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Technical Notes

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Hydrogen Peroxide Gas Generator with Dual Catalytic Beds for Nonpreheating Startup

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Nomenclature

A_t = throat area
C^*_{exp} = experimental characteristic velocity
C^*_{the} = theoretical characteristic velocity
$\dot{m}$ = mass flow rate
P_C = chamber pressure
η_{C^*} = decomposition efficiency

I. Introduction

INTERESTS in rocket-grade hydrogen peroxide have been renewed in recent years as a new demand for a nontoxic alternative to rocket propellants arises. The use of high-concentrated hydrogen peroxide as a propellant in propulsion dates back to the 1940s. After the Second World War, it was used as a monopropellant and as an oxidizer in a bipropellant system for thrusters. Hydrogen peroxide was eventually replaced by higher-performing propellants such as hydrazine and N_2O_4. In the middle of the 1990s, there was renewed interest in hydrogen peroxide due to low toxicity, clean products, and enhanced versatility [1,2].

The performance of the catalyst is crucial in the design of the propulsion devices that use the decomposition of hydrogen peroxide. Silver has been the most widely used catalyst despite many shortcomings, including low melting point, nonuniform flow path, high-pressure loss, and need of preheating [2].

In addition, silver cannot withstand the high decomposition temperatures of hydrogen peroxide at concentration levels higher than 92% [3]. Alternative catalysts including manganese oxides [3–6] and perovskites [7] have been tested with varying degree of effectiveness. Perovskite material such as $La_{0.8}Sr_{0.2}CoO_3$ (hereafter referred to as LSC) had superior characteristics at elevated temperature but displayed very slow reactivity at room temperature [8]. On the other hand, permanganate-based catalysts displayed very high reactivity at room temperature but were not stable at elevated temperature [9].

In the gas generator proposed in the present study (Fig. 1), hydrogen peroxide goes through two distinct reaction phases: catalytic and thermal decomposition [10]. In the inlet region, the liquid-phase hydrogen peroxide decomposes mainly by catalytic decomposition upon contact with the catalyst surface. In this region, unreacted hydrogen peroxide vaporizes by the heat of the decomposition process. The vapor content of the partially decomposed hydrogen peroxide increases along the axial direction of the reactor bed. Down the reactor bed, the unreacted hydrogen peroxide in vapor state decomposes by further catalytic reaction. Good startup performance and catalytic reactivity are required in the inlet region, and high catalytic reactivity and thermal stability at high temperature are required in the outlet region. The LSC catalyst has good thermal stability and high reactivity at high temperature, but is hard to start up at room temperature [8]. To use the LSC catalyst for the high-temperature region, various catalysts for a vaporizer catalyst bed were selected and evaluated using a constant volume reactor and gas generator. Finally, the gas generator with a dual catalytic bed was tested and evaluated.

II. Catalytic Activity in Constant Volume Reactor

A. Catalyst Preparation

To select the catalyst having good decomposition characteristics, reactivity tests were performed with various catalysts at low temperature. The candidate catalysts for the vaporizer catalyst bed were various manganese oxides and platinum. A cordierite monolith with a cell density of 300 cells per square inch was used as the catalyst support. A honeycomb monolith, used widely as the catalyst support in automotive industry, has excellent mechanical properties [3,11]. The surface area of the cordierite monolith was further increased by the washcoat process. The washcoat layer has a high resistance to thermal shock and a good chemical stability during the catalyst decomposition. A sol slurry of γ-alumina powder was prepared and coated on the monolith [12]. The dip-coated monolith was heated in a microwave oven for 30 min to remove moisture [13]. To improve the adhesion of the washcoat material and monolith support, the washcoated monolith was calcined in a furnace at 500°C for 4 h. The loaded weight of the washcoat material was 5% of the total weight of the monolith. The total weight of the monolith used for the reactivity test was 1.0 g.

