Catalysis Today 155 (2010) 45–50

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

The preparation of a metal foam support of Pt/Al_2O_3 for combustion of hydrogen

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ARTICLE INFO

Article history:
Available online 7 June 2009

Keywords:
Hydrogen catalytic combustion
Passive autocatalytic recombiner (PAR)
Metal foam
Support
Hydrogen risk
Nuclear power reactor

ABSTRACT

A catalyst bed is an essential component of a passive autocatalytic recombiner (PAR) used to remove hydrogen that is accidentally released during a meltdown of a nuclear reactor power plant. Metal foam was selected as a catalytic support in this study, due to its excellent thermal conductivity and its high surface-to-volume ratio. The support surface area was additionally increased by the application of an Al_2O_3 washcoat. An investigation of optimum coating conditions of the Pt/Al_2O_3-coated metal foam was performed with respect to the hydrogen conversion rate and the thermal behavior, with the goal of achieving high hydrogen removal rates. The experimental results showed that the hydrogen conversion rates were affected by washcoat weights and platinum weights, and the majority of the experimental conditions of the Pt/Al_2O_3-coated metal foam showed hydrogen conversion rates over 95%. For cost-effective fabrication, the optimum conditions are an Al_2O_3 washcoat weight of 45 wt.%, and a platinum weight of 3 wt.%. These will lead to a complete removal of the hydrogen at a hydrogen concentration of 4 vol.%. Furthermore, since a region of high hydrogen concentrations has a temperature lower than about 560 °C, which is the ignition limit at a hydrogen concentration of 4 vol.% and ambient pressure, the hydrogen risk can be avoided using the metal foam support.

1. Introduction

Safety regulation on nuclear reactors requires passive autocatalytic recombiners (PAR) to remove hydrogen in the event of a severe accident in a nuclear power plant. These devices are driven by the catalytic recombination of hydrogen and oxygen in air that results in the generation of water vapor and heat. Existing PARs use a series of plate type reactors covered by Al_2O_3 as a catalytic support and platinum as a catalyst; however, with these PARs, the exothermic reaction may lead to an unintended ignition of the hydrogen–air mixture due to the local overheating of the catalyst elements. Several research groups have observed unintended ignitions occurring with high hydrogen concentration levels above 10% [1,2]. Thus, the potential ignition risk of hydrogen is the most important issue for the safety regulation of PARs.

In a recent experimental investigation of existing plate-type PARs with a hydrogen concentration of 4 vol.%, it was shown that temperatures of the catalyst bed reached about 560 °C, which is the ignition limit [3]. Especially, temperatures at the leading edge, a region with high hydrogen concentrations, were much higher than those at the trailing edge. This well-known phenomenon is due to the high diffusivity of hydrogen in air at the case of $Le < 1$ [4]. These results indicate that there is a strong possibility of unintended ignition at hydrogen concentrations above 4 vol.%, and that present-day PARs should be reviewed to avoid the potential ignition risk.

Porous catalyst elements consisting of coated steel meshes have been investigated as a means to limit the heat release [3]. Although temperatures occurring with hydrogen concentrations above 10 vol.% could be controlled so as to avoid unintended ignitions, the conversion rates are not sufficient for massive amounts of hydrogen, since the catalyst material directly coated on the substrate surface limits the reaction rates of the hydrogen recombination process.

The above issues have motivated the present study, which investigates the use of Al_2O_3-coated metal foam as a catalytic support. The metal foam has structural stability and a high surface-to-volume ratio; moreover, it has a high thermal conductivity and it effectively dissipates the accumulated heat. The objectives of the present study are to investigate the preparation of the catalyst bed based on the Al_2O_3-coated metal foam, and to evaluate its performance with respect to hydrogen conversion rates and thermal behavior.

2. Experimental

2.1. Preparation of catalytic support and catalyst

In this study, metal foam with a high thermal conductivity and porosity of the material was considered as a catalytic support.

