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Sensing characteristics of mixed-potential-type zirconia-based sensor attached with NiO-based sensing electrode prepared by ball-milling

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A stabilized zirconia-based sensor attached with an oxide sensing-electrode (SE) was developed for the selective detection of propylene (C_3H_6), representative hydrocarbon (HC), at high temperature. Among six kinds of commercial oxides examined, NiO–SE gave the highest sensitivity to C_3H_6 at 600°C under the wet condition. However, other sensing characteristics, such as the C_3H_6 selectivity, the response and recovery times, of this sensor were not satisfactory. Thus, to improve the C_3H_6 sensing characteristics, NiO–SE was successively mixed with different oxides. For better reproducibility of response, all the single- or mixed-oxide SEs were prepared by ball-milling. As a result, the sensor attached with $NiTiO_3$–SE (the initial mixture of 50 mol% NiO and 50 mol% TiO_2) exhibited highly selective and sensitive response to C_3H_6 at 650°C, accompanying with relatively quick response and recovery. In addition, by the comparison of sensing performances of $NiTiO_3$–SEs fabricated by the different methods, the ball-milling method was found to be the most appropriate from the viewpoint of obtaining high selectivity and sensitivity to C_3H_6.

Key-words : Gas sensor, Mixed-potential, Automotive exhaust, Propylene, YSZ

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1. Introduction

A major amount of harmful air pollutants is nowadays emitted from various industrial furnaces and automobiles. Since a number of automobiles has been drastically increasing for last two decades, the developed countries, such as USA, Japan and those in European Union, set more and more stringent emission standards for automotive exhausts. Among different gases emitted into an environment, highly reactive saturated and unsaturated hydrocarbons (HCs) are considered as one of the hazardous air pollutants because of their severe affect on an environmental ecosystem (photochemical smog and greenhouse effect). Therefore, in order to control the concentration of HCs exhausted from automobiles and to fulfill the strict emission regulations, the development of high-performance and reliable gas sensor is strongly required.

The electrochemical solid-state gas sensors based on yttria-stabilized zirconia (YSZ) seems to be one of realistic candidates for detection of HCs, because of their simplicity of fabrication and the ability to operate at high temperature even under rather harsh conditions. More importantly, YSZ-based sensors have been already proven to operate in a real automotive exhaust for detection of oxygen (λ-sensor) or total NO_x ($NO + NO_2$) concentrations. So far, several kinds of HCs sensors have been examined and reported.[1)–13)] Among them, the mixed-potential-type YSZ-based sensors[14)] are of great concern due to the possibility to detect different gases sensitively and selectively as well as the long-term stabilities of both base and sensing signals.

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Thus, in the present study, the mixed-potential-type YSZ-based sensors using each of several oxide-based SEs were fabricated and examined, aiming at sensitive and selective detection of propylene (C_3H_6), as a representative highly reactive and dangerous HC. In order to obtain the best C_3H_6 sensing characteristics (high sensitivity and selectivity, fast response/recovery, and good reproducibility), the composition of oxide-based SEs was optimized by mixing with various oxides using a ball-milling approach.

2. Experimental

2.1 Preparation and characterization of SE materials

For the initial tests, each of the as-received commercially-available NiO, SnO_2, Cr_2O_3, ZnO (Kojundo Chemical Laboratory Co., Ltd.), Fe_2O_3, In_2O_3 (Wako Pure Chemical Industries, Ltd.), and TiO_2 (Kishida Chemical Co., Ltd.) powders was used for fabrication of SE. Then, the parent oxides and their appropriate mixtures were obtained by means of ball-milling method (using a planetary ball-mill, Fritsch, Pulverisette 7, Germany) in ethanol solution (10 cm^3) at 750 rpm for 2 h using zirconia balls (2 mm in diameter). The each of resulting suspension was filtered and dried at 130°C for 2 h. For comparison, the equimolar mixture (1:1 molar ratio) of the as-received commercial NiO and TiO_2 was prepared by sonication in ethanol solution (10 cm^3) for 2 h (without ball-milling). The obtained suspension was also filtered and dried at 130°C for 2 h.

All the obtained compounds were identified by means of X-ray diffraction analysis (XRD, 2100VLR/PC, Rigaku Co.) using Cu Kα radiation and a scan speed of 1 degree/min. Morphology of the fabricated SEs was observed by a field-emission scanning

electron microscope (FE–SEM, JSM–6340F, JEOL Ltd.). Specific surface area of the prepared oxide-based materials was measured by a BET method using a nitrogen sorption isotherm apparatus (HM–Model 1201, Mountech).

