Effects of catalytic combustion behavior and adsorption/desorption properties on ethanol-sensing characteristics of adsorption/combustion-type gas sensors

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ABSTRACT

Adsorption/combustion-type gas sensors, subspecies of catalytic combustion-type gas sensors, show large dynamic responses to volatile organic compounds (VOCs) under the operation with a mode of pulsed temperature heating, because of the flash catalytic combustion of target VOCs adsorbed on the gas-sensing films. Catalytic combustion behavior of ethanol over γ-Al₂O₃ powders loaded with and without 1 wt% Pt and/or 10 wt% metal oxide (MO: CeO₂ or Bi₂O₃) and their adsorption/desorption properties of ethanol (adsorption temperature: 150°C) were investigated, and then the ethanol-sensing characteristics of the sensors utilizing the gas-sensing materials (low and high temperatures under dynamic operation: 150°C and 450°C, respectively) have been discussed on the basis of the findings on both their catalytic combustion behavior and adsorption/desorption properties. Especially, the co-loading of Pt with CeO₂ onto γ-Al₂O₃ was the most effective in enhancing the dynamic response, because the small amounts of various compounds that were adsorbed on the surface at 150°C efficiently oxidized at the initial stage of the pulse-driven heating to form CO₂. The effects of low and high temperatures under the pulse-heating operation on the ethanol-sensing properties of the sensor utilizing γ-Al₂O₃ co-loaded with Pt and CeO₂ were also clarified on the basis of the above findings.

1. Introduction

Catalytic combustion-type gas sensors are operated by monitoring the heat, which is generated by the combustion of target gases, and thus they have generally been used for monitoring inflammable gases such as hydrogen, carbon monoxide, methane, and propane [1–5]. The practical sensors are quite useful in different application fields, because the magnitude of responses to the inflammable gases is almost proportional to the gas concentration up to the explosive limit (LEL). Recently, the sensors have also been adopted as hydrogen detectors for fuel-cell vehicles as well as common gas-leak detectors for multiple uses. However, the catalytic combustion-type gas sensors do not show so much larger responses to the small amounts of volatile organic compounds (VOCs) under general operation. To overcome the drawback, Sasahara et al. proposed adsorption/combustion-type gas sensors, which actively utilize the dynamic sensor signal profile under pulse-heating operation, although the sensor structure is based on the catalytic combustion-type gas sensors [6–11]. The expected gas-sensing mechanism is as follows. First, VOC molecules adsorb on both the sensing and reference films of the adsorption/combustion-type gas sensors at a low temperature for a certain period. Next, the adsorbed VOC molecules burn especially on the sensing film at the initial stage of the pulse high-temperature heating, while they mainly just desorb from the inactive reference film. The sensor-signal profile obtained typically shows a quite large dynamic output by the flash catalytic combustion of VOC molecules adsorbed on the sensing film. The microsensor platform with extremely small thermal capacity, which is fabricated by MEMS (Micro Electro Mechanical Systems) technology, has been utilized to detect even a slight amount of heat generated by the combustion of the low concentration of VOCs adsorbed on the sensing film. Sasahara et al. have thus far demonstrated that the adsorption/combustion-type gas sensors can sufficiently detect as low as 40 ppb formaldehyde [8] and 10 ppb toluene [9,10] in ambient air by optimizing the composition of the sensing-film materials as well as the operating conditions. Besides, the adsorption/combustion-type gas sensors show specific dynamic sensor-signal profiles largely dependent on the kinds of target VOCs [6,7] and detect the amounts of total VOCs generated in a newly constructed building [10] as well as at early stages of fire [11] sensitively. More recently, our group have reported that the compositional and microstructural control of the gas-sensing materials is quite effective in drastically enhancing the magnitude of dynamic responses of the adsorption/combustion-type gas sensors [12–18]. Our fundamental strategy to improve the VOC-sensing properties is to increase the VOC adsorptivity and VOC-oxidation activity of the gas-sensing materials while maintaining the thermal conductivity. Mesoporous γ-alumina (γ-Al₂O₃) powders with large specific surface area, which were prepared by microwave-assisted solvothermal technique, were promising as base materials of the sensing and reference films [12], and the simultaneous loading of Au and Pd onto the γ-Al₂O₃ powder even by impregnation technique was effective in improving
2. Experimental

