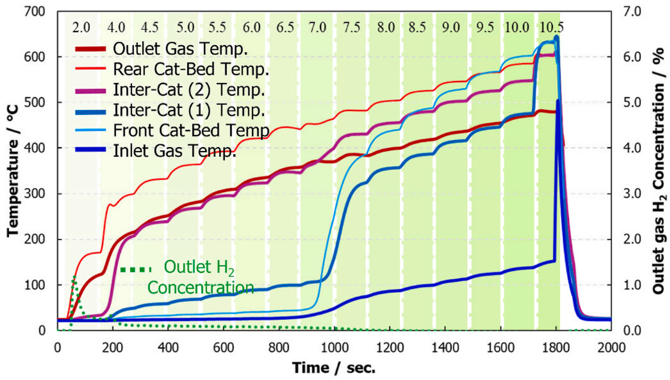

Fig. 8. Multi-stage catalyst set #07 (Pt–Fe/Al_2O_3 ×2 + Pt–Fe/CZY-L).

Here, the resistance to carbon monoxide, the most typical poison for precious metal catalysts, was evaluated [25–27]. The H_2 oxidation activity of the pelletized powder catalyst was measured in the presence of CO and low O_2 concentration. 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 a precious metal loading of 0.5 wt%, were compared (Fig. 9) [14,28–33].

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 showed the lowest reaction temperature, followed by Pd and Pt. The oxidation reactions of H_2 and CO occurred almost simultaneously. Next, catalysts using CZY support are discussed. It should be noted that the Pt/CZY already showed a conversion of 60% from the beginning 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 selectivity of the reaction towards hydrogen. The intelligent catalyst designed for automotive emissions control exhibited dynamic activity even at low temperatures.

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 catalysts supported on alumina, even under this condition, Rh exhibited the lowest reaction temperature, followed by Pd and Pt, with the difference in activity becoming more pronounced. In the case of Pt/Al_2O_3, it was clarified that the oxidation of H_2 started after the removal of CO, a poisoning substance, through oxidation. With the combination of CZY support, the catalysts Pt, Pd, and Rh showed significant improvements in low-temperature activity, conversion rate, and selectivity towards hydrogen oxidation. The intelligent catalysts designed for automobile exhaust gas control demonstrated the ability to

