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Long-term stability of Pt/alumina catalyst combustors for micro-gas sensor application

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Abstract

Long-term stability of thick-film type Pt/alumina catalyst combustors integrated on the micro-thermoelectric hydrogen sensor (micro-THS) has been investigated. We prepared the catalyst thick films with three different thicknesses to investigate their combustion performance on the micro-device. To enhance the long-term stability, a self-heating treatment of the catalyst aging of the sensor with its micro-heater has been carried out. The performance of the sensor with the 15-μm thick catalyst which was the thickest one in this study was less temperature dependent, and more stable for long-term operation. While the sensor without aging treatment failed to detect 100 ppm H_2 in air in a month, the sensor after aging treatment have detected 100 ppm H_2 in air over 3 months. The degradation of its signal level for 1 vol.% and 100 ppm was below 10% and 15%, respectively. Nano-level microstructure observation of the catalyst investigating the Pt nano-particle dispersion has been carried out to discuss with mechanism of the performance degradation and the role of aging treatment on the stability of the sensing performance of the sensor.

Keywords: Catalytic stability; Sensors; Electrical properties; Pt/Al_2O_3; Combustors

1. Introduction

Platinum-based catalysts such as Pt-loaded on oxide show a high activity in the selective catalytic oxidation of hydrogen. Among them, the Pt-loaded alumina (Pt/alumina) ceramic catalyst is the most famous and has been used as a catalyst combustor for hydrogen. Also for the chemical sensor application, the Pt/alumina catalyst beads have been used for catalytic-combustion-type gas sensors for several decades because of its advantages such as activity and stability. However, because the sintering of Pt particles in the catalyst occurs in the Pt/alumina catalyst used at high temperature, it is expected that the activity of the catalyst decreases significantly with this degradation of Pt particle sintering.[1–4] Therefore, the development of the catalyst which has the better stability is important for the development of the robust gas sensor.

Micro-thermoelectric hydrogen sensor (micro-THS)[5] operates on the basis of the oxidation of hydrogen by the Pt/alumina catalyst combustor, similar to the catalytic-combustion-type sensor, so that the sensor performance directly depends on the activity and stability of the Pt/alumina catalyst.[6] When the Pt/alumina catalyst oxidizes H_2 gas and releases the combustion heat, the temperature gradient is developed between the hot-side and the cold-side junction. This temperature gradient is converted into voltage by the Seebeck effect of a thermoelectric SiGe thin film. This micro-THS device is the very promising platform device for evaluating the performance of a catalytic combustor. Since the heat energy due to the catalytic combustion is directly converted into the output voltage in the sensor, the catalytic performance can be evaluated by the sensing properties.

Recently many developments of this micro-THS have been performed to integrate a ceramic Pt/alumina catalyst combustor into the micro-sensor device to enhance the sensitivity[7,8] and the long-term stability.[9,10] In this study, we have carried out a long-term stability test of the micro-THS with the ceramic Pt/alumina catalyst, and verified the effect of the heating treatment so-called aging. Also the effect of the catalyst thickness on the stability has been studied, because the thicker catalyst films ensure the better stability commonly. Furthermore, we have discussed the structure–performance relationship by the nano-level microstructure analysis on the ceramic

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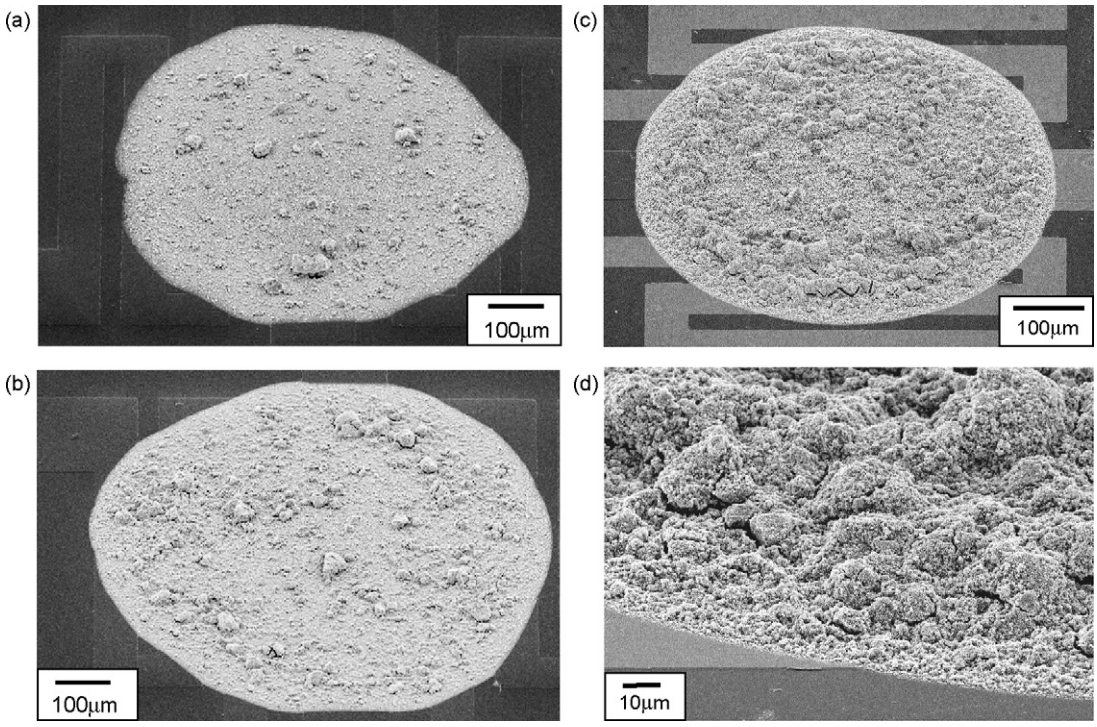