2.1. Preparation of mesoporous γ-Al₂O₃ and MO-loaded γ-Al₂O₃ powders (MO: metal oxide)

Aluminum secondary butoxide (4.2 × 10⁻² mol) and behenic acid (mesopore-template material, 1.0 × 10⁻² mol) were mixed with 1-propanol (300 cm³). After de-ionized water (10 cm³) was added to the solution, it was stirred at room temperature for 45 h to hydrolyze the aluminum secondary butoxide. Then, the solution was solvothermally treated at 110°C for 1 h. After the obtained precipitates were centrifuged at 2500 rpm for 10 min and then washed with ethanol, the mesoporous γ-Al₂O₃ powder was prepared after firing the precipitates at 700°C for 2 h in air [12]. In some cases, an appropriate amount of Ce(NO₃)₃ · 6H₂O or Bi(NO₃)₃ · 5H₂O was subsequently mixed with the γ-Al₂O₃ powder in a small amount of de-ionized water, they were evaporated to dryness, and then the obtained precipitates were fired at 700°C for 1 h in air. The obtained MO-loaded γ-Al₂O₃ powders (MO: CeO₂ or B₂O₃) were denoted as nMO/γ-Al₂O₃ (n: the amount of MO loaded, 10 (wt%) in this study).

2.2. Loading with Pt nanoparticles onto the surface of γ-Al₂O₃ and 10MO/γ-Al₂O₃ powders

We have already demonstrated that the noble-metal loading onto γ-Al₂O₃ by utilizing sonochemical reduction technique was quite effective in increasing the ethanol response, in comparison with that by general impregnation technique [14]. Therefore, Pt nanoparticles were synthesized by the sonochemical reduction technique, in this study. The appropriate amount of the dihydrogen hexachloroplatinate(IV) hexahydrate was dissolved into de-ionized water, and then the 10 mM aqueous solution obtained (10 cm³) and a 4 mM polyethylene glycol monostearate (C₁₇H₃₅ CO(CH₂CH₂O)₄OH) aqueous solution (10 cm³) were mixed with de-ionized water (40 cm³). The precursor solution obtained was irradiated with strong ultrasonic wave (200 kHz, 6 W cm⁻²) at 20°C for 30 min in a container filled with argon, and then the colloidal dispersion containing Pt nanoparticles was obtained in this container [19–21]. The appropriate amount of the γ-Al₂O₃ or MO/γ-Al₂O₃ powder was added into the Pt colloidal dispersion, and then the pH was adjusted to about 4. After the Pt nanoparticles were adsorbed on the powders, the powders obtained were filtered and dried at 40°C for 12 h. The obtained γ-Al₂O₃ and MO/γ-Al₂O₃ powders loaded with Pt were denoted as mPt/γ-Al₂O₃ and mPt/10MO/γ-Al₂O₃ (m: the amount of Pt loaded), respectively. The amount of Pt loaded was fixed at 1 wt% in this study, because it is technically difficult to load the larger amount of Pt by the sonochemical reduction technique. However, the small amount of Pt loading was luckily suitable for investigating the effects of co-loading of metal oxide on the ethanol-sensing properties of the sensors [15,16]. It was confirmed that the average size of Pt nanoparticles loaded on the oxide surface was ca. 2 nm, by transmission electron microscopy (TEM; JEOL Ltd., JEM2010) [15].