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doi:10.1016/j.cattod.2009.04.021

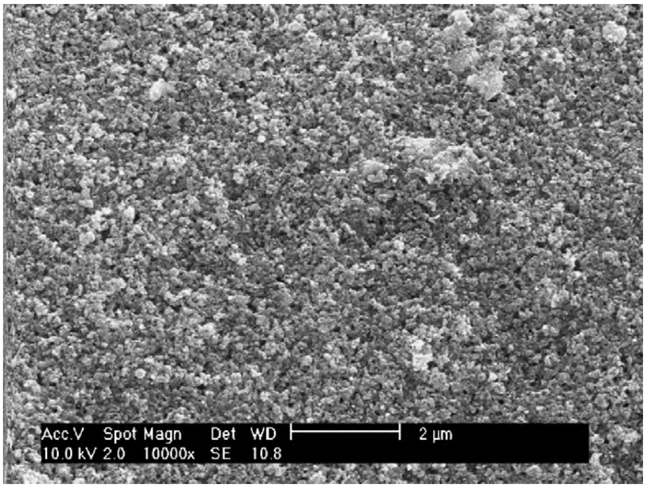

Fig. 1. Surface SEM images of the Al_2O_3 washcoat on the nickel foam used as a catalytic support (10,000×).

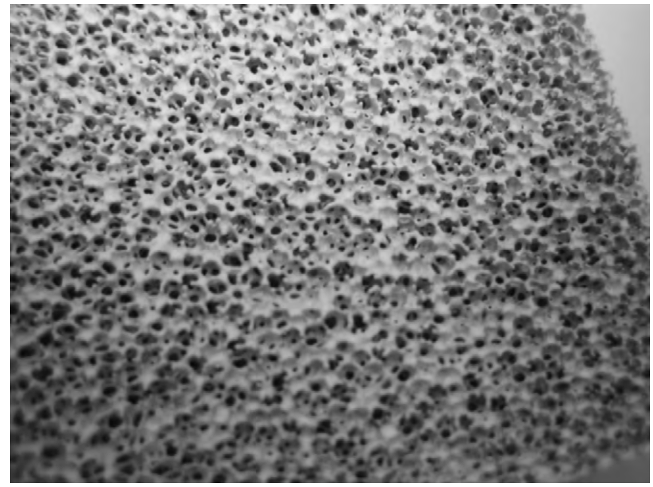

Fig. 2. Clogging phenomenon of metal foam pores at the Al_2O_3 washcoat weight of 75 wt.%.

Nickel foam which has porosity of 90–92% was chosen, with an average pore density of 40 ppi, thermal conductivity of 90.9 W/m K and a thickness of 10 mm to ensure structural stability and a minimal pressure drop.

Washcoat of γ-alumina (Al_2O_3) was applied to the surface of the metal foam using the modified Sol–Gel method, in order to further increase the active surface [5,6]. Fig. 1 shows SEM images of the surface of the Al_2O_3-coated metal foam; the very rough surface indicates that its suitability as a catalytic support has increased, as expected.

Platinum was applied to the washcoat surface by the incipient wetness method, using hexachloroplatinic acid ($H_2PtCl_6 \cdot nH_2O$) as the precursor. A predetermined weight of hexachloroplatinic acid was dissolved in acetone, and after stirring, the solution was dropped onto the washcoat surface. After a few minutes, the acetone has quickly evaporated in air, leaving particles of hexachloroplatinic acid uniformly attached to the washcoat surface. After the metal foam has undergone the Al_2O_3 and platinum coating processes, it is calcined at 500 °C to remove impurities such as organic substances. A reduction is performed to activate the platinum catalyst, under flowing 4% of H_2/N_2 at 500 °C.

To determine the optimum preparation condition of the catalyst bed, its hydrogen recombination performance was measured against two experimental parameters: the Al_2O_3 washcoat weight percentages and the platinum weight percentages. These two parameters affect the hydrogen conversion rates and the thermal behavior. If the Al_2O_3 washcoat weight percentage is too low, the active surface of the metal foam will be reduced and may be insufficient to recombine all of the hydrogen generated, thus there will be a low hydrogen conversion rate. If the Al_2O_3 washcoat weight percentage is too high, the pores of the metal foam will clog (Fig. 2), resulting in a decrease of the metal foam surface and an increase in the pressure drop across the metal foam. Similarly, in order to guarantee a high hydrogen conversion rate, the platinum as a catalyst must be sufficiently applied to the metal foam coated Al_2O_3 washcoat. The platinum weight percentage, however, will be limited by the cost of the catalyst bed, since platinum is an expensive material. Table 1 lists the fabrication conditions of the Al_2O_3 washcoat weight and the platinum weight that were prepared in order to evaluate their effects on hydrogen recombination performance.