Fig. 1. SEM images of the Pt/alumina catalyst deposited on the sensor device after baking with the different thickness catalyst: (a) thin catalyst, (b) intermediate-thick catalyst, (c) thick catalyst and (d) magnified view of the thick catalyst.

catalysts on the sensor device before and after the long-term operation.

2. Experimental

Micro-THS devices with the chip size of 5 mm × 5 mm were fabricated on the basis of the previous studies.[7–10] The Pt/alumina catalyst was prepared by impregnation of a commercial alumina powder (α-alumina, 100 nm, Taimicron, Taimei Chemicals Co., Ltd.) with an aqueous solution of platinum (IV) chloride pentahydrate. The details of the catalyst preparation have been reported previously.[11] The powder catalyst was mixed with an organic vehicle (a blend of terpineol and ethyl cellulose) to make ceramic pastes.

Various methods to deposit catalyst on the devices are well reviewed elsewhere.[12] A drop of the ceramic paste was dispensed using a dispenser technique (FAD320s, MUSASHI Engineering Inc.). Before the dispensing, the viscosity of the ceramic catalyst paste was measured by Rheometer (RS300, Thermo Haake) at 25 °C. The size of a catalyst was controlled to keep constant as 0.8 mm diameter by controlling the dispensing time and the air pressure. After the deposition, the ceramic paste was baked in air at 300 °C for 2 h. Then the chip was packaged.

The Pt content of the Pt/alumina catalyst in this study was fixed at 40 wt%, which was found to be optimum by the previous study.[6] The grain size of Pt metal was estimated to be 3 nm by transmission electron microscopy (TEM) observation after baking.

Two types of sensor device samples were prepared to investigate the effect of the aging treatment; one is with a fresh catalyst as prepared and the other is with an aged catalyst. The aging treatment is that the catalyst on the micro-THS was heated up by the micro-heater at 160 °C for 14 days, at room temperature atmosphere.

The hydrogen response performance was investigated using gas-flow-type which has been used in the previous works[7–10] and gas-diffusion-type test chambers. A 30-L volume gas-diffusion-type test chamber[13] was mainly used for long-term stability test. Humidity in the diffusion chamber was controlled at 60–65% RH by placing the NaBr saturated solution in the box and temperature in the chamber was kept to be 25–30 °C. For the gas response measurement, an appropriate amount of pure hydrogen gas was injected into the 30-L chamber, for example, 300 mL in 2 s for 1 vol.% H_2, through the rubber inlet using a syringe with a needle.

The microstructures of the catalysts were investigated by Transmitted Electron Microscopy (TEM, JEM2010, JEOL), and the size and thickness of the catalysts was estimated by the optical microscope with 3D measurements system (ST-HZ stage with CT-7, resolution: 0.5 μm, KH-300, HiROX Inc.).

3. Results and discussion

3.1. Temperature dependence of the sensor performance

To investigate the effect of the catalyst thickness on the sensor performance, we have deposited the catalysts with different thickness on the micro-device. The thickness of the thick-film catalyst can be controlled by changing the viscosity of the ceramic paste, which is increased with the concentration of the catalyst powder particles.

Fig. 1 shows SEM images of the baked Pt/alumina catalyst with the catalyst of three different thicknesses deposited on the micro-devices: (a) thin catalyst, (b) intermediate-thick catalyst, and (c) thick catalyst. The particle concentrations of the catalyst pastes used in the deposition process were (a) 1.94 vol.%, (b) 3.83 vol.% and (c) 7.37 vol.%. The viscosity of these catalyst pastes were (a) 3.5 Pa s, (b) 5.5 Pa s and (c) 9.5 Pa s at the shear rate of 0.2 s^{-1}. The thickness of these catalysts after the baking at 300 °C was measured to be estimated approximately at (a) 5 μm, (b) 10 μm and (c) 15 μm. The microstructure of these catalyst thick films including hierarchical micropore structures from ca. 100 nm to several micrometers were as same to the previous observation and as the process parameters of sintering temperature, 300 °C. As the thickness increases, the crack becomes prominent (d).