2.2 Fabrication of sensor device

A commercially-available one-end-opened YSZ tube (8 mol% Y_2O_3-doped ZrO_2, Nikkato Co.) was used for fabrication of a sensor device. The length of the tube was 300 mm and its inner and outer diameters were 5 and 8 mm, respectively. Each of the as-received commercial pure oxides as well as each of their ball-milled or sonicated mixtures was thoroughly mixed with α-terpineol in a weight ratio of 1:1. Each resulting paste was applied on the outer surface of the YSZ tube to form SE. In all cases, the width of the painted area of the belt-like SE around the YSZ tube was about 3 mm. The commercial Pt paste (Tanaka Kikinzoku Kogyo) was applied on the top of the inner surface of the YSZ tube to obtain a reference electrode (RE). Then, the YSZ tube attached with outer oxide-based SE and inner Pt–RE was sintered at 1100°C for 2 h in air to fabricate a final sensing device. The thickness of SE was estimated to be about 30 μm.

2.3 Evaluation of sensing characteristics

The measurements of gas sensing characteristics for the fabricated sensors were carried out in a conventional gas–flow apparatus equipped with an electric furnace operating in the temperature range of 550–750°C. The wet synthetic air (containing 5 vol% water vapor) was used as a base gas. The sample gas containing each of the various reducing/oxidizing gases (C_3H_6, C_3H_8, CH_4, H_2, NO_2, NO, NH_3 and CO; 100 ppm each) was prepared by diluting each of parent gases with the base gas. The response transients to C_3H_6 were obtained in the concentration range of 10–800 ppm. Pt–RE was always exposed to an ambient atmospheric air. The electromotive force (*emf*) between SE and RE was measured as a sensing signal by means of a digital electrometer (Advantest, R8240) upon switching a gas flow (100 cm^3/min) over SE from the base gas to the sample gas and backwards. The measurements of current-voltage (polarization) curves were performed by the use of a potentiostat (Hokuto Denko, HZ–3000) under potentiodynamic mode at a constant scan rate of 2 mV/min.

3. Results and discussion

Sensing performances of mixed-potential-type YSZ-based sensors usually depend on a kind of SE material used due to the fact that each of metal oxide-based SE has different catalytic activities to the anodic and cathodic reactions occurring at the interface of SE/YSZ and to the gas-phase oxidation/reduction reaction in the bulk of SE. Therefore, to find the most appropriate SE for the sensitive and selective C_3H_6 detection, the sensors using each of five different commercially-available oxide SEs were fabricated and their sensing characteristic to various gases were examined. It should be noted that initially all these oxides were used as-received without additional treatment. **Figure 1** shows the dependence of sensitivity (Δemf) to 100 ppm C_3H_6 on the operating temperature in the range of 550–750°C for the YSZ-based sensors attached with each of as-received metal oxide SEs sintered at 1100°C. Hereinafter, the gas sensitivity (Δemf) is defined as follows

$$\Delta emf = emf\,(\text{sample gas}) - emf\,(\text{base gas}). \qquad (1)$$

It is seen that all the examined oxide-SEs gave relatively high sensitivity to 100 ppm C_3H_6, especially in the temperature range of 550–600°C. And then, with increasing operating temperature, the Δemf values tended to decrease. This is a typical behavior for the mixed-potential-type YSZ-based sensor reported elsewhere.[2),8),11)] Among the different oxide-SEs studied, the sensor attached with NiO–SE gave the highest sensitivity (–136 mV) against 100 ppm C_3H_6 at 600°C. However, unfortunately, the overall sensing performance of this sensor was not satisfactory, since it revealed high cross-sensitivities to other interfering gases, such as CO, NH_3 and H_2, as shown in **Fig. 2**. Additionally, although very high C_3H_6 sensitivity was observed, the 90% response and recovery times to 100 ppm C_3H_6 were found to be as long as ca. 70 s and ca. 250 s, respectively.

To improve the C_3H_6 sensing characteristics, NiO was successively mixed with each of other oxides used in the present study in a molar ratio of 1:1. As it was already mentioned above, the sensor attached with each of the single-oxide SEs showed relatively high C_3H_6 sensitivity at 600°C. Thus, it was speculated that the mixing of two oxides (NiO + each of other oxides) might bring about the improvement in C_3H_6 sensitivity and selectivity as well as the increase in response and recovery rates. Additionally, the ball-milling pretreatment was applied to all the oxide mixtures to obtain the unique morphology and grains size.

