

STACY: International collaboration towards liquefied hydrogen safety

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Significance and Relevance

Liquefied hydrogen has three characteristics compared to gases in the event of a leak: (1) cryogenic temperatures, (2) high expansion and low oxygen concentration, and (3) high energy density. A passive autocatalytic recombiner (PAR) to ensure the safety requires (1) improved low-temperature activity, (2) enhanced response, (3) suppression of spontaneous ignition, and additionally (4) robustness against surface contamination. A brand-new PAR was designed by devising the crystal structure of a new catalyst at the atomic level, prototyping the actual catalyst in a laboratory, and conducting repeated reaction experiments using various equipment, including large high-pressure vessels.

Preferred choice for the topic: H₂ storage and transportation, green H₂ production, hydrogen vectors

2nd choice for the topic: Sustainable and clean energy production and transport

Preferred presentation: Oral only / Oral preferred

Introduction and Motivations

Global efforts aim to decarbonize the energy sector by increasing the share of renewable energies in the energy mix. Energy storage technologies are needed to store surplus energy generated from fluctuating energy sources and make it accessible when needed. In this context, large-scale storage and transportation of liquefied (cryogenic) hydrogen (LH₂), which has a high storage density, is expected to play a fundamental role in a potential hydrogen economy of the future.

To realize the economic benefits and societal acceptance of LH₂, an international research collaboration between Germany, France and Japan has been working since 2022 on the development of technologies that contribute to the safety of the storage and transportation of liquefied hydrogen. The project name is "Towards the safe storage and transportation of cryogenic hydrogen" and the acronym is "STACY". The results of three years of research are summarized here.

Results and Discussion

Powder catalysts with various chemical compositions such as Pd/Al₂O₃, Pt/Al₂O₃, Pt/CeZrYO_{2-δ}, and CaZrPtO₃ were prepared, and oxidation and reduction pretreatments were compared to explore the effect of different surface conditions on cryogenic catalytic activity [1-2]. In particular, differences in the mechanisms of hydrogen oxidation activity of various catalysts at sub-zero temperatures were investigated using isotope of oxygen. Furthermore, catalysts coated on honeycomb supports with various cell densities were prepared, and the effect of hydrogen concentration on the hydrogen oxidation reaction rate was clarified (Figure 1).

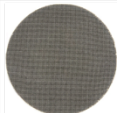


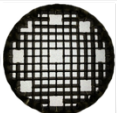

Coanfig. No.	#900	#100	#30	#7	#3
Cell Configuration					
Cell density / cell cm ⁻²	139.5	15.5	4.4	1.1	0.5
Cell (hole) size / cm	0.08	0.25	0.45	0.91	1.43
Note	900 cell-inch ⁻²	100 cell-inch ⁻²	30 cell-inch ⁻²	4-cell holes of #30	9-cell hole of #30

Figure 1. Configuration of honeycomb-type catalysts

The catalytic reactivity can be controlled to the desired value by the cell configuration. It was shown that reducing the cell density can generate natural convection for the oxidation of hydrogen accumulated in a closed space, improving the amount of hydrogen oxidation (Figure 2) [3-4].

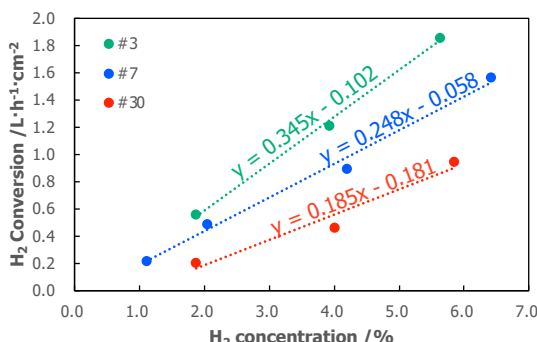


Figure 2. H₂ conversion rate by natural convection using exothermic H₂ oxidation reaction

On the other hand, there is a concern that if high-concentration hydrogen is oxidized all at once, the exothermic reaction may exceed the hydrogen auto-ignition temperature. To mitigate the sudden heat generation, the concept of multi-stage catalysts was investigated, and its effectiveness was experimentally confirmed. It was also shown that Pt-Fe/CZY can selectively catalyze hydrogen at room temperature in the presence of CO, a catalyst poison that inhibits catalytic reactions [5]. Thus, a comprehensive guideline for catalyst design as a PAR in the event of an LH₂ leak has been compiled.

References

1. Nishihata, Y., Mizuki, J., Akao, T., Tanaka, H., Uenishi, M., Kimura, M., Okamoto, T., Hamada, N., Self-regeneration of a Pd-perovskite catalyst for automotive emissions control, *Nature*, 418, p.164-167 (2002). DOI: 10.1038/nature00893
2. Tanaka, H., Taniguchi, M., Uenishi, M., Kajita, N., Tan, I., Nishihata, Y., Mizuki, J., Narita, K., Kimura, M., Kaneko, K., Self-regenerating Rh- and Pt-based perovskite catalysts for automotive-emissions control, *Angew. Chem. Int. Ed.*, 45, p.5998-6002 (2006). DOI: 10.1002/anie.200503938
3. Reinecke, E.-A., Takenaka, K., Ono, H., Kita, T., Taniguchi, M., Nishihata, Y., Hino, R., Tanaka, H., Performance tests of catalysts for the safe conversion of hydrogen inside the nuclear waste containers in Fukushima Daiichi, *Inter. Jour. of Hydrogen Energy*, 46 p.12511-12521 (2021). DOI: 0.1016/j.ijhydene.2020.08.262
4. Ono, H., Takenaka, K., Kita, T., Taniguchi, M., Matsumura, D., Nishihata, Y., Hino, R., Reinecke, E.-A., Takase, K., Tanaka, H., Research on hydrogen safety technology utilizing the automotive catalyst, *E-Journal of Advanced Maintenance*, Vol.11, No.1, p.40-45 (2019). ISSN-1883-9894/10
5. Inagawa, K., Matsumura, D., Taniguchi, M., Uegaki, S., Nakayama, T., Urano, J., Aotani, T., Tanaka, H., Development of hydrogen oxidation reaction catalysts to overcome CO poisoning and elucidation of reaction mechanism, *J. Phys. Chem. C*, 127, p.11542-11549 (2023). DOI: 10.1021/acs.jpcc.3c02237

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