Fig. 2 shows the hydrogen sensing performance of the micro-THS with the different thickness catalyst (a) thin catalyst, (b) intermediate-thick catalyst and (c) thick catalyst, to 1 vol.% H_2 in air at various catalyst surface temperatures of the sensor, which is monitored by IR camera. We call this catalyst surface

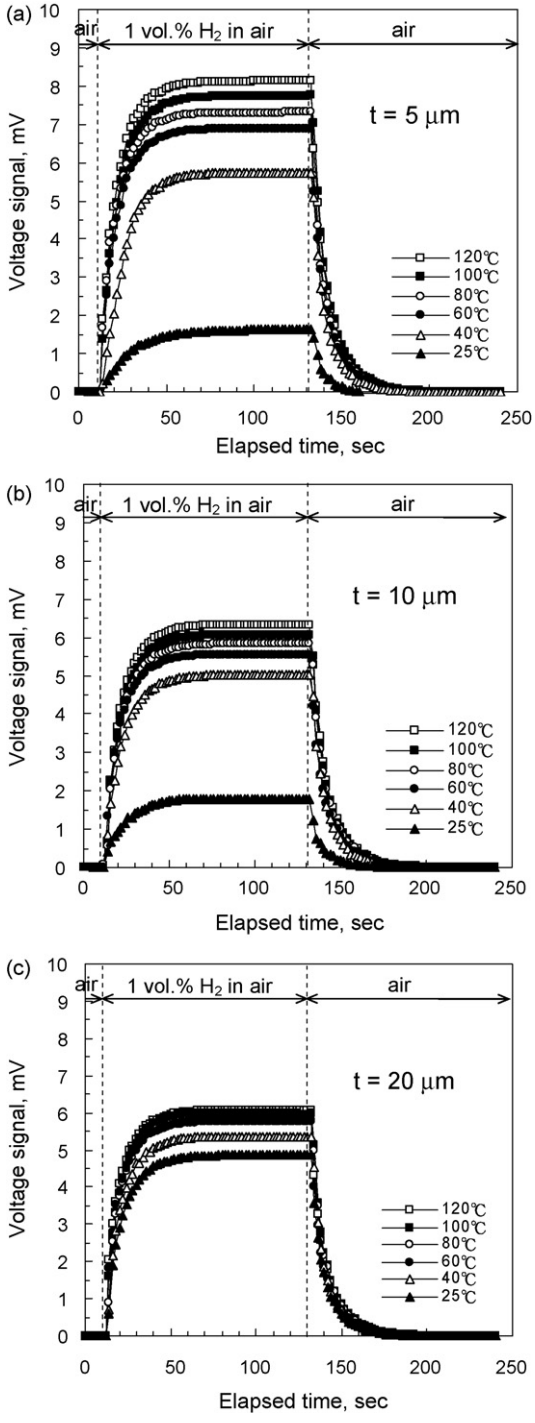

Fig. 2. Hydrogen sensing performance of the micro-THS with the different thickness catalyst, (a) thin catalyst, (b) intermediate-thick catalyst and (c) thick catalyst, for 1 vol.% H_2 in air at various operating temperatures.