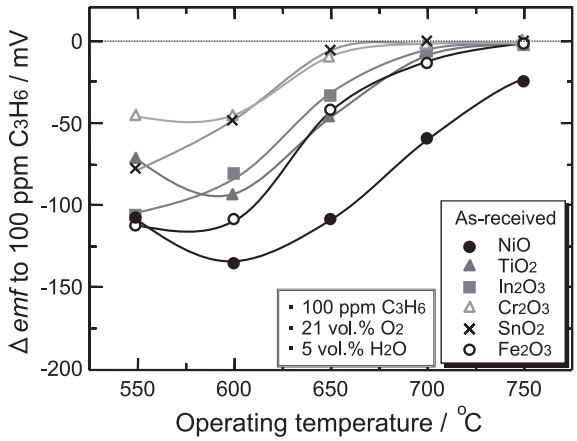

Fig. 1. Dependence of the sensitivity (Δemf) to 100 ppm C_3H_6 on operating temperature for the YSZ-based sensors attached with each of various as-received oxide-SEs.

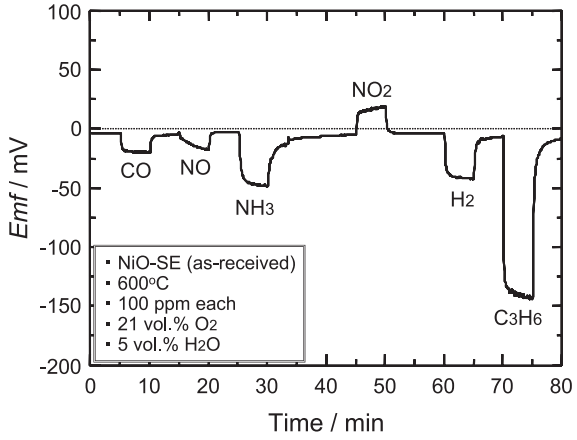

Fig. 2. Response transients to various gases (100 ppm each) for the YSZ-based sensor using as-received NiO–SE operating at 600°C under the wet condition.

According to the XRD patterns (not shown here), after sintering at 1100°C, NiO reacted fully with TiO_2, Cr_2O_3 and Fe_2O_3 forming $NiTiO_3$ (JCPDS No.: 33–0960), $NiCr_2O_4$ (JCPDS No.: 23–1272) and $NiFe_2O_4$ (JCPDS No.: 10–0325) mixed oxide, respectively. In the other cases (In_2O_3 and SnO_2 additives), no reaction seemed to be observed and the obtained samples were composed of the mechanical mixtures of two parent oxides even after annealing at 1100°C.

Each of the newly formed ball-milled mixed oxides and mechanical mixtures was then examined as SE for the mixed-potential-type YSZ-based gas sensor. As a result, among them, the ball-milled $NiTiO_3$–SE (the initial mixture of 50 mol% NiO and 50 mol% TiO_2) was found to give the most selective response to C_3H_6. **Figure 3** shows the response transients to various gases for the YSZ-based sensor using $NiTiO_3$–SE operating at 600°C under the wet condition. As shown in this figure, apart from the improvement in C_3H_6 selectivity, the response and recovery rates of the present sensor were also enhanced in comparison with those for the sensor attached with the as-received pure NiO–SE (see Fig. 2). In addition, the value of sensitivity to 100 ppm C_3H_6 for the sensor attached with the ball-milled $NiTiO_3$–SE was almost same as that for the sensor using NiO–SE.

The attempt of further improvement in the C_3H_6 sensing characteristics was undertaken by mixing the parent NiO with TiO_2 in various molar ratios (80:20, 60:40, 40:60 and 20:80). In each case, the deviation from stoichiometric $NiTiO_3$ single phase ($NiO:TiO_2$ = 50:50) resulted in the appearance of excess second phase. If the molar ratio of NiO is higher than that of TiO_2, the resulting mixture was composed of $NiTiO_3$ and NiO, and vice versa ($NiTiO_3$ and TiO_2) in the case of TiO_2 excess. Regarding the sensing performance, it was found that appearance of any second component in excess resulted in poorer selectivity towards C_3H_6 (not shown here) and only the sensor attached with the single-phase $NiTiO_3$–SE ($NiO:TiO_2$ = 50:50) gave highly selective and sensitive response to C_3H_6. Therefore it can be speculated that the newly formed $NiTiO_3$ single phase seems to be responsible for the highly selective detection of C_3H_6 at high temperature even under the wet condition. Hence, the detailed C_3H_6 sensing characteristics were further examined for the YSZ-based sensor attached with the $NiTiO_3$–SE prepared by the ball-milling pretreatment.