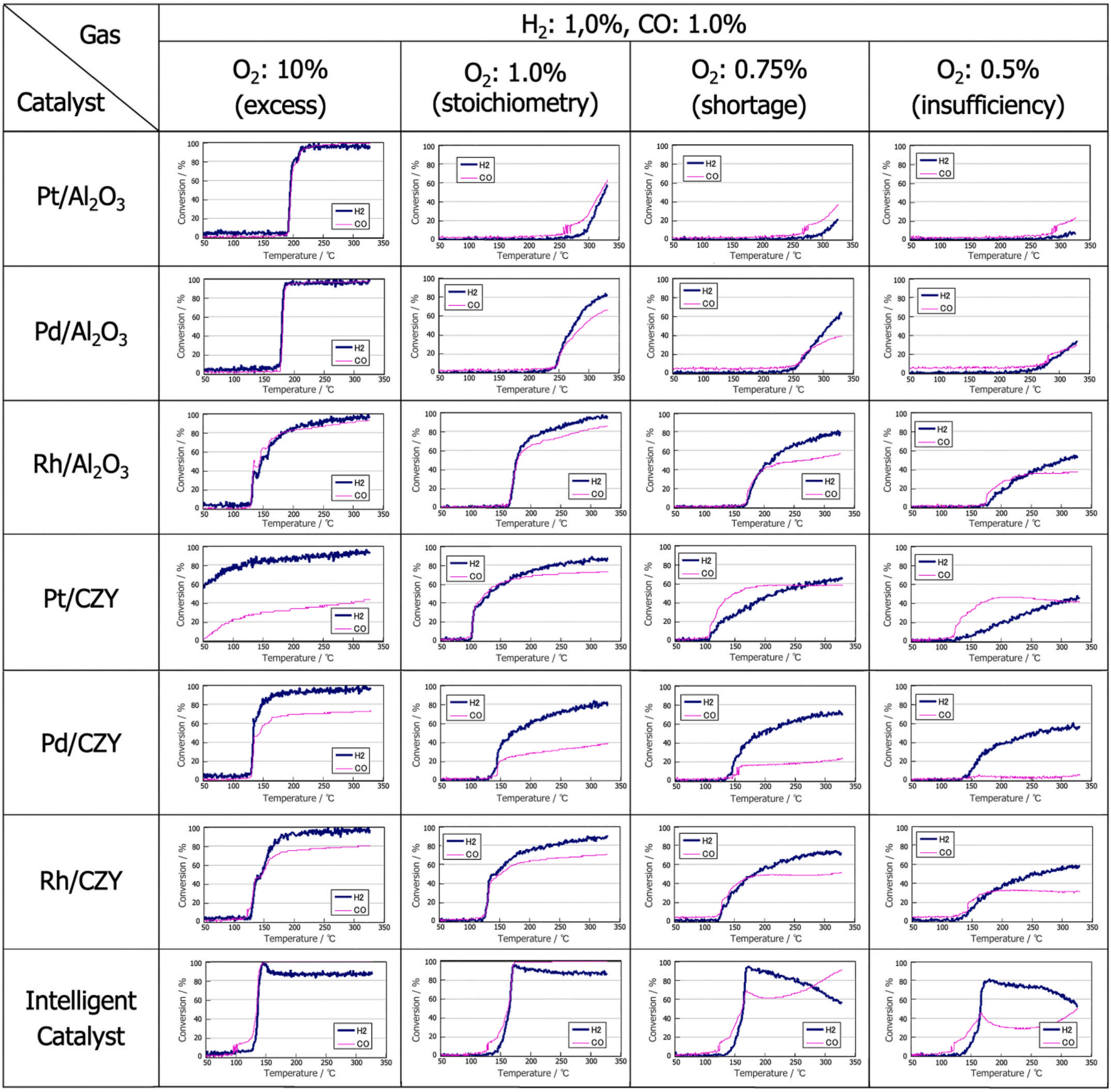

Fig. 9. H_2 and CO oxidation activity in CO coexistence and various O_2 concentrations.

completely oxidize hydrogen below 200 °C, distinguishing them from other catalysts.

Short and insufficient oxygen conditions: Activity was discussed when not enough O_2 was supplied to oxidize H_2 and CO, specifically at 75% or 50% of the stoichiometric ratio. Pt/Al_2O_3 exhibited minimal reactivity, while Pd showed slight activity, and Rh oxidized H_2 and CO in proportion to the supplied oxygen. All three catalysts initiated the oxidation of H_2 after CO was removed through oxidation. On the other hand, Pt/CZY demonstrated significant improvements in catalytic performance. Notably, the oxidation of H_2 started after the CO was eliminated through oxidation. In Pt/CZY, the selectivity towards H_2 appeared in oxygen-excess, and CO selectivity appeared in oxygen-deficient environments. Compared to Pd/Al_2O_3, Pd/CZY exhibited enhanced catalytic activity at lower temperatures and favored hydrogen oxidation selectivity. O_2 was not consumed by CO and the reaction favored H_2 oxidation. For Rh/CZY, a common feature was observed where the oxidation reactions 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 both Rh catalysts with different support materials exhibited stable and efficient oxidation properties. Even in an oxygen-deficient environment, the intelligent catalyst started CO oxidation around 125 °C, followed by H_2 oxidation from 150 °C. A phenomenon was observed where H_2 conversion reached a peak of over 80% and then decreased at higher temperatures, indicating the occurrence of the water-gas shift reaction in this elevated temperature range.

Summary of CO poisoning prevention catalysts:

All catalysts exhibited good oxidation activity for H_2 in the presence of excess O_2, even under CO-poisoning environment. The decrease in H_2 oxidation activity with decreasing O_2 concentration was interestingly different depending on the catalyst specification; in the case of Al_2O_3 support, H_2 and CO oxidation activities were Rh > Pd > Pt, suggesting that the formation of an oxide layer on the precious metal surface is effective for CO tolerance. In Pt/Al_2O_3, H_2 is oxidized after CO is oxidized.