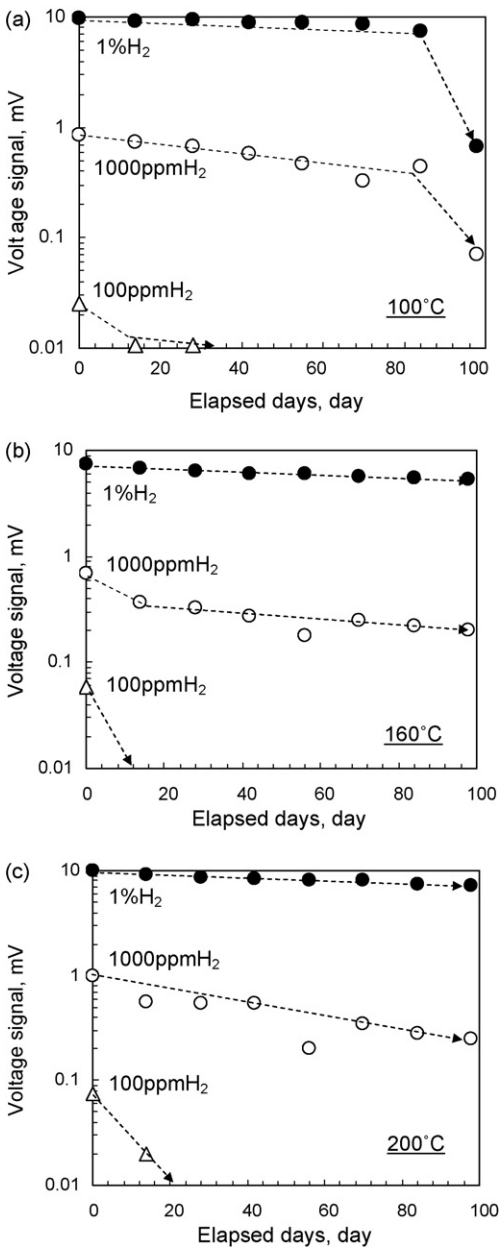

Fig. 3. Difference of the hydrogen sensing performance of the micro-THS with the intermediate-thick catalyst at operating temperatures of 100 °C (a), 160 °C (b) and 200 °C (c). These performance tests were conducted by the gas-diffusion-chamber under the controlled humidity condition, 60–65% RH, through three consecutive months.

temperature on the device acquired by IR camera in air flow as sensor operating temperature. The operating temperature dependence of the output voltage signal depends on the thickness of the catalyst. The performance of the micro-THS with thin catalyst (a) shows high output voltage at around 100 °C but large temperature dependence exists compared to those of the sensors with thicker catalysts. The performance of the micro-THS with the thick catalyst (c) has shown less temperature dependence. This behavior of the sensor with the thick catalyst makes the sensing performance stable against any abrupt change of atmospheric temperature. Considering the results above on the sensor stability, the sensors with the rather thick catalyst, intermediate-thick and thick, Fig. 2(b) and (c), were selected for the long-term stability test.

3.2. Long-term stability

The degradation of the Pt/alumina catalyst is considered to be caused by the sintering of Pt particles mainly. The migration and coalescence of the particles cause the growth of Pt grain size and the loss of the active surface area, to lose its activity and stability.[1–4] The aging treatment is considered effective to prevent this degradation of catalyst performance. Before determining the aging temperature and period, we have heated the catalyst up to 160 °C and checked the change of the performance of the sensors.

Fig. 3 shows the changes of hydrogen sensing performance over 3 months for the two sensors with the intermediate-thick catalyst at operating temperature of (a) 100 °C, (b) 160 °C and (c) 200 °C. The long-term stability test was conducted on the basis of the diffusion-type test method using a 30-L chamber as reported previously.[13] The sensor device was set up in the gas-diffusion chamber under the controlled humidity condition, 60–65% RH, through the test period.

The hydrogen sensing performance of the micro-THS with the intermediate-thick catalyst (Fig. 3(a)) for 1 vol.% and 1000 ppm H_2 in air gradually decreased from the start, and decreased again drastically after 80 days. For the low concentration of 100 ppm hydrogen in air, the sensing performance of the sensor decreased fast from early stage, and no response was observed after 28 days On the other hand, the performance of the sensor operating at higher temperature (Fig. 3(b) and (c)) for 1 vol.% and 1000 ppm H_2 in air, were rather stable even after 80 days. For 100 ppm H_2 in air, no clear signal was observed from the sensor with the intermediate-thick catalyst after 28 days. At a glance, the results of Fig. 3 tell us that both 160 °C and 200 °C operating have diminished the gas sensing performance for 100 ppm H_2 in air. While the aging treatment at 200 °C for 2 weeks has destroyed a couple of devices no response even for

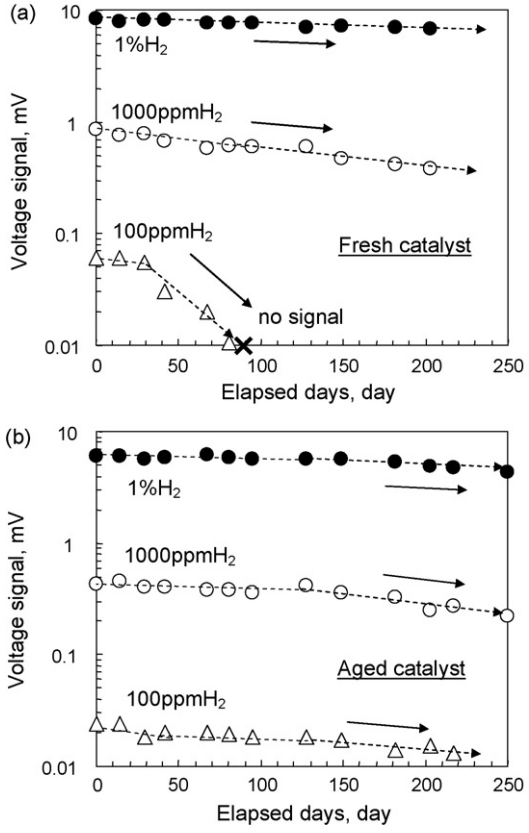

Fig. 4. Difference of the hydrogen sensing performance of the thick catalyst (a, fresh catalyst) and the thick catalyst after the aging treatment (b, aged catalyst) at operating temperature of 100 °C. These performance tests were conducted by the gas-diffusion-chamber under the controlled humidity condition, 60–65% RH, through three consecutive months.