2.2. Experimental setup

Fig. 3 illustrates the experimental setup. The 1 m long mixing chamber was filled with 1 cm glass beads, and it was used to completely mix the relatively small amount of hydrogen with the air. The hydrogen–air mixture enters the reaction chamber at the bottom; after it reacts with the catalytic layer, the products leave the reaction chamber at the top. The hydrogen concentrations at the inlet and the outlet of the reaction chamber were measured using a gas analyzer that can detect up to 10 ppm of hydrogen by a TCD (thermal conductivity detector), and these measurements can be used to determine the hydrogen conversion rates.

A detail of the reaction chamber is shown schematically in Fig. 4. The reaction chamber was made of stainless steel and its diameter and length were about 12 cm and 14 cm, respectively. A 4 cm × 4 cm square of the Pt/Al_2O_3-coated metal foam was inserted into the reaction chamber. Temperatures were measured at the bottom and at the top of the metal foam layer.

Experiments were performed for different hydrogen feeding rates: 1.78 g/s m^2, 3.55 g/s m^2, and 7.11 g/s m^2. Corresponding total flow rates at a hydrogen concentration of 4 vol.% were about 25 l/m, 50 l/m and 100 l/m. The inlet temperature was 20 °C (room temperature) and the reactor chamber was not insulated. The test mixture ratio of hydrogen in air ranged from 1 vol.% to 8 vol.%; these amounts were selected since one purpose of the catalyst bed in this study is to reduce hydrogen concentrations to less than the extinction limit of the hydrogen–air mixture, with an inflammability limit of 4 vol.%.

3. Results

3.1. Effect of Al_2O_3 coating

The hydrogen conversion rates in the reactor chamber can be influenced by the washcoat weight of the metal foam, because it is a surface reaction between the hydrogen–air mixture and the catalyst. To investigate the effects of the Al_2O_3 weights, various tests were performed with three metal foams, coated with

Table 1
Experimental conditions of Al_2O_3 washcoat and platinum weight percentages.

No.	Al_2O_3 weights[a] [wt.%]	Platinum weights[b] [wt.%]
1	45	5
2	45	3
3	45	1
4	26	3
5	63	3

[a] Coated washcoat weight/initial metal foam weight × 100.
[b] Coated platinum weight/coated washcoat weight × 100.

