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Research on hydrogen safety technology utilizing the automotive catalyst

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ABSTRACT

Safety management technology of hydrogen gas is extremely important not only for nuclear power generation but also for future society. This is international research and development on hydrogen safety technology in which industry, government and academia collaborate. A brand-new passive autocatalytic recombiner (PAR) system utilizing the monolithic “intelligent catalyst” has been studied for the long-term storage of high-concentration radioactive materials related to the decommissioning of nuclear reactors. In a small lab scale test, it was found that this monolithic catalyst can start a hydrogen oxidation reaction from a low temperature of minus 20 °C. The monolith-type automotive catalyst showed high hydrogen conversion activity from a room temperature in a large-scale reactor of REKO-4 in Jülich (FZJ). It became clear that natural convection by reaction is greatly improved by roughening the cell density of the monolith catalyst especially under static environmental conditions such as in a storage container. Furthermore, this natural convection is strengthened by adopting a chimney, and the hydrogen oxidation reaction per unit time has improved about three times. Taking advantage of this superior catalytic property, we aim to complete the safety technology for storage containers at an early stage and advance the development of highly active catalyst from further low temperature.

KEYWORDS

hydrogen safety, nuclear power plant, catalyst, recombiner, monolith

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1. Introduction

In 2011, Fukushima Daiichi nuclear power plant lost the external power supply because of the giant tsunami, subsequently, the zirconium alloy cladding of a fuel rod and water vapor caused chemical reaction and a large amount of hydrogen molecules were produced in the reactor. From this, the pressure vessel and the containment vessel were damaged, and the hydrogen gas leaked out from them. Hydrogen concentration in the reactor building increased and the hydrogen explosion was caused. Proper treatment of hydrogen gas is important not only managing the nuclear power plants but also for the long-term storage of high-concentration radioactive materials at decommissioning of reactor. Under the government project, research and development for safe and long-term storage of fuel debris have been conducted. A passive autocatalytic recombiner (PAR) system has been researched as a strong candidate that does not need the external power supply to recombine the hydrogen and oxygen.[1-4] The monolithic “intelligent catalyst” which is equipped with the automobiles showed the great availability about applying to the PAR.[5-7] In this paper, the cell density, the catalyst thickness and the chimney height were investigated to acquire the knowledge for designing the catalyst and the container that is suitable for the long-term storage of high-concentration radioactive materials.

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2. Experimental condition

2.1. Catalyst preparation

Various kinds of monolith catalysts which have different cell density and thickness were prepared using mass-produced automotive catalyst technology named “intelligent catalyst” containing P-, Pd- and Rh-perovskite type compound oxides. The configurations of monolith catalysts are shown in Table 1, and their appearances are shown in Fig. 1. Cell density is called by the unit of cell/inch^2 (cpsi: cell par square inch) in the automotive industry.

Table 1. The configurations of monolith catalysts

Number	Cell density / cpsi	Catalyst thickness / mm	Diameter / mm
(i)	30	10	29.4
(ii)	100	10	29.4
(iii)	900	10	29.4
(iv)	30	10	70
(v)	100	10	70
(vi)	900	10	93
(vii)	900	5	93
(viii)	30	3.5	93
(ix)	30	5	93
(x)	30	10	93

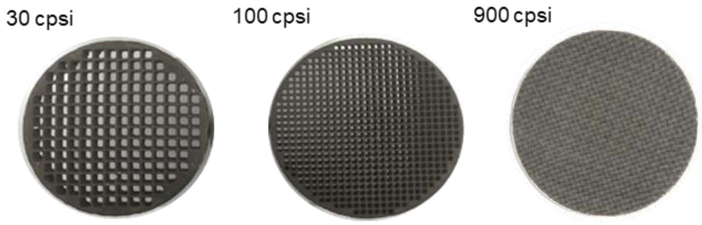

Fig. 1. The catalyst appearance which have different cell density

2.2. Laboratory scale catalytic reaction (forced flow)

Mixture gas (4%-H2, 10%-O2, Balance-N2) was flowed at 4.0 L/min to the monolith catalyst which have different cell density ((i), (ii) and (iii)). The schematic picture of the experimental equipment is shown in Fig. 2 (a). By blowing liquid nitrogen from the outside of the glass reactor, the catalyst was once cooled down to minus 50 °C and then blowing the liquid nitrogen was stopped. The temperature of the catalyst naturally increased toward room temperature without any external power supply. And the temperature further increased due to the start of the hydrogen oxidation reaction. In this test, the amount of hydrogen oxidized by the catalyst with each cell density was observed.