2.3. Sensor fabrication and measurement

A schematic drawing of the adsorption/combustion-type gas sensor fabricated is shown in Fig. S1. The sensing material (10MO/γ-Al₂O₃, 1Pt/γ-Al₂O₃ or 1Pt/10MO/γ-Al₂O₃ powder) or unloaded γ-Al₂O₃ powder was mixed with an organic vehicle (a mixed solution of di-n-butyl phthalate (36.4 g) and terpineol (53.6 g) containing polyvinyl butyral resin (mean polymerization degree: 700, 10 g)) at a concentration of ca. 20 wt%, followed by ball milling for 30 min. The pastes containing the sensing material and the unloaded γ-Al₂O₃ were applied on a pair of Pt heaters of microsensor chip fabricated by MEMS technique, as sensing and reference films, respectively, by drop coating technique employing an air-pulse dispenser fluid.
dispenser (Musashi Eng., In., MS-10DX) with a suitable size of syringe, and then the microsensor chips attached with these films were fired at 700°C for 2 h in air. The heat treatment increased the average size of Pt nanoparticles by 20 nm [15]. The sensors obtained are referred to as the kind of VOC-sensing materials in this study.

The sensing properties of the adsorption/combustion-type gas sensors fabricated were measured in an acrylic chamber (inner volume: 50 dm³), in which 10–1000 ppm ethanol was evaporated with a compact heater. The sensor was incorporated into a bridge circuit with two fixed resistive elements, which was used to get output signals from the sensor. All sensors were operated with a mode of pulsed temperature heating (high temperature \(T_h\) at 250–450°C for 0.4 s after low temperature \(T_c\) at RT–150°C for 9.6 s with a cycle of 10 s) by applying rectangular pulse voltage, as shown in Fig. S2(a) and Fig. S2(b). The rate of temperature rise in the sensing and reference films on a microsensor chip was quite fast (the period required for the rapid increase in temperature from RT to 450°C: merely ca. 30 ms [6]). Figure S2(c) shows a typical sensor-signal profile of an adsorption/combustion-type gas sensor. The wave profile of the sensor response generally has one dynamic signal mainly by flash combustion of ethanol and the related compounds adsorbed on the sensing-film surface and a subsequent static signal by general catalytic combustion of ethanol during the pulsed high-temperature heating. The magnitude of general ethanol response, \(\Delta V_{MAX}\), was defined as the maximum of the difference between output voltages in ethanol balanced with air and that in air. Besides, two kinds of response values calculated by integrating the wave profiles, i.e. approximately integrated dynamic response (IDR) and approximately integrated static response (ISR) were also defined as shown in Fig. S2(d).

2.4. Catalytic combustion activity and temperature-programmed desorption and oxidation properties

All the powders were pressed into a disc, and then crushed into granules (ca. 9–20 mesh). The granules obtained (ca. 0.6 g) were fixed in a glass reactor connected with a flow apparatus. After they were pre-treated at 500°C for 1 h and then cooled down to selected temperatures (30–500°C, rates of temperature rise and temperature drop: 3°C min⁻¹ and −3°C min⁻¹, respectively) in dry air (30 cm³ min⁻¹), the catalytic combustion behavior of 923 ppm ethanol over all samples was characterized at each temperature in dry air (30 cm³ min⁻¹, space velocity (SV): 1664 h⁻¹). Temperature-programmed desorption (TPD) and temperature-programmed oxidation (TPO) properties of all samples were also investigated by using the same experimental setup. After they were pre-treated at 500°C for 1 h in dry air (30 cm³ min⁻¹), they were cooled down to 150°C (rate of temperature drop: −3°C C min⁻¹), which is the typical low-power heating temperature under sensor operation. The flow gas was changed from dry air to 923 ppm ethanol balanced with dry air, and then all the samples were treated at 150°C for 1 h in 923 ppm ethanol balanced with dry air (30 cm³ min⁻¹). After an abrupt drop in temperature to 30°C in helium (for TPD) or dry air (for TPO), the TPD or TPO profile was measured at a rate of temperature rise of 3°C min⁻¹ in the same gas (30 cm³ min⁻¹, space velocity: 1664 h⁻¹). The kind and concentration of outlet gases were analyzed by using a gas chromatograph/mass spectroscopy (GC-MS; Shimadzu Corp., GCMS-QP5050 (capillary column used: PorapLOT Q)) and a GC equipped with an FID detector (Shimadzu Corp., GC-2010 (capillary column used: DB-5)).