A specimen MnO_2 catalyst was prepared by submerging washcoated monolith in $Mn(CH_3COO)_2 \times 4H_2O$ solution. The solution was prepared by dissolving 2.0 g of $Mn(CH_3COO)_2 \times 4H_2O$ (Aldrich) in 25 ml of water. A specimen of K_xMnO_y catalyst was prepared by submerging the monolith in the solution of $KMnO_4$ (Aldrich) and high-purity acetone (DC Chemical Co.) for one day

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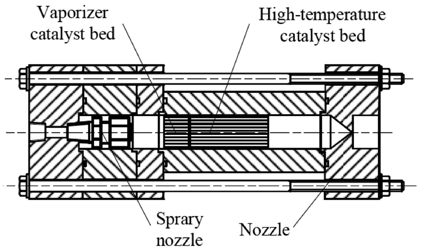

Fig. 1 Gas generator with a dual catalytic bed.

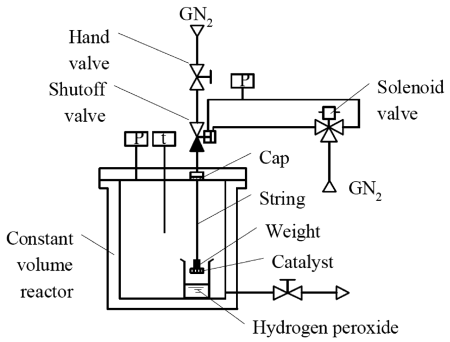

Fig. 2 Schematic for the reaction test.

[14]. The support specimen of the Na_xMnO_y catalyst was prepared by submerging the monolith in the solution of $NaMnO_4$ (Aldrich) and high-purity acetone (DC Chemical Co.). Each solution was prepared by dissolving 2.0 g of permanganate with 25 ml of acetone. The soaked monoliths were then dried at 120°C for 2 h and calcined at 500°C for 4 h in a convection oven. To increase the loading of active material, the coating process was repeated several times. The weight percentage of loaded active material was 4.8% of MnO_2, 6.2% of K_xMnO_y, and 6.0% of Na_xMnO_y. The platinum catalyst was prepared by impregnation of the washcoated monolith in a H_2PtCl_6 solution. The soaked monolith was then dried at 70°C for 6 h and calcined at 300°C for 6 h in the convection oven. The platinum-loaded monolith was then reduced in a steady flowing hydrogen environment at 300°C for 6 h. Two specimens of platinum were prepared with weight percentages of loaded platinum at 6.6 and 11%. The LSC catalyst was synthesized and coated for support by the sol-gel procedure [8].

B. Catalytic Activity in a Constant Volume Reactor

Some studies investigated the activity of various catalysts in a constant volume reactor or a constant pressure reactor [15,16]. However, there are few reports on the catalytic activity of the catalysts supported on a cordierite monolith with similar loading of active materials.

To evaluate the catalytic activity, a constant volume reactor with a cylindrical shape was built, as shown in Fig. 2. The inside diameter and height of the reactor are 100 and 125 mm. The catalyst was suspended at the ceiling of the reactor by steel string and a cap made of polyurethane foam. The weight of 5 g was attached to the catalyst-loaded specimen to prevent it from floating on the hydrogen peroxide during the decomposition. Hydrogen peroxide was placed in a small container located at the bottom of the reactor. When the solenoid valve was activated by the digital timer, nitrogen gas opened the shutoff valve. Then the small pressure ($\sim$0.1 bar) of nitrogen gas between the hand valve and the shutoff valve expanded, pushed the cap, and finally dropped the catalyst into the hydrogen peroxide container. The operation of the shutoff valve (open and close) was completed within 0.5 s. The increase of the reactor pressure by nitrogen gas used for dropping the catalyst was less than the measurement range. The pressure and temperature of the reactor during the decomposition process, as well as nitrogen pressure for valve operation, were recorded by thermocouples and pressure transducers. The pressure for the shutoff valve operation was used as the catalyst dropping time. All of the measured parameters were recorded at the sampling rate of 100 Hz. The temperature was measured by K-type thermocouple (Omega). The pressures were measured by the pressure transducer (500 psi-BME-1100, Kulite), which was calibrated using the deadweight calibration device.