2.3. Large scale catalytic reaction (natural convection)

2.3.1. Steady state test

Two types test, the steady state test and the dynamic test, were conducted in the REKO-4 that stands at Jülich, in Germany which has the 1.4 m diameter, the 3.7 m height and the 5,330 L volume. The schematic picture of the experimental equipment is shown in Fig. 2 (b). Hydrogen was constantly feeded until reaching steady state of the temperature and hydrogen concentration at 1, 2, 4 and 6%, respectively. [8] The objective of this test is to know the flow rate of natural convection. The amount of hydrogen oxidized by the catalyst is obtained from hydrogen injection amount, the flow rate of natural convection is calculated from them.

2.3.2 Dynamic test

For the dynamic test using the chimney in 300 mm height, hydrogen gas was injected into the reactor to reach the concentration about 6%, then injection of hydrogen gas was stopped and the valve was closed. The objective of the test is to know the catalytic ability for oxidizing hydrogen.

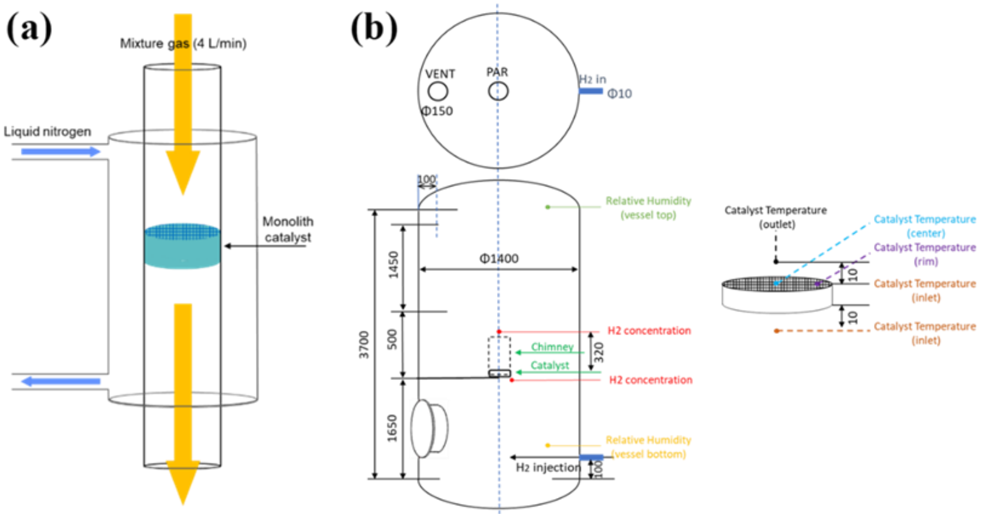

Fig. 2. The schematic picture of the catalytic reaction experimental equipments ((a): laboratory scale, (b): Large scale)

3. Results and Discussion

3.1. Laboratory scale catalytic reaction (forced flow)

The result of laboratory scale catalytic reaction (forced flow) is shown in Fig. 3. It showed the temperature dependence of the hydrogen conversion rate. All three catalysts showed good activity, and the conversion efficiency reached 90% or more, at the room temperature. It is further noted that activation from a low temperature of about minus 20 ° C. Hydrogen conversion rate was getting high as the temperature increased. From hydrogen oxidation reaction started below freezing point, it turned out that hydrogen oxidation reaction could be sufficient by using an intelligent catalyst without any heating. The results showed the ability of applying the monolithic intelligent catalyst to PAR.