The use of CZY support promoted the oxidation reaction compared to Al_2O_3. In particular, Pt/CZY was the only one that showed high H_2 oxidation activity from room temperature under excess O_2, even in the presence of CO. It is noteworthy that Pd/CZY selectively oxidized H_2 without oxidizing CO under oxygen deficient conditions. Rh showed excellent H_2 oxidation activity regardless of the carrier material.

Intelligent catalysts designed for automotive emissions control showed excellent properties for both H_2 and CO oxidation under a wide range of boundary conditions.

X-ray Absorption Spectroscopy by Synchrotron Radiation in SPring-8: X-ray absorption fine structure (XAFS) measurements were performed to analyze the local structure of Pt catalysts [34–36]. The valence state of Pt was estimated from X-ray absorption near edge structure (XANES) spectrum at Pt L_{III}-edge. Pt/CZY catalyst in He atmosphere, after reduction treatment, exhibited a clean metallic platinum profile, which represents the standard state (Fig. 10). By introducing O_2, CO, and H_2 separately into He atmosphere, the adsorption structures of Pt nanoparticles changed respectively. When O_2 was introduced, an increase in white-line intensity indicated a highly oxidized state of Pt, corresponding to an increase in the average valence. When CO was adsorbed, a broad overhang on the high-energy side of the peak was observed, which is sometimes referred to as a peak shift. On the other hand, when H_2 was adsorbed, the tail in the energy range of 11,572–11,575 eV was lifted. The adsorbed species on the Pt surface can be understood by comparing the profile when the mixed gas is flowed with the profile when O_2, CO, and H_2 are individually adsorbed on the metallic state Pt (see Fig. 11).

In-situ observation of adsorbed species on Pt surface: XAFS spectra were measured in a mixed gas flow that closely resembles the real environment, allowing for the observation of surface-adsorbed species of platinum. In total, there were four types of mixed gas conditions: two without CO and two with CO added (Table 3).

Fig. 11 (a) shows Pt L_{III}-edge XANES spectra of Pt/Al_2O_3 under four different gas conditions as indicated in Table 3. In condition 1 (excess oxygen), the white line intensity increases, indicating that Pt is in an oxidized state. In condition 2 (stoichiometry), Pt appears to be mostly in a metallic state, and hydrogen oxidation occurs even at room temperature, indicating a clean Pt surface. A slight increase in absorption intensity in the range of 11,572–11,575 eV suggests hydrogen adsorption, potentially due to slight oxygen deficiency in the experimental equipment settings, such as the mass flow controller. The profiles of conditions 3 (excess oxygen) and 4 (insufficient oxygen) with CO coexistence are nearly identical, indicating adsorption of CO observed as an overhang on the high-energy side. Even under excess oxygen (condition 3), the entire Pt surface is covered with the CO adsorption layer, preventing oxidation of the Pt surface and inhibiting the reaction.

Fig. 11 (b) shows Pt L_{III}-edge XANES spectra of Pt/CZY under four different gas conditions mentioned in Table 3. In condition 1 (excess oxygen), the white line intensity significantly increases, indicating a highly oxidized state of Pt. Condition 2 (stoichiometry) exhibits similar characteristics to Pt on Al_2O_3, where Pt on CZY is predominantly in a metallic state and hydrogen adsorption is observed. In condition 4 (oxygen deficiency) with the coexistence of CO, the overhang in the spectrum confirms the adsorption of CO on the Pt surface, consistent with Pt/Al_2O_3. Notably, condition 3 (excess oxygen) with CO coexistence reveals a distinct feature where Pt on CZY undergoes oxidation. This observation suggests that the surface of Pt on CZY remains unpoisoned even in the presence of CO at room temperature, given sufficient oxygen supply.