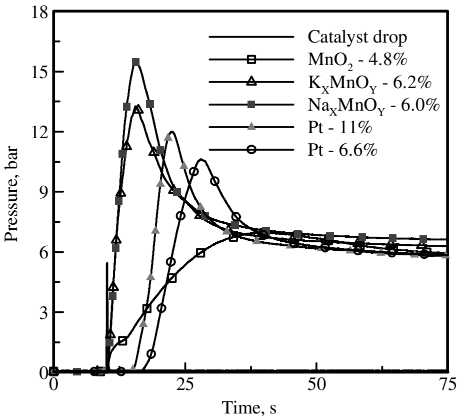

Fig. 3 Comparison of pressure increase vs time for various catalysts.

Hydrogen peroxide of 80% concentration that was obtained by distilling 30% hydrogen peroxide was used for the catalyst reactivity test. No information on the stabilizing agents was available. The reaction tests were carried out using 20 g of hydrogen peroxide and the initial temperature of hydrogen peroxide was 10°C.

Results of reaction tests with different catalysts are shown in Fig. 3 and Table 1. The reaction rate was measured by the pressure increase. Temperatures were not used for the reaction rate evaluation, because they showed uneven behavior. Na_xMnO_y showed the best reaction performance in terms of reaction delay, slope of pressure rise, and maximum chamber pressure. Na_xMnO_y and K_xMnO_y reacted without reaction delay. For Na_xMnO_y, maximum pressure was 15.48 bar and the pressure slope was 2.91 bar/s. For K_xMnO_y, the maximum pressure was 13.25 bar and the pressure slope was 2.43 bar/s. For 11 wt % platinum, the reaction delay was 3.98 s, the maximum pressure was 12.01 bar, and the pressure slope was 1.41 bar/s. MnO_2 showed 0.14 s of reaction delay and low pressure slope. If 20 g of 80% hydrogen peroxide was completely decomposed in the reactor and the final temperature is 40°C, the calculated pressure is 6.23 bar, and all of the reaction pressure converged approximately to 6 bar.

In the catalytic activity test using the constant volume reactor, manganese-oxide-based catalysts showed good performance. Particularly, manganese oxides alkalized with group 1 metals Na and K showed very high catalytic activity [4]. Platinum showed superior performance as the loaded amount increased. All of the

Table 1 Results of constant volume reactor test

Catalyst	Active metal, wt %	T_{max}, °C	Ignition delay, s	P_{max}, bar	Pressure slope, bar/s
K_xMnO_y	6.2	184	0.10	13.25	2.43
Na_xMnO_y	6.0	310	0.14	15.48	2.91
MnO_2	4.8	188	0.14	6.97	0.23
Pt	11	183	3.98	12.01	1.41
	6.6	208	5.43	10.62	0.84

catalysts tested showed reasonable performance at room temperature. With slight variation in reactivity, these catalysts can be used to initiate the gas generator without preheating.

C. Catalytic Activity in a Steady Flow Condition

Before incorporating into a dual bed catalytic reactor, further tests were carried out in a steady flow condition of hydrogen peroxide. When the monolith was used as a catalyst support, the flow distribution at the inlet is very important for the performance of the gas generator. A hollow cone type of spray nozzle was used as an injector. For even distribution of atomized hydrogen peroxide, the catalyst bed was located 25 mm from the nozzle exit. The inner diameter of the gas generator was 25 mm, and the cell density of the monolith was 300 cpsi. The converging nozzle with a diameter of 1.7 mm at the exit was connected to the rear part of the reactor bed (Fig. 1). The schematic of the experimental apparatus is shown in Fig. 4. Hydrogen peroxide was supplied to the gas generator by high-pressure gaseous nitrogen. The mass flow rate was adjusted either by controlling the nitrogen pressure or by adjusting the needle valve located at the inlet of the gas generator. The mass flow rate was calculated using the pressure difference between the spray nozzle, which was calibrated by water. All of the measured data were recorded at the sampling rate of 100 Hz.