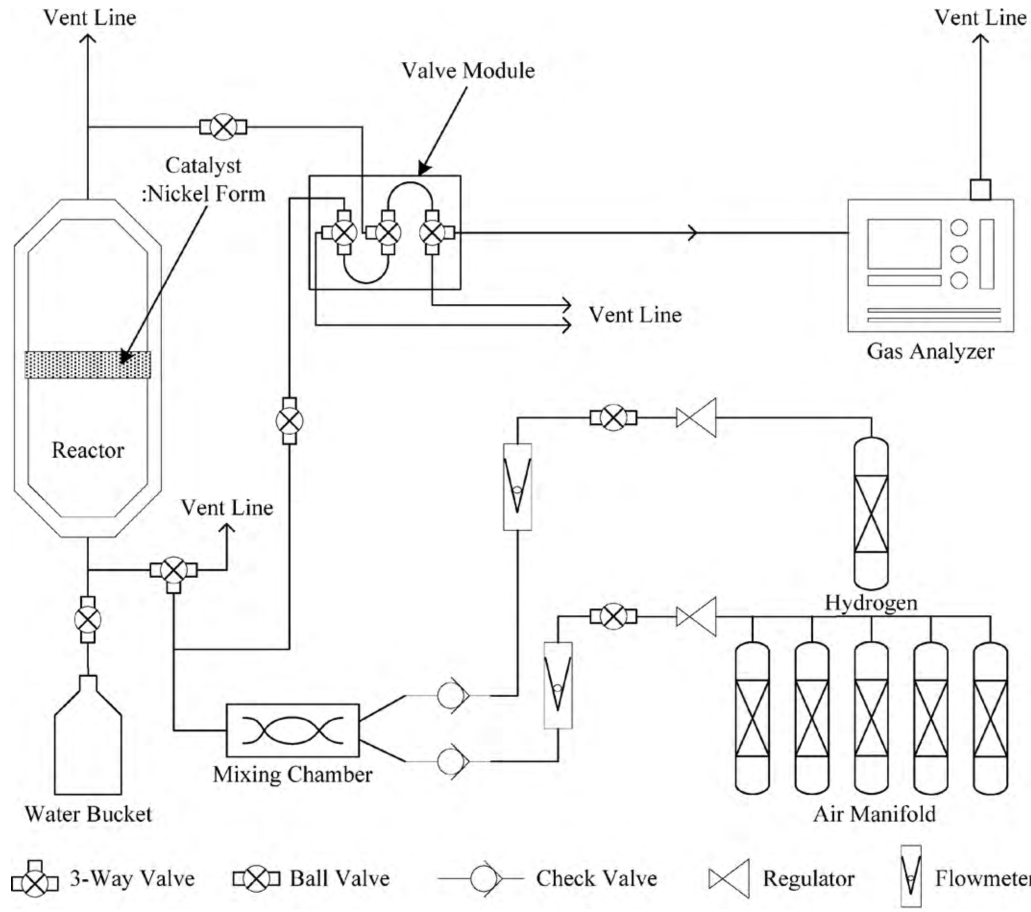

Fig. 3. Schematic diagram of the experimental setup for the metal foam coated Pt/Al_2O_3.

different washcoat weight percentages and a constant platinum weight condition of 3 wt.%.

Fig. 5 shows the results of the hydrogen conversion rates at different inlet hydrogen concentrations. Each graph in Fig. 5 corresponds to a different value of the hydrogen feeding rates. Overall, the hydrogen conversion rates increase with increasing washcoat weights, due to the increased support surface area; most rates were above 96% with these experimental conditions. With a washcoat weight of 26 wt.%, the hydrogen conversion rate decreased dramatically to 68%, at a hydrogen concentration of 1 vol.%. The relatively small surface area resulted in low reactivity

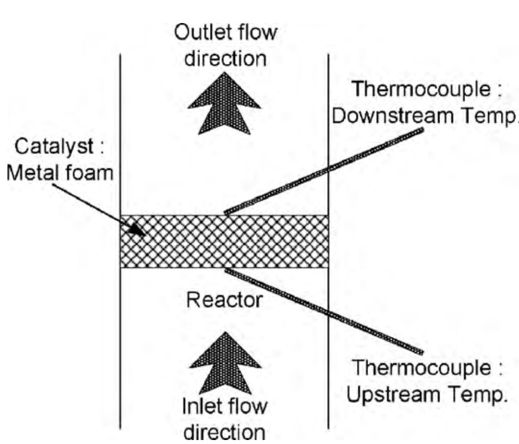

Fig. 4. Schematic diagram of the reaction chamber and the flow direction of the hydrogen–air mixtures.

of the catalyst, so that there was low generated heat. Since the reaction rate is strongly affected by temperature, the hydrogen conversion rate at a washcoat weight of 26 wt.% was too low compared with the other washcoat weight conditions.

During a severe accident, the massive hydrogen released must be removed rapidly. To address this, the capacity of the Pt/Al_2O_3-coated metal foam layer was investigated using three different conditions of hydrogen feeding rates. Similar to the vertical dotted lines in Fig. 5, the limit of a complete reaction zone moves toward the direction of high hydrogen concentrations as the hydrogen feeding rate increases, because this reduces the space time. These space times were calculated based on the thickness and the cross-sectional area of the metal foam layer at 4 vol.% hydrogen concentration. The space times corresponding to hydrogen feeding rates of 1.78 g/s m^2, 3.55 g/s m^2, and 7.11 g/s m^2 were calculated to be about 19 ms, 10 ms, and 5 ms, respectively. In other words, as the contact time between the hydrogen–air mixture and the platinum catalyst is reduced, the hydrogen conversion rate decreases. This result indicates that if the metal foam is coated with constant weights of washcoat and catalyst, its capacity will be determined by the hydrogen feeding rates.

A few seconds after introducing the hydrogen–air mixture, the temperatures of the upstream and downstream sides of the metal foam layer rise dramatically. During the next 2 min, these temperatures reached a nearly steady-state condition. As seen in Fig. 6, the temperatures of the metal foam layer at constant hydrogen concentrations barely change with washcoat weight. The one exception occurs with a washcoat weight of 26 wt.% and a hydrogen concentration of 1 vol.%; in this case, the temperature of the metal foam was observed to be slightly lower due to a lower