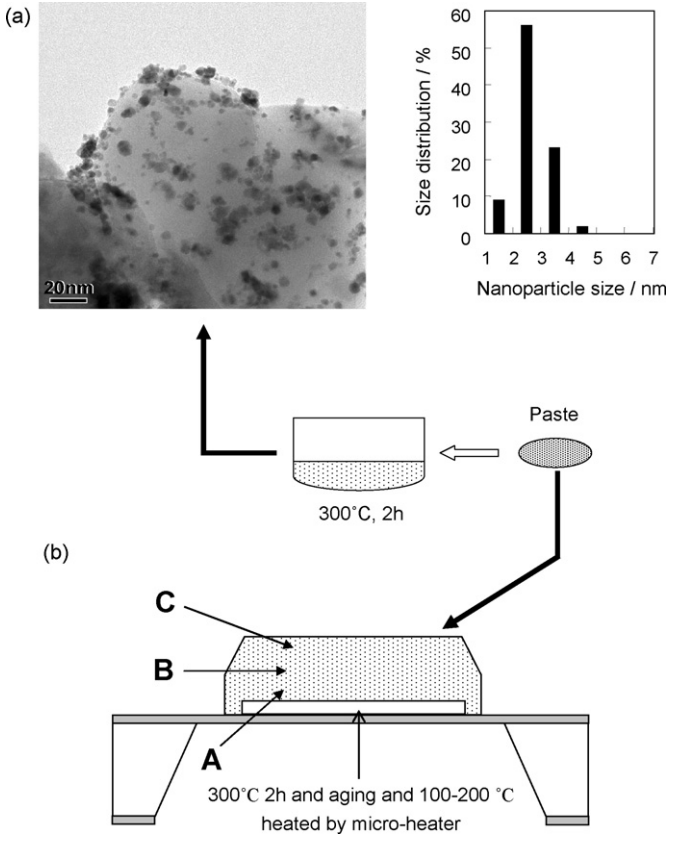

Fig. 5. (a) TEM image and Pt particle distribution of the Pt/alumina fresh catalyst after the firing in the crucible at 300 °C, 2 h. (b) Schematic illustration of the catalyst part under cross-sectional TEM observation on the micro-device.

1% H_2, the aging treatment at 160 °C succeeded at first trial and seems to be safe and controllable. We have decided to continue the long-term test by carrying out the aging treatment with the condition of 160 °C and 14 days.

Fig. 4 compares the long-term hydrogen sensing performance of the micro-THS with the thick catalyst without aging treatment (a, fresh catalyst) and the thick catalyst after the aging treatment at 160 °C for 14 days (b, aged catalyst). For 1 vol.% and 1000 ppm H_2 in air, the performance of the sensor with the fresh catalyst decreased gradually, and became less than half of the starting level after 7 months for 1000 ppm H_2 in air. For 100 ppm H_2 in air, the performance of the sensor decreased fast after 28th day, and no response was observed after 3 months. On the other hand, for 1 vol.% and 1000 ppm H_2 in air, the performance of the sensor with the aged catalyst was stable compared to the other one with the fresh catalyst. For 100 ppm H_2 in air, the sensor with the aged thick catalyst responded for almost 8 months, even though the signal decreased gradually.

These results demonstrate that the aging process is effective and important treatment to stabilize the hydrogen sensing performance of a micro-THS for long-term operation. We suggest that the aged catalyst is considerably stable keeping its sensing performance for lower concentration, such as 100 ppm H_2 in air, because the aging treatment prolongs the activity of the thick catalyst to lower level hydrogen concentration.

3.3. Microstructure analysis of the catalyst after long-term operation

The decrease of the sensor performance is due to the degradation of the catalyst so that the gas sensing performance of the micro-THS is directly related to the catalytic activity of the ceramic catalyst. The degradation of the Pt/alumina catalyst seems to be mainly due to the growth of grain size of Pt, which reduces the active surface area. It is expected that the difference of the long-term stability between two micro-THSs with the fresh catalyst and the aged catalyst is originated from the difference of the microstructure of their catalysts. We have carried out the cross-sectional microstructure observation by TEM for the Pt/alumina ceramic thick-film catalyst on the membrane of the micro-THS.