Fig. 12 provides an illustrative depiction of the surface changes in Pt metal nanoparticles and the ability to overcome CO poisoning. A remarkable suggestion has been put forward for the design of an "anti-CO catalyst" to overcome CO poisoning. The XAFS results provide evidence that CO poisoning can be prevented by facilitating the formation of an oxygen and/or oxide layer on the surface of Pt catalysts. CZY, a cerium-based composite oxide support material with oxygen storage capacity, promotes the formation of such layers on Pt. Additionally, in laboratory tests, it is observed that the H_2 oxidation activity and the formation of oxygen/oxidized layers on the surface of precious metals are improved in the presence of CO, with the order of Pt < Pd < Rh. The ability of intelligent catalysts for automotive emissions control to exhibit H_2 oxidation performance in diverse environmental conditions can be attributed to their design aimed at delivering performance in environments with varying redox conditions.

5. Conclusions

Through international collaboration between industry, government, and academia, potential risks in the storage and transportation of liquefied hydrogen have been identified, and effective safety measures are being developed. To improve the safety of hydrogen, a passive autocatalytic recombiner (PAR), which does not require external power for heating, has been developed by applying automotive monolith catalyst technology.

In response to the unique characteristics of liquefied hydrogen, such as its extremely low temperatures, high energy density, and significant expansion during leaks, research has progressed from atomic-level crystal structure design to prototyping actual catalysts and conducting evaluations at scales ranging from laboratory to large-scale systems.

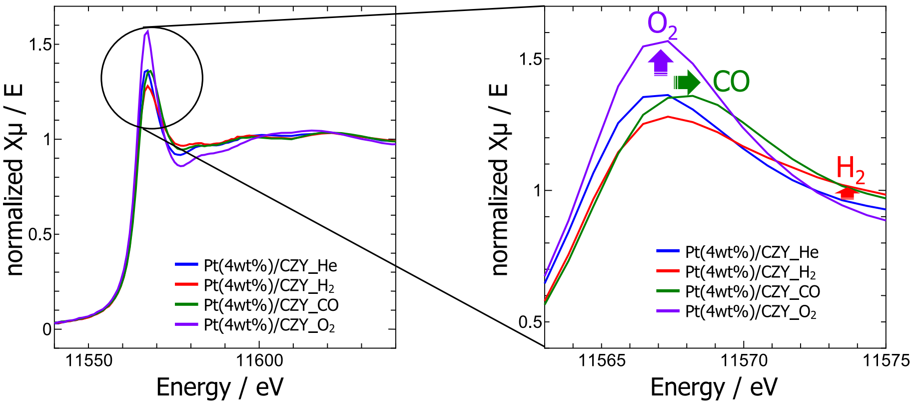

Fig. 10. Pt L_{III}-edge XANES spectra of Pt/CZY under individual gas atmospheres at room temperature.

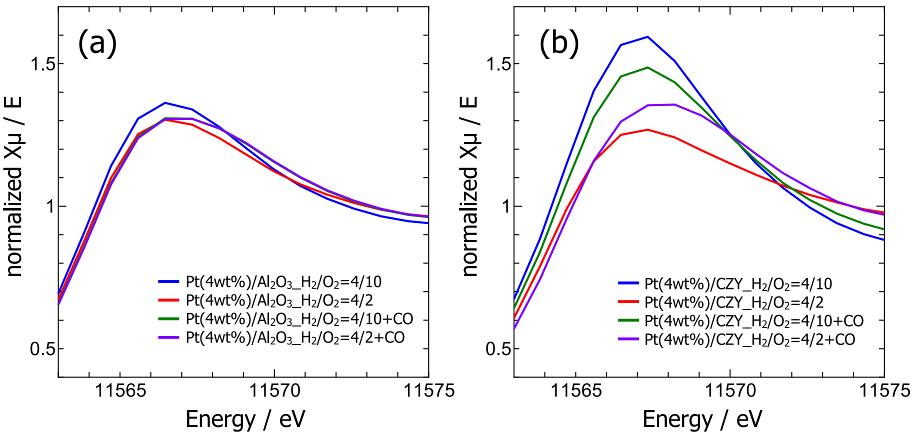

Fig. 11. Pt L_{III}-edge XANES spectra of (a) Pt/Al_2O_3 and (b) Pt/CZY.