Figure 4 depicts the comparison of the cross sensitivities to various gases (100 ppm each) in the operating temperature range of 550–750°C for the sensor using the ball-milled $NiTiO_3$–SE. Since it was already mentioned that the sensitivity to each gas usually decreases with increasing operating temperature, the most appropriate operating temperature range was 600–650°C from the viewpoint of high sensitivity and selectivity to C_3H_6. However, the recovery for the present sensor was much faster at 650°C rather than that at 600°C. Thus, the operating temperature of 650°C seems to be the optimum for the present sensor. At this temperature, the sensitivity, the 90% response and recovery times against 100 ppm C_3H_6 were about –100 mV, 9 s and 19 s, respectively.

Figure 5 shows the response transients to various concentrations of C_3H_6 at 650°C for the sensor attached with the ball-milled $NiTiO_3$–SE. It is seen that the present sensor can respond fast to each C_3H_6 concentration upon switching from the base gas to the sample gas attaining the stable steady-state *emf* values in a few seconds. After introducing the base gas over the sensor, the sensor's signal returns rather quickly back to the zero level. The present sensor exhibited the relatively high sensitivity (about –30 mV) even to 10 ppm C_3H_6 and gave the good repeatability of the *emf* response to 800 ppm C_3H_6. More importantly, as for the reproducibility, the accuracy of sensitivity to 100 ppm C_3H_6 was found to be less than 10% for the five sensors fabricated. The

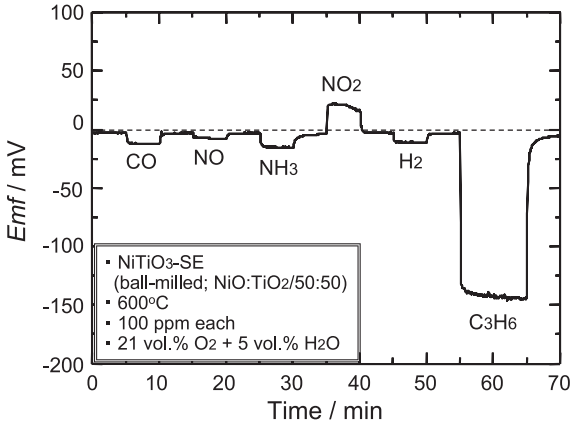

Fig. 3. Response transients to various gases (100 ppm each) for the YSZ-based sensor using the ball-milled $NiTiO_3$–SE (initial equimolar mixture of NiO and TiO_2) operating at 600°C under the wet condition.

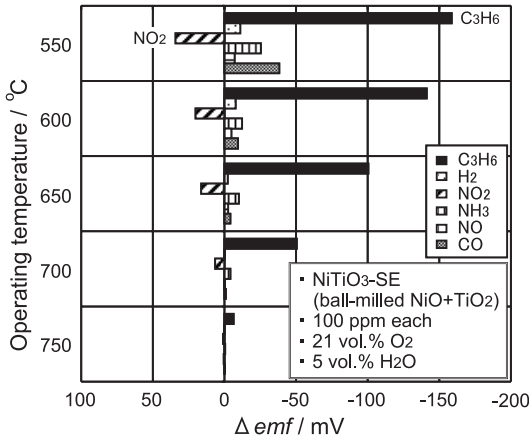

Fig. 4. Cross sensitivities to various gases (100 ppm each) at various operating temperatures for the sensor attached with the ball-milled $NiTiO_3$–SE.

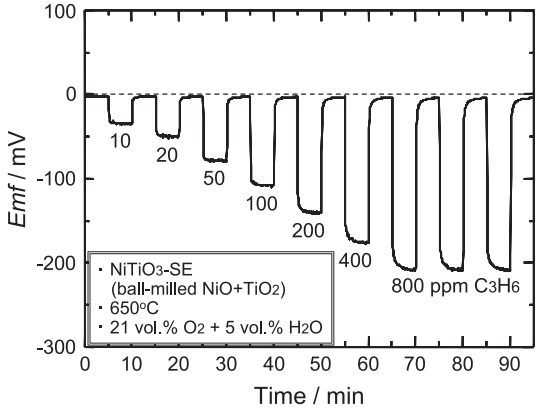

Fig. 5. Response transients to various concentrations of C_3H_6 for the YSZ-based sensor using the ball-milled $NiTiO_3$–SE operating at 650°C under the wet condition.