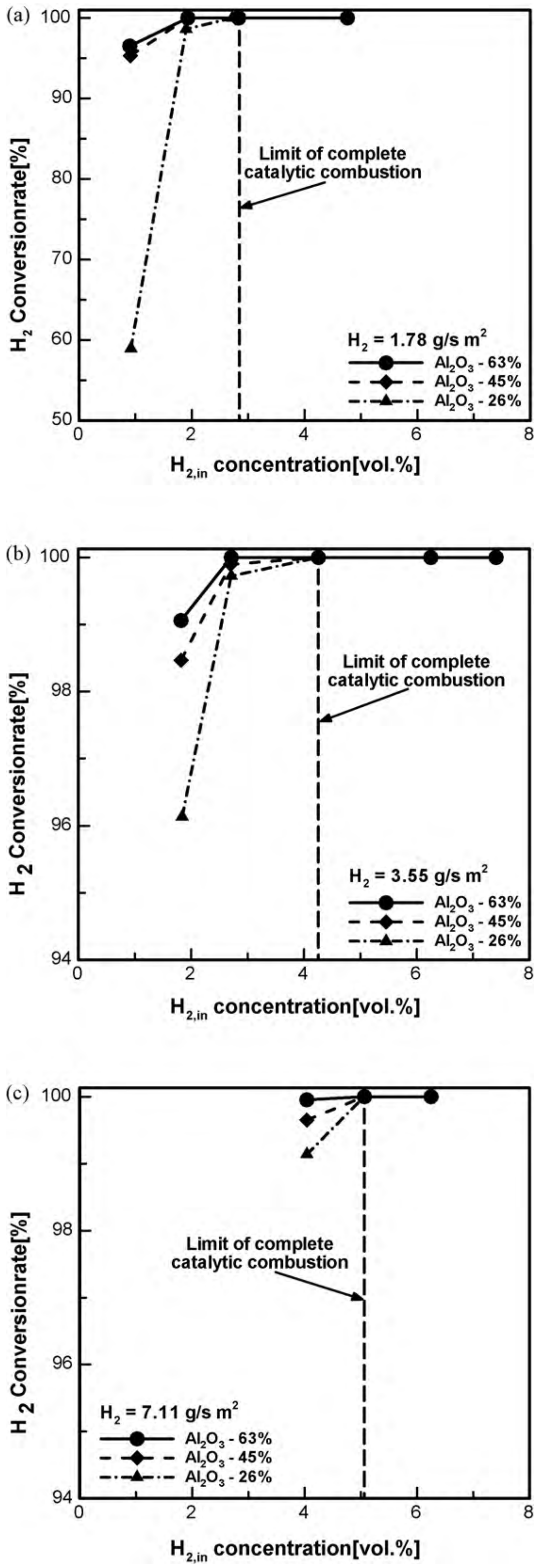

Fig. 5. Hydrogen conversion rates at different Al_2O_3 washcoat weight percentages with 3 wt.% constant platinum weight. Hydrogen feeding rates are (a) 1.78 g/s m^2, (b) 3.55 g/s m^2, and (c) 7.11 g/s m^2.

hydrogen conversion rate. As a result of this temperature trend, the inlet hydrogen concentrations have by far the most dominant effect on the temperature distribution in the high hydrogen conversion rate region.

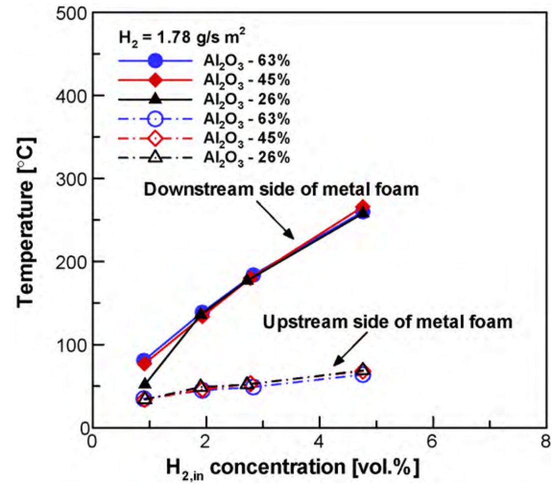

Fig. 6. Steady-state temperature distribution of the metal foam layer at different inlet hydrogen concentrations.

3.2. Effect of platinum coating

The weight of the platinum as a catalyst has a direct effect on the performance and the fabrication cost of the Pt/Al_2O_3-coated metal foam. These effects were investigated using three different values of the platinum weights. The experiments were conducted with a constant Al_2O_3 washcoat weight of 45 wt.%.