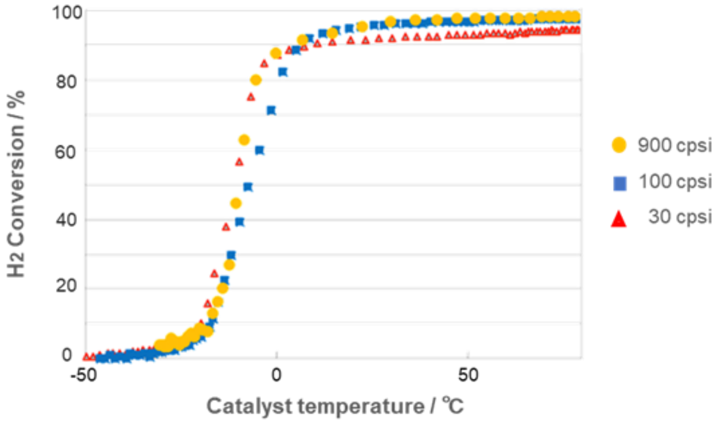

Fig.3. The temperature dependence of hydrogen conversion at each cell density

3.2. Large scale catalytic reaction (Natural convection)

3.2.1 Steady state test

The results of steady state test at large scale catalytic reaction, according to the test condition shown in Table 1, are shown in Fig. 4 (a). The flow rate of natural convection was calculated from the amount of hydrogen injection and hydrogen concentration. When the catalysts (iv), (v) and (vi) were used, the flow rate were 0.187, 0.0873 and 0.007 m/s, respectively. Under the forced flow in laboratory scale, the catalyst with finer cell density showed higher hydrogen oxidation rate. While under natural convection, the catalyst with coarser cell density showed the much better flow rate. It was found that by designing optimization the catalyst from 900 cpsi to 30 cpsi, the flow rate can be improved by 27 times. It is thought that optimization the cell density reduced the airflow resistance. A comparison of influence of catalyst thickness is shown in Fig. 4 (b). When the catalyst (vi) was used, the flow rate was 0.007 m/s. In comparison with the catalyst (vii) was used, the flow rate became about one tenth. It is thought that increasing the airflow resistance was caused by using the catalyst which has the fine cell density and the high thickness. On the other hand, when the catalysts which have the different thickness ((viii), (ix) and (x) ）were used, the flow rate were 0.239, 0.227 and 0.217 m/s. It is considered that applying the catalyst which has 30 cpsi to PAR is useful because the influence of airflow resistance what is caused by catalyst thickness can be reduced. The result of the test using the chimney which have different height is shown in Fig. 4 (c). When the hydrogen concentration was 6%, using the 300 mm chimney, the flow rate was 0.227 m/s. It was about twice as large as the flow rate using the 50 mm chimney. Furthermore, compared to without the chimney, the flow rate improved by three times. Thus, the flow rate increased as the chimney height became high. Furthermore, it can be inferred that there is little relationship between hydrogen concentration and flow rate.

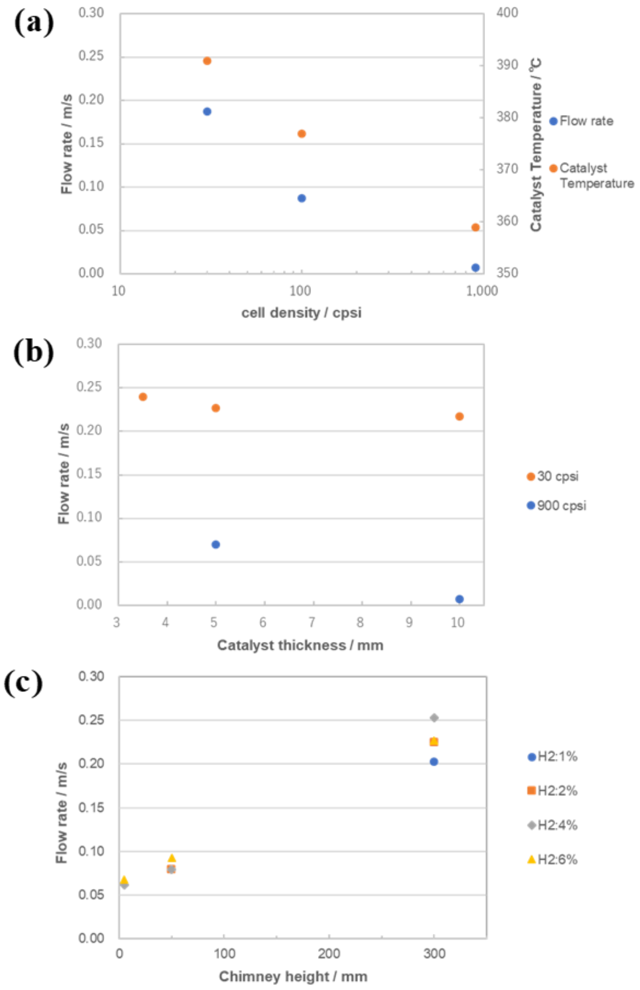

Fig. 4. (a)The cell density dependence of flow rate of natural convection and the catalyst temperature, using the catalyst that have 5 mm thickness and 300 mm height chimney. Hydrogen concentration was kept at 6%. (b)The cell thickness dependence of flow rate of natural convection, using the 300 mm height chimney. Hydrogen concentration was kept at 6%. (c) The chimney height dependence of flow rate of natural convection, using the catalyst that have 5 mm thickness and 30 cpsi cell density.