Fig. 5(a) shows the microstructure and the Pt particle dispersion of the fresh catalyst after baking of the ceramic paste at 300 °C, 2 h. The grain size of Pt metal particle was estimated to be 3 nm by TEM observation, and the high dispersion of the Pt particle was kept. Fig. 5(b) shows the cross-sectional schematic illustration of the catalyst on the micro-device. A, B and C represent the bottom part just above the micro-heater, the center part and the surface of the catalyst, respectively. The catalyst was heated by the micro-heater controlling the surface temperature of catalyst (A) at 100–200 °C.

Fig. 6(a) shows the microstructure of the fresh catalyst after long-term operation, the bottom part just above the micro-heater

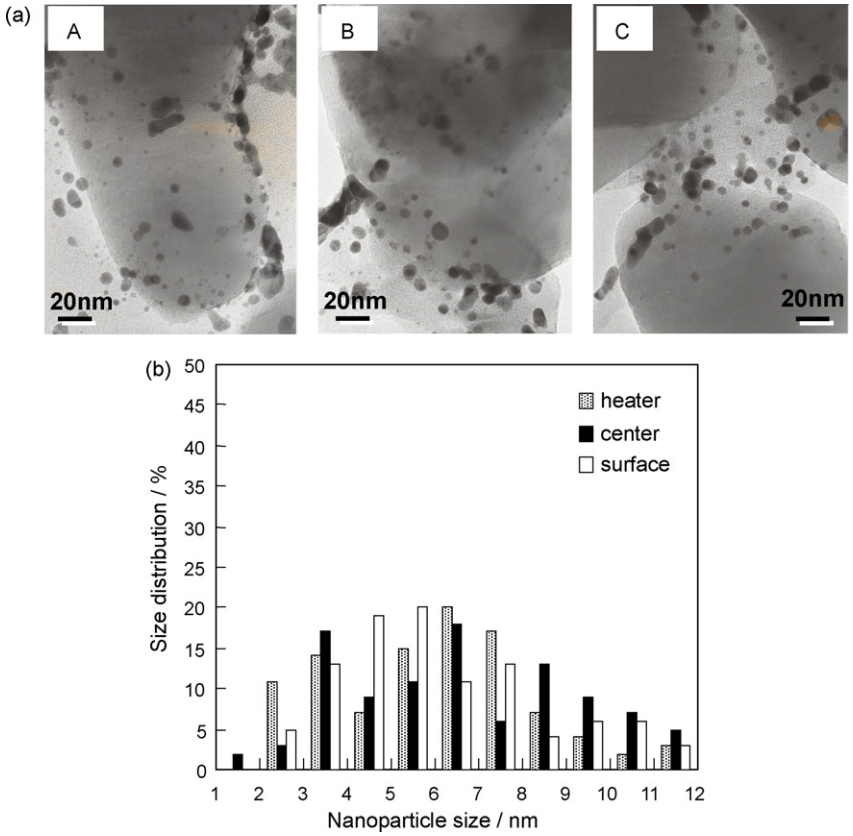

Fig. 6. (a) TEM images of the catalyst microstructure on the bottom part just above the micro-heater (A), the center part (B) and the surface part (C) of the fresh catalyst after long-term operation. (b) Distribution of the Pt particle size measured from these TEM images.

(A, heater), the center part (B, center) and the surface part (C, surface). To discuss the dispersion of Pt particle more quantitatively, we have estimated the size of Pt particle in this TEM image. The Pt particles size distribution analyzed from these TEM images are plotted in Fig. 6(b). It is found that the Pt particle size of the catalyst varied greatly and the average Pt particle size increased to ca. 6 nm. However, no significant special difference of Pt particle size was observed between the top and bottom part of the thick-film catalyst even after the long-term operation, and it seems that the sintering of Pt particles occurs in similar manner over the whole catalyst area.

Fig. 7(a) shows the microstructure of the catalyst after the aging treatment (A) heater, (B) center and (C) surface. For the catalyst after aging treatment, the high dispersion of the Pt particle was kept in all area of the thick film, and any film-type particle growth above the micro-heater was not observed. The Pt particles size distribution estimated from these TEM images is plotted in Fig. 7(b). The average Pt particle size just above the micro-heater and the center of the catalyst were not changed (∼4 nm) as compared with the prepared one. However, the Pt particles on the surface of the catalyst grew larger as same as the fresh catalyst after the long-term operation, and the sintering of the Pt particles seemed to be caused only to the surface of the catalyst.