Gas generator performance in terms of pressure rise as a result of the catalytic decomposition of hydrogen peroxide is displayed in Fig. 5 with various catalyst beds under the same test condition. The length of the catalyst beds was 50 mm, with the weight of the loaded catalyst at 9.1% for platinum, 2.8% for K_xMnO_y, 2.6% for MnO_2, 2.5% and 29% for Na_xMnO_y. All catalysts showed good startup performance at room temperature. Na_xMnO_y showed better performance than K_xMnO_y, with similar loading of active material. As the loading of active material was increased, the performance and durability of Na_xMnO_y were improved. In the steady flow reactor, the fine atomization of H_2O_2 at the spray injector reduces the ignition delay and results in improved catalytic activity. Platinum had superior adhesion to the support surface. On the other hand, adhesion of Na_xMnO_y on the surface of the catalyst support was inadequate, although its catalytic reactivity is higher. The selection of platinum as the catalyst was made by consideration of these two aspects.

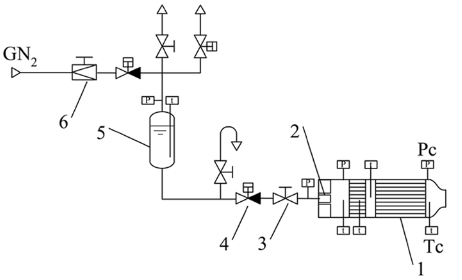

Fig. 4 Test apparatus: 1) gas generator, 2) spray nozzle, 3) needle valve, 4) shutoff valve, 5) hydrogen peroxide bottle, and 6) regulator.

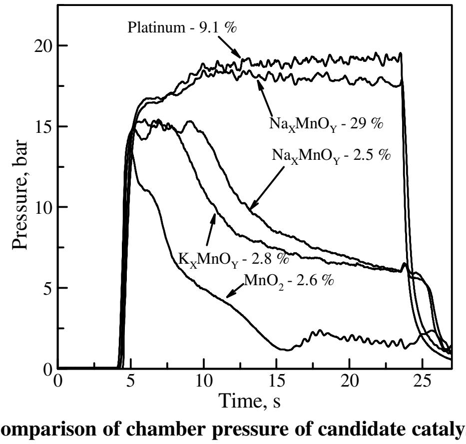

Fig. 5 Comparison of chamber pressure of candidate catalysts with a 50-mm bed length.

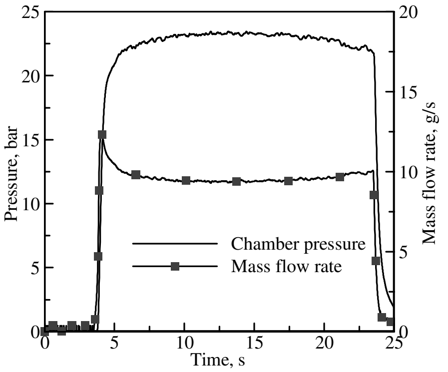

Fig. 6 Chamber pressure and mass flow rate vs time for a 20-mm platinum catalytic bed.

To understand the decomposition performance of platinum, a catalyst bed with a 20-mm length and 9.5% catalyst loading was prepared and tested. Three consecutive tests were carried out with adjusting the needle valve at constant pressure. The chamber pressure rose rapidly as the hydrogen peroxide was supplied into the gas generator, as shown in Fig. 6. The measured decomposition temperatures were from 200 to 225°C and the mass flow rates were from 6.5 to 10 g/s.

III. Gas Generator Experiment with a Dual Catalytic Bed

In the steady flow test, the platinum catalyst bed with a 20-mm length could vaporize 10 g/s of hydrogen peroxide up to 225°C, and the length of the vaporizer catalyst bed was determined to be 20-mm long. The length of the high-temperature catalyst beds were 30, 40, and 50 mm. The loading of the catalyst was 9.5% for the vaporizer catalyst bed and $12 \sim 13\%$ for the high-temperature catalyst bed (LSC catalyst).