3.2.2 Dynamic test

A passive autocatalytic recombiner (PAR) is required to react at room temperature. And the required condition for the upper limit of the hydrogen concentration was set to 2%, which is half the explosion limit. The results of dynamic test at large scale catalytic reaction, the catalyst (vii) and (ix) were used, is shown in Fig. 5. It took 12 hours to reduce the hydrogen concentration down to 1.5% for catalyst (vii). While, it took only 3 hours to reduce the hydrogen concentration down to 0.6% for catalyst (ix). By using the catalyst which has coarse cell density, both the reaction rate and the ultimate concentration were improved in the hydrogen oxidation reaction.

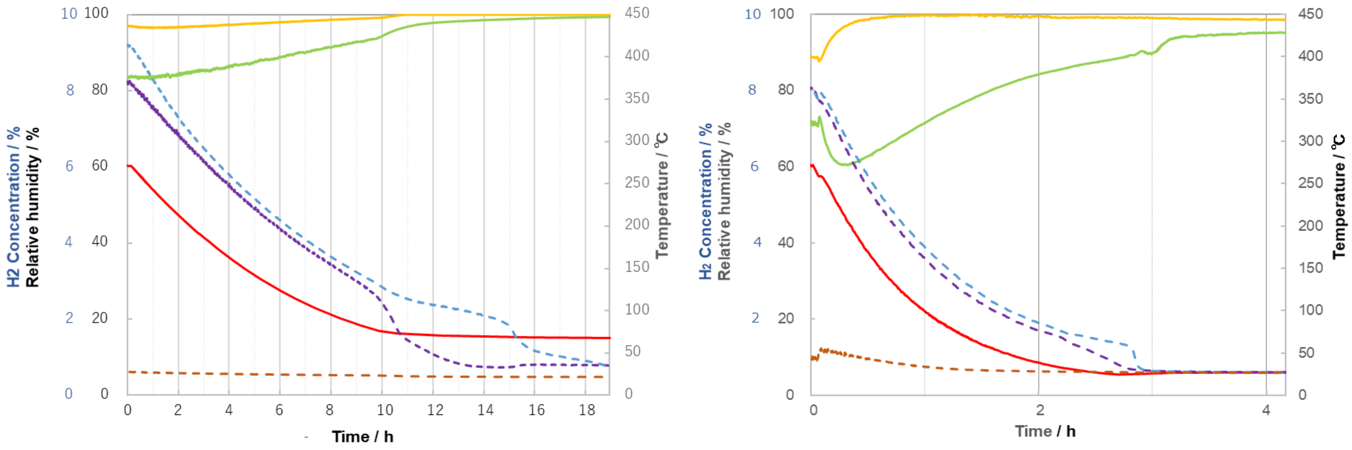

Fig. 5. The result of dynamic test at large scale catalytic reaction ((a): 900 cpsi, (b): 30 cpsi)

— H2 concentration — Relative humidity (vessel top) — Relative humidity (vessel bottom)

- - Catalyst temperature (rim) - - Catalyst temperature (center) - - Catalyst temperature (inlet)

4. Conclusion

1. The applicability of the monolithic intelligent catalyst to PAR was experimentally confirmed.
2. In forced flow, the catalysts showed that the starting hydrogen conversion from below freezing point.
3. In natural convection, the flow rate can be greatly improved by design optimization from automotive (900 cpsi) to PAR (30 cpsi) because the airflow resistance is widely reduced by using the catalyst which has coarse cell density.
4. It was confirmed that installing the chimney with height, the flow rate of natural convection increased.
5. It can be inferred that there is little relationship between hydrogen concentration and flow rate of natural convection.
6. Parameter necessary for designing the container to long-term storage high-concentration radioactive materials were clarified by catalytic reaction experiments using the monolithic intelligent catalyst.

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