Fig. 8(a) shows the microstructure of the catalyst after the 2 weeks aging treatment and the long-term operation (A) heater, (B) center and (C) surface. For the catalyst after the aging treatment and long-term operation, the high dispersion of the Pt particle was kept in all area of the thick film, and any film type particle growth just above the micro-heater was not observed. The Pt particles size distribution estimated from these TEM images are shown in Fig. 8(b). The average Pt particle size on the direct top of the heater and the center of the catalyst were increased to 5 nm, while that of as prepared was 3 nm.

The results shown in Fig. 6 tell us that the fresh catalyst without the aging treatment would sinter by migration of nano-size Pt particles along the surface of the alumina support, causing the coalescence of metal particles[14]. Considering the sintering temperature of the previous reports that Pt particles of the Pt/alumina catalyst sintered at 600–700 °C,[1–4] the operating temperature of 100 °C of the sensor in this study seems to be too low to trigger the coalescence of the Pt in the ceramic catalyst on the sensor. However, the Pt content in the ceramic catalyst, 40 wt% in this study is much larger than those of the typical catalyst over 10–40 times. Because the inter-particle distance is much shorter in the catalyst of higher Pt content, the migration may start at much lower temperature such as 100 °C. Furthermore, the 1 vol.% H_2 exposure during the test may elevate the temperature of the local areas of Pt particle coagulation and the sintering may progress also.

On the other hand, the catalyst after the aging treatment hardly sintered for long-term operation. As the bonding between Pt and alumina is weak,[15,16] it seems that some weak-bond Pt particles

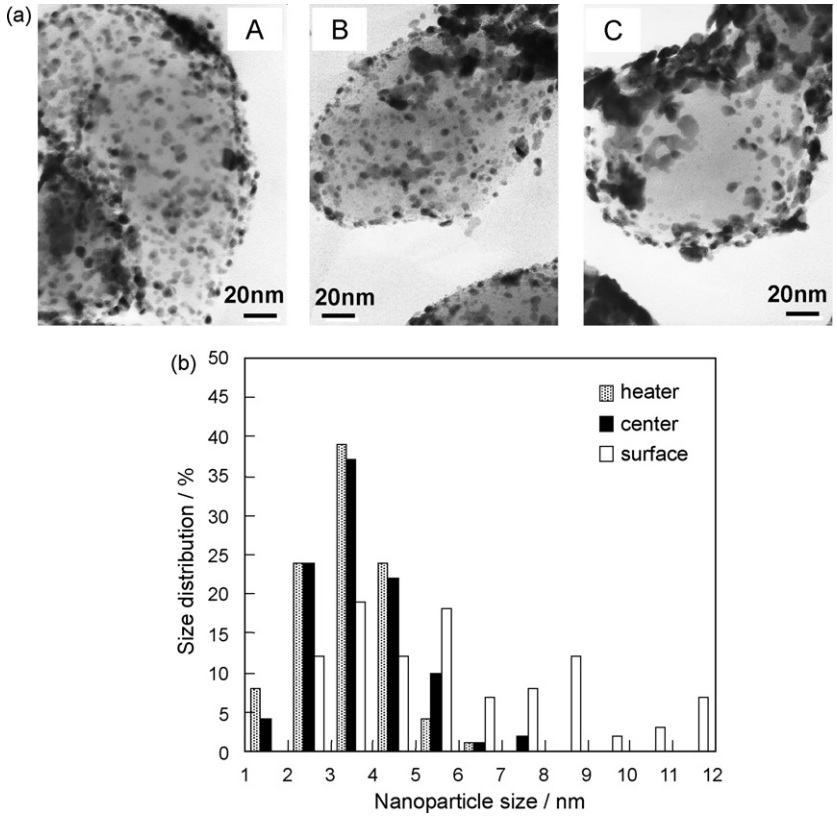

Fig. 7. (a) TEM images of the catalyst microstructure on the bottom part just above the micro-heater (A), the center part (B) and the surface part (C) of the catalyst after aging treatment. (b) Distribution of the Pt particle size measured from these TEM images.