As shown in Fig. 7, the effects of the platinum weight are similar to those resulting from the variation of the Al_2O_3 weights discussed above. The hydrogen conversion rates increase with increasing platinum weight percentages, because the quantity of the platinum as a catalyst influences the contact area with the hydrogen–air mixture. If the platinum on the catalytic support is too low, part of the hydrogen–air mixture passes through the metal foam without undergoing catalytic reaction. Except for the case with a platinum weight of 1 wt.% at a hydrogen concentration of 1 vol.%, these test conditions measured hydrogen conversion rates over 95%. This means that the reactivity of the Pt/Al_2O_3-coated metal foam is determined by both the platinum weights and the inlet hydrogen concentrations. Consequently, a platinum weight of 3 wt.% could be selected which would be cost-effective and would result in high conversion rates.

To investigate the effects of the hydrogen feeding rates with respect to the platinum weight percentages, experiments were performed using the same space times as with the tests for the Al_2O_3 weights. As the hydrogen feeding rate increases, the limit of the complete reaction zone moves towards the direction of high hydrogen concentrations, similar to the vertical dotted lines in Fig. 7. This phenomenon, which was similarly observed in the Al_2O_3 weight experiments, shows that sufficient space time is required to obtain high hydrogen conversion rates. Considering the effects of the platinum and washcoat weights combined, the allowable capacity of the Pt/Al_2O_3-coated metal foam will be determined by hydrogen feeding rates at constant platinum and washcoat weight percentages.

3.3. Discussion

It is interesting to note that there were differences between the temperatures of the upstream and downstream sides of the metal foam layer, and that the temperature of the upstream side was lower than the temperature of the downstream side. That means that the rich hydrogen region can be maintained at a temperature less than the 560 °C which is the ignition limit. According to Pfefferle et al. [4], temperature distributions in the