Table 3
Mixed gas conditions for XAFS experiments.

Condition	H_2	O_2	CO	atmosphere
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

This work has clarified the following key tasks required of catalysts:

Task 1. Cryogenics: Hydrogen oxidation catalytic activity was observed even at extremely low temperatures around −90 °C.

Task 2. High-flow & Low O_2: It was confirmed that catalysts can maintain high catalytic activity even in high-flow, low-oxygen environments.

Task 3. Prevent Ignition: The multi-stage catalyst concept is expected to be effective in treating the heat generated by oxidizing high-energy-density hydrogen.

Task 4. Robustness: It was found that the surface contamination of catalytic precious metals can be controlled by changing the support.

Furthermore, it has been confirmed that the passive autocatalytic recombiner is an effective technology for preventing hydrogen explosions in the event of a liquefied hydrogen leak. Ongoing research is expected to further contribute to the realization of the economic advantages and societal acceptance of liquefied hydrogen.

CRediT authorship contribution statement

Hirohisa Tanaka: Writing – original draft, Visualization, Supervision, Project administration, Investigation, Funding acquisition, Conceptualization. **Ernst Arndt Reinecke:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition. **Nabiha Chaumeix:** Supervision, Project administration, Investigation, Funding acquisition. **Ahmed Bentaib:** Supervision, Project administration, Funding acquisition. **Masashi Taniguchi:** Investigation, Data curation, Conceptualization. **Daiju Matsumura:** Methodology, Investigation, Data curation. **Shannon Krenz:** Data curation. **Itsuki Jinjo:** Data curation. **Tomohito Nakayama:** Data curation. **Shinya Uegaki:** Data curation. **Takuro Aotani:** Data curation. **Tomoaki Kita:** Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial

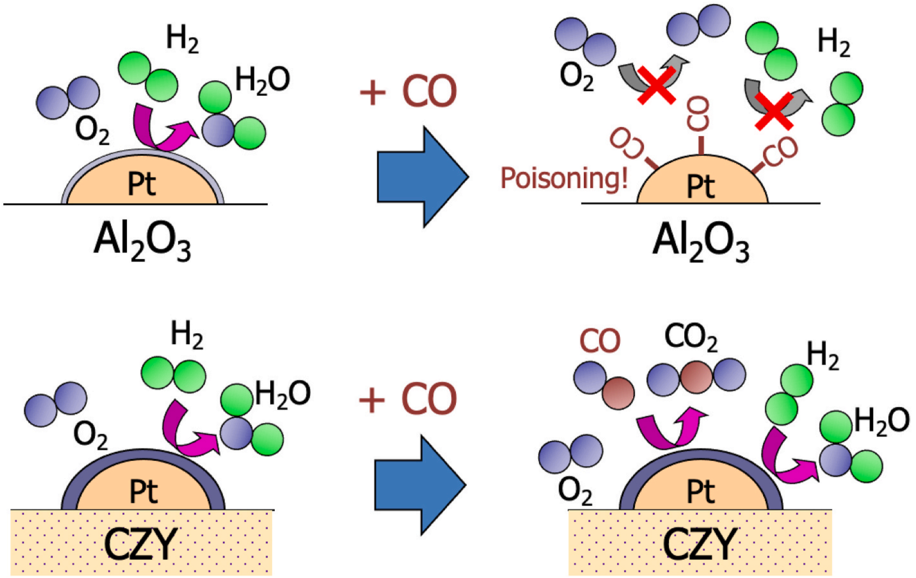

Fig. 12. Image diagram of reaction termination due to CO poisoning in Pt/Al_2O_3 catalysts, and hydrogen recombination overcoming CO poisoning in Pt/CZY catalysts.

interests or personal relationships that could have appeared to influence the work reported in this paper.

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