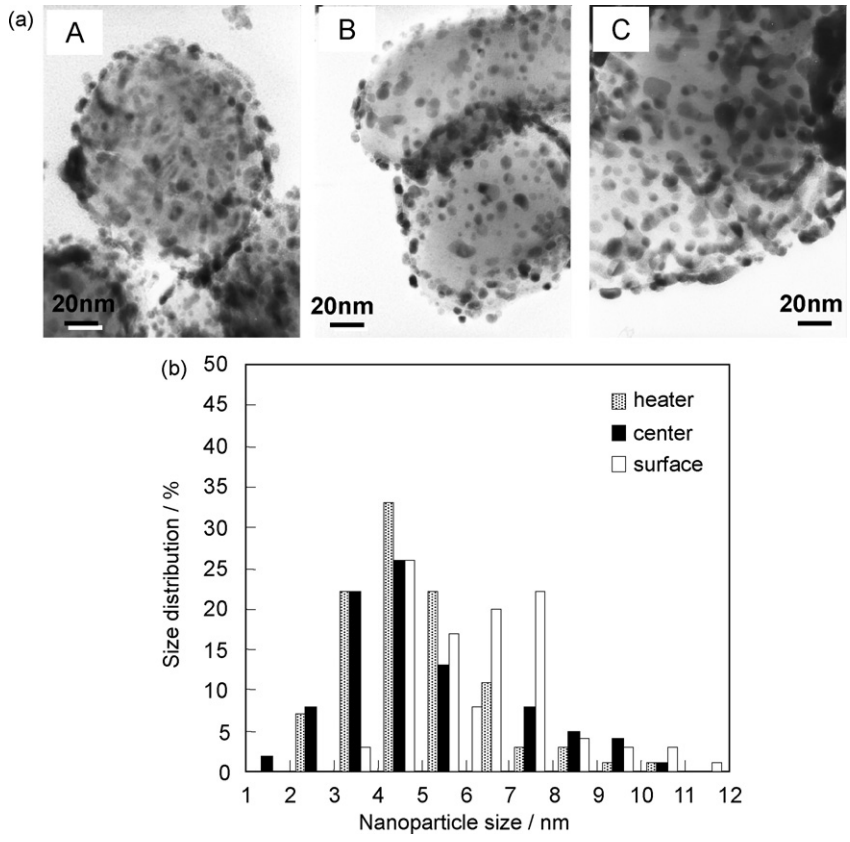

Fig. 8. (a) TEM images of the catalyst microstructure on the bottom part just above the micro-heater (A), the center part (B) and the surface part (C) of the catalyst after the aging treatment and long-term operation. (b) Distribution of the Pt particle size measured from these TEM images.

move on the surface of the alumina by thermally activated migration during the aging treatment at 160 °C and is fixed to stable site by the anchor effect.[15] Therefore, it seems that the aging treatment prevents the further migration of Pt particles and the catalyst after the aging treatment is stable for long-term operation. However, this aging treatment could degrade the catalytic activity of the ceramic catalyst because the Pt particles on the surface of the catalyst cause the sintering a little by this treatment, as shown that the voltage signal of the fresh and aged sensor in Fig. 4 are different.

Furthermore, the nature of the alumina surface is very important regarding the nucleation and growth of the metal particles on its surface. The difference of the phase of alumina also has been reported to affect the size of the nano-size Ag particles in other report.[17] The preparation process of Pt/alumina catalyst in this study is very similar to that of this report and it is worth to be checked.

From the experiment we have carried out with other crystal phase of alumina, β- and γ-, not only with α-phase, the bad dispersion of these oxides in the aqueous solution was the problem which we have failed to get a proper paste for the deposition process. The dispersion of the β- and γ-alumina was too bad to be used for the ceramic catalyst paste preparation. Furthermore, it has been reported by our previous report that the size of Pt metal particle on the alumina surface was not dependent on the preparation method of the catalyst,[11] if it is prepared from the Pt solution or Pt nano-clusters.

4. Conclusion

Pt/alumina ceramic catalyst was integrated on the hot-plate of thin membrane of the micro-THS device to investigate the long-term stability of the catalyst combustor. The temperature dependence of the hydrogen sensing performance of the micro-THS was related with the thickness of the catalyst. The performance of the sensor with the thin catalyst showed large temperature dependence compared to that of thicker one. The performance of the sensor with the thick catalyst was less temperature dependence down to room temperature.

The aging treatment at 160 °C for 14 days was effective and important to stabilize the hydrogen sensing performance of the sensor for long-term operation. The performance of the sensor with the thick catalyst after aging was considerably stable and sensitive even from 100 ppm to 1 vol.% H_2 in air for almost 8 months. The degradation of its voltage signal for 1 vol.% and 100 ppm was below 10% and 15%, respectively.

Though the fresh catalyst after long-term operation showed the low dispersion of the Pt particles, the catalyst after the aging treatment showed the high dispersion of the Pt particle, and no significant difference of the Pt particle size were observed in all area of the catalyst. Furthermore, the catalyst after the aging treatment and the long-term operation was similar to the dispersion of Pt particle of the catalyst after aging treatment. We considered that the aging treatment at 160 °C fixed some weak-bond Pt particles to stable site by the anchor effect.[15]

As discussed above, we conclude that the thick catalyst after the aging treatment is considerably stable and sensitive even from 100 ppm H_2 in air. Moreover, we suggest that the aging treatment prevents the migration of Pt particles in the catalyst, and the aged catalyst is stable for long-term operation. The micro-THS device with the thick catalyst after the aging treatment can be a robust sensor with long-term operation.

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