sensitivity varied almost linearly with the logarithm of C_3H_6 concentration in the examined range of 10–800 ppm, suggesting that the sensing mechanism of the present sensor is based on the mixed-potential model.[14] The mixed-potential arises when the following cathodic

$$O_2 + 4e^- \rightarrow 2O^{2-} \quad (2)$$

and anodic

$$(2/9)C_3H_6 + 2O^{2-} \rightarrow (2/3)CO_2 + (2/3)H_2O + 4e^- \quad (3)$$

reactions proceed simultaneously at the interface between $NiTiO_3$–SE and YSZ. Thus, the mixed-potential mechanism for the present sensor can be rationalized by the measurements of current-voltage (polarization) curves in the base gas (wet synthetic air) and in the sample gas (100 ppm C_3H_6 + the base gas). As a result, the estimated mixed-potential value from the intersection of both modified polarization curves measured at 650°C was about –97 mV that is in good agreement with the experimentally observed *emf* value of –101 mV. Such a close coincidence between the estimated and observed *emf* values confirms that the present sensor is operating under the mixed-potential model.[2),8),14)]

In addition to the electrochemical reactions (2) and (3), the sensing characteristics of the present sensor can be also affected by the catalytic activity of SE to the gas-phase oxidation reaction

$$C_3H_6 + (9/2)O_2 \rightarrow 3CO_2 + 3H_2O \quad (4)$$

which occurs while gas is passing through the $NiTiO_3$–SE matrix. This means that grain size and the porosity of the $NiTiO_3$–SE play a very important role in the achievement of highly selective and sensitive response to C_3H_6. Thus, for the comparison with the $NiTiO_3$–SE fabricated by means of the ball-milling pretreatment, the same SE material was prepared by sonication of the mixture of as–received commercial NiO and TiO_2 (molar ratio of 1:1) in ethanol for 2 h (hereinafter, the sonicated $NiTiO_3$–SE). Both the ball-milled and the sonicated $NiTiO_3$–SEs were then examined for the YSZ-based sensors and the obtained results of cross sensitivities to various gases (100 ppm each) at 650°C under the wet condition are shown in **Fig. 6**. It is clearly seen that the sensing performances of these two SEs fabricated by the various experimental methods were completely different from each other. In comparison with the highly selective and sensitive C_3H_6 sensor using the ball-milled $NiTiO_3$–SE, the sensor attached with the sonicated $NiTiO_3$–SE showed poor C_3H_6 selectivity.

To examine a reason of such a large difference in C_3H_6 selectivity, SEM observation of the surface morphologies and the measurements of the specific surface areas were carried out. **Figure 7** shows the representative SEM images for the surface of (a) the ball-milled and (b) the sonicated $NiTiO_3$–SEs, followed by annealing at 1100°C for 2 h. It is clear that the ball-milled $NiTiO_3$–SE has much denser microstructure than that for the sonicated one. Furthermore, the ball-milled $NiTiO_3$–SE has a very uniform morphology, whereas the SE fabricated by sonication method has a wide variation in the grain size. The specific surface areas of the equimolar (NiO + TiO_2) mixtures undergone by the ball-milling and the sonication prior to the annealing at high temperature were about 14.9 m^2/g and 3.25 m^2/g, respectively. After sintering at 1100°C, these values were found to be about 1.01 m^2/g and 0.880 m^2/g, respectively. Based on these results, it can be speculated that, after the ball-milling pretreatment, the (NiO + TiO_2) mixture was composed of a large number of highly homogeneous oxides particles which then formed very close-packing microstructure of the ball-milled $NiTiO_3$–SE during the annealing at high temperature (see Fig. 7(a)). Regarding the sensor performance, it means that all the sample gases can be much easier oxidized to CO_2 and H_2O in SE matrix, resulted in much higher C_3H_6 selectivity and slightly lower C_3H_6 sensitivity for the sensor attached with the ball-milled $NiTiO_3$–SE (see Fig. 6). On the contrary, the (NiO + TiO_2) mixture obtained by the sonication pretreatment was composed of much larger oxides particles which then formed more porous structure and gave a wide variation of grain size after annealing at 1100°C (Fig. 7(b)). As a result, the sensor using the sonicated $NiTiO_3$–SE gave poor C_3H_6 selectivity, because all the sample gases examined could