Each catalytic bed was tested at three different mass flow rate ranges. The test duration was 20 s for each test. The performance of the catalyst bed is evaluated in terms of C^* efficiency η_{C^*}, the pressure drop across the catalyst bed, and the appearance of the plume [3]. In the present study, the C^* efficiency that was defined next was used to determine the relative performance of the reactor bed.

$$\eta_{C^*} = \frac{C^*_{\text{exp}}}{C^*_{\text{the}}} \times 100 \tag{1}$$

$$C^*_{\text{exp}} = \frac{P_c \cdot A_t}{\dot{m}} \tag{2}$$

C^*_{the} was determined from the CEA code [17]. For hydrogen peroxide at a concentration of 80% the theoretical value of C^* is 821 m/s. The experimental characteristic velocity was determined using the measured chamber pressure in Pa, the mass flow rate of hydrogen peroxide in kg/s, and the throat area in m^2.

Figure 7 shows the calculated C^* efficiency of the single and dual catalyst beds. The dual catalyst bed shows more improved C^* efficiency and stable performance than the single catalyst bed. Figure 8 shows the C^* efficiency comparison between single and dual catalyst beds. Note that the C^* efficiencies of dual catalyst beds were $10 \sim 20\%$ higher than the 20-mm-long platinum catalyst. The performance of the vaporizing section of the catalyst bed has crucial effects on the overall decomposition process of the reactor. As the hydrogen peroxide mostly in liquid phase in the vaporizing section of the catalyst bed has relatively low velocity, sufficient contact time between hydrogen peroxide and the catalyst surface is allowed. After vaporizing, the contact time between gas-phase hydrogen peroxide

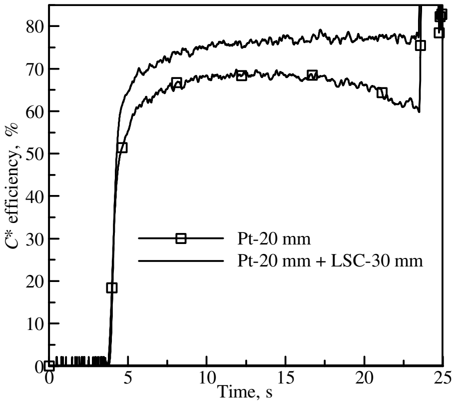

Fig. 7 C^* efficiency vs time for single and dual catalytic beds.

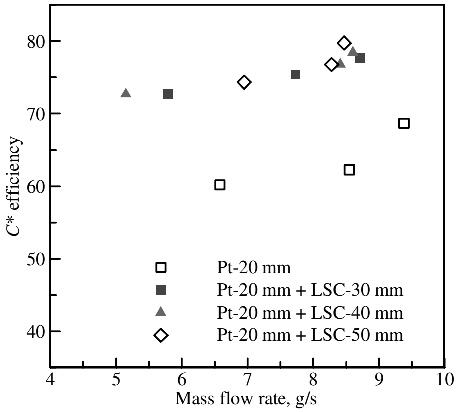

Fig. 8 Comparison of C^* efficiency vs mass flow rate for single and dual catalytic beds.

and the catalyst surface becomes insufficient, because the relative speed of the gaseous hydrogen peroxide against the catalyst surface is high. The reaction products also prevent sufficient contact between gaseous hydrogen peroxide and the catalyst surface. As the length of the LSC bed was increased, the residence time of hydrogen peroxide was increased and resulted in the improved decomposition performance.

IV. Conclusions

A new type of gas generator with hydrogen peroxide as a monopropellant was developed and tested. To overcome the shortcomings of a conventional catalyst bed of the gas generator that requires preheating and/or protection of the catalyst from excessive temperature rise, a dual catalyst reactor bed was proposed and investigated. The catalyst reactor bed was divided into two parts that were loaded with different catalysts that performed best in the respective location in the catalyst bed. By a reactivity test in a constant volume reactor and in a steady flow reactor, platinum was selected as the catalyst for initiation of vaporization of hydrogen peroxide, and the LSC was loaded in the rear part of the catalyst bed, in which stability under high temperature was important. The dual catalyst reactor bed was a 70-mm-long cordierite monolith; the leading 20 mm was loaded with platinum and the rear 50 mm was coated with LSC. The reactor bed was inserted in a gas generator with a converging nozzle. The fabricated gas generator showed good startup capability at room temperature without preheating and demonstrated improved C^* efficiency.

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