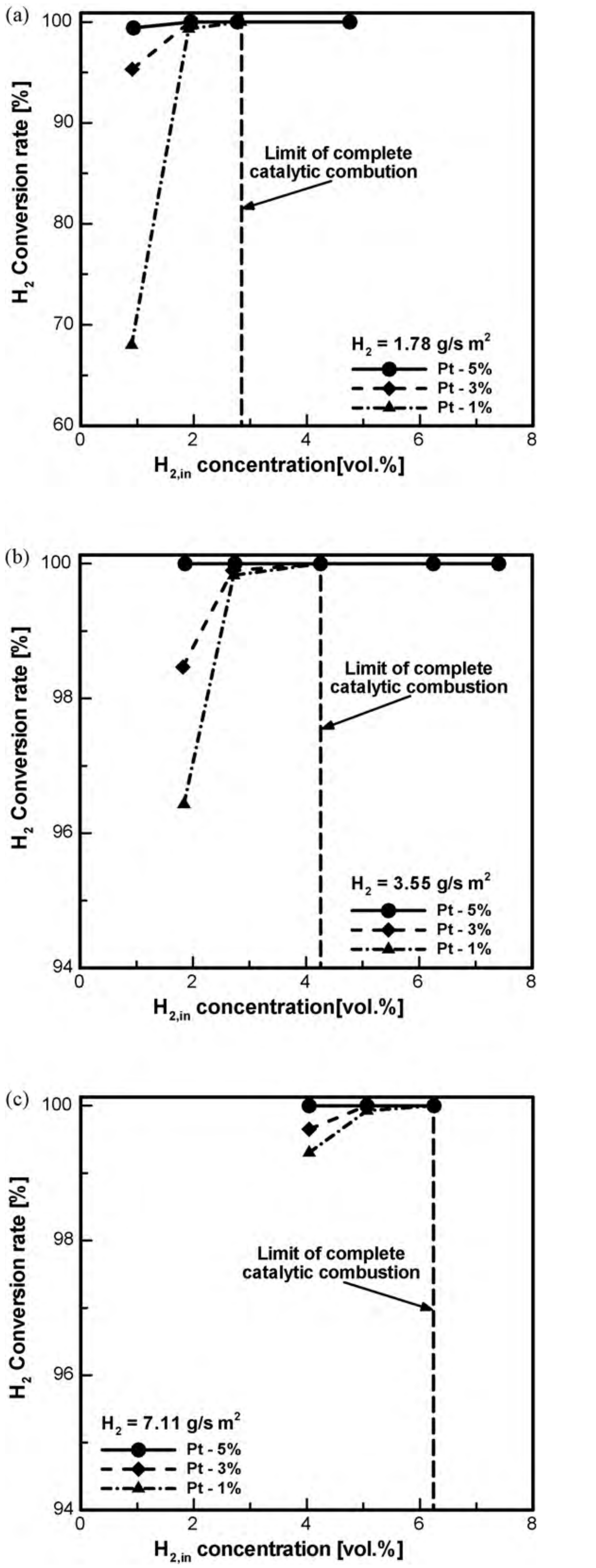

Fig. 7. Hydrogen conversion rates at different platinum weight percentages with 45 wt.% constant Al_2O_3 washcoat weight. Hydrogen feeding rates are (a) 1.78 g/s m^2, (b) 3.55 g/s m^2, and (c) 7.11 g/s m^2.

case of hydrogen combustion can be affected by high thermal conductivity catalyst supports, heat losses, and kinetically controlled catalytic reactions. Unlike an industrial PAR system using a plate-type catalytic support, thermal conductivity

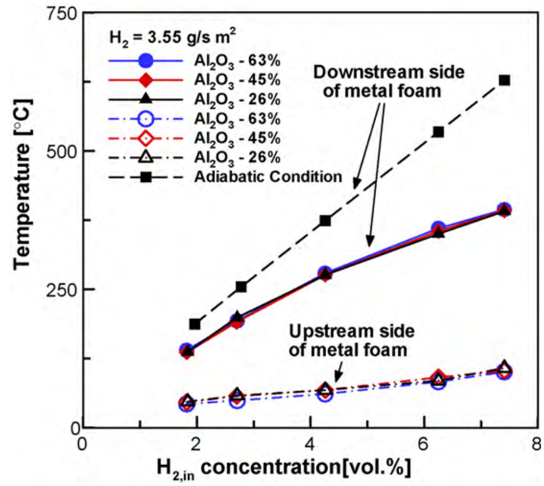

Fig. 8. Comparison between the expected adiabatic temperatures and the experimental results at the exit of the reaction chamber.

induced by using a metal foam layer would be a main factor of favorable temperature distributions in this study. Since all of the hydrogen–air mixtures should pass through the pores of the metal foam, the heat from the product gas will dissipate through the metal foam and will be pushed to the downstream side of the reactor. This temperature characteristic of metal foam is an attractive advantage which can be used to avoid unintended ignition.

The expected adiabatic temperature at the exit of the reactor is shown in Fig. 8. In comparison, the experimental results were measured at somewhat lower values because of heat loss. Since this heat loss increases with increasing inlet hydrogen concentrations, the difference between the adiabatic and measured temperatures becomes more pronounced.

Although the Pt/Al_2O_3-coated metal foam has been proposed in this paper as a means to prevent hydrogen risk and to enhance hydrogen removal rates, additional considerations include material reliability and duration. The PAR system is operated by natural convection induced by the temperature difference between the upstream and downstream of the catalyst elements. With metal foam, the permeability and pore density will influence the total mass flow rates of the hydrogen–air mixture, due to the induced pressure drop across the metal foam. Consequently, further research on metal foams as a catalytic support are needed to design optimized recombiner systems.

4. Conclusions

The objectives of this research were to investigate the feasibility of a PAR system based on a Pt/Al_2O_3-coated metal foam, and to optimize the Al_2O_3 washcoat and platinum weights so that high performance is obtained for hydrogen removal and thermal safety in a high hydrogen concentration region. The experimental results showed that the hydrogen conversion rates were affected by both the washcoat weights and platinum weights, and that the temperatures of the metal foam layer were mainly determined by inlet hydrogen concentrations. The majority of the experimental conditions resulted in hydrogen conversion rates of over 95%, with a lower temperature at the upstream side of metal foam compared with the downstream side. For these reasons, the hydrogen risk of inducing an unintended ignition can be prevented using the Pt/Al_2O_3-coated metal foam. Moreover, since the low flammability limit of the hydrogen–air mixture is about 4 vol.%, a washcoat weight of 45 wt.% and a platinum weight of 3 wt.% would allow for cost-effective fabrication, and can ensure complete catalytic combustion at hydrogen concentrations above 4 vol.%.

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MEST) through NRL (No. R0A-2007-000-20065-0)

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