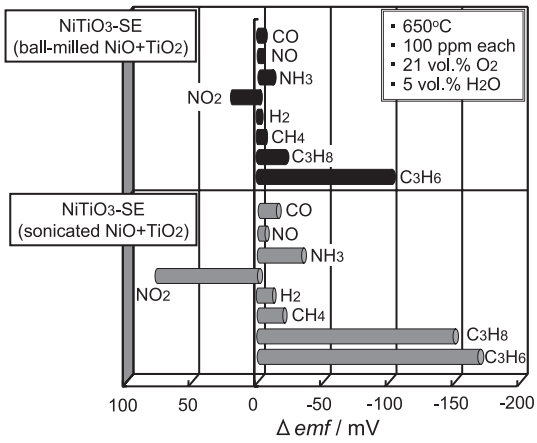

Fig. 6. Comparison of the cross sensitivities to various gases (100 ppm each) at 650°C under the wet condition for the sensors using each of the ball-milled and the sonicated $NiTiO_3$–SEs.

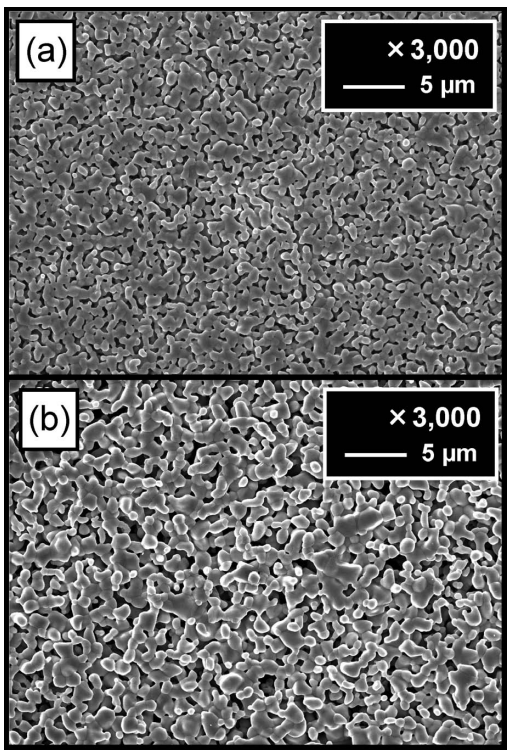

Fig. 7. Representative SEM images for the surfaces of the ball-milled (a) and sonicated (b) $NiTiO_3$–SEs, followed by annealing at 1100°C for 2 h.

reach the interface of SE/YSZ to some extent and generate the sensor's signal. In addition, we have already reported about the effect of grain size on the sensing characteristics of the mixed-potential-type NO_x sensors.[15] Thus, it seems that the preparation of highly homogeneous and highly reactive oxides particles by applying, for example, the mechanical pretreatment (ball-milling) could be one of very useful techniques for the fabrication of high-performance SEs for the mixed-potential-type YSZ-based sensors.

4. Conclusions

The mixed-potential-type YSZ-based sensors attached with various oxide-based SEs were fabricated and examined for highly sensitive and selective detection of C_3H_6. Among them, the sensor using the as-received commercial NiO–SE sintered at 1100°C showed the highest sensitivity to 100 ppm C_3H_6 at 600°C under the wet condition (5 vol% water vapor). However, apart from high C_3H_6 sensitivity, other sensing characteristics were found to be poor and required to be further optimized. After sequential mixing of NiO with other oxides and application of the ball-milling pretreatment to the oxide mixtures, the sensor using the ball-milled $NiTiO_3$–SE (initial NiO + TiO_2 mixture in 50:50 mol% ratio) exhibited highly selective and sensitive response to C_3H_6 at 650°C under the wet condition. Such attractive C_3H_6 sensing characteristics of the present sensor seem to be attributed to the formation of highly uniform morphology of the ball-milled $NiTiO_3$–SE which can give the high catalytic activities to the gas-phase oxidation reactions.

The sensitivity of the present sensor varied linearly with the logarithm of C_3H_6 concentration in the examined range of 10–800 ppm at 650°C. Furthermore, the relatively high sensitivity (about –30 mV) even to 10 ppm C_3H_6 was observed. More importantly, the sensor attached with the ball-milled $NiTiO_3$–SE showed highly repeatable and reproducible behavior, indicating the obvious advantage of ball-milling pretreatment for the preparation of SE with a rather uniform final close-packing morphology.

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