3. Results and discussion

3.1. Ethanol-sensing properties of 1Pt/γ-Al₂O₃, 10MO/γ-Al₂O₃, and 1Pt/10MO/γ-Al₂O₃ sensors

Figure 1(a) shows sensor-signal profiles of all sensors to 10, 100, and 1000 ppm ethanol in air under the pulse-heating operation (\(T_h\): 150°C, \(T_c\): 450°C). The loading of 10 wt% MO (CeO₂ or Bi₂O₃) onto γ-Al₂O₃ was hardly effective in obtaining a large response to ethanol. Both the 10MO/γ-Al₂O₃ sensors showed quite small dynamic responses even to 1000 ppm ethanol, and the magnitude of the responses decreased with a decrease in the ethanol concentration. However, these sensors continued to positively respond to a high concentration of ethanol during the pulse-driven heating of 0.4 s, whereas the magnitude of responses negatively shifted to a lower concentration of ethanol just after the dynamic response with the negligible static response. The loading of 1 wt% Pt onto γ-Al₂O₃ drastically improved both the dynamic and static ethanol responses. Moreover, the co-loading of Pt with CeO₂ was further effective in improving the magnitude of dynamic response, while the co-loading of Pt with Bi₂O₃ reduced the magnitude of the dynamic response of the 1Pt/γ-Al₂O₃ sensor. On the other hand, the magnitude of static response remained almost unchanged, even though each MO (CeO₂ or Bi₂O₃) was loaded with Pt onto γ-Al₂O₃. Figure 1(b) shows ethanol-concentration dependences of three kinds of responses, \(\Delta V_{MAX}\), IDR, and ISR of all the sensors. In particular, the magnitudes of \(\Delta V_{MAX}\) and IDR of 1Pt/γ-Al₂O₃ and 1Pt/10MO/γ-Al₂O₃ sensors, which mainly originate from their dynamic responses, seem to be intimately related to the adsorption of ethanol and/or the related components onto these surfaces, because the relationship between “\(\Delta V_{MAX}\) or IDR” and “concentration” was quite similar to general adsorption isotherm [22–24]. On the other hand, the magnitude of ISR of the sensors was roughly
proportional to ethanol concentration, and the behavior approximately corresponds to that of general catalytic combustion-type gas sensors [25,26].

### 3.2. Catalytic combustion properties

Figure 2 shows catalytic combustion behavior of 923 ppm ethanol over unloaded γ-Al₂O₃, 1Pt/γ-Al₂O₃, 10MO/γ-Al₂O₃, and 1.0Pt/10MO/γ-Al₂O₃ in dry air (dependences of ethanol-conversion ratio, CO₂-production ratio (the ratio of the amount of CO₂ produced to the amount of total carbon in 923 ppm ethanol), and the concentration of products on temperature). Besides, various parameters on their catalytic combustion behavior are shown in Table 1.

The conversion onset temperature of ethanol, \( T_{CO(E)} \), and the complete conversion temperature of ethanol, \( T_{CC(E)} \), of the γ-Al₂O₃ were quite high (ca. 120°C and ca. 280°C, respectively), and thus the γ-Al₂O₃ showed the lowest oxidation activity of ethanol (the temperature at which 50% of ethanol was converted, \( T_{SO(E)} \): ca. 170°C) among all the samples. On the other hand, the production onset temperature of CO₂ (\( T_{PO(CO₂)} \), ca. 120°C) was quite comparable to \( T_{CO(E)} \), while the complete production temperature of CO₂ (\( T_{CP(CO₂)} \), ca. 300°C) were much higher than \( T_{CC(E)} \). Therefore, the temperature at which 50% of ethanol was oxidized to CO₂ (\( T_{SO} \) (CO₂), ca. 235°C) was much higher than \( T_{SO(E)} \) (ca. 170°C). Three kinds of gases (ethylene, acetaldehyde, and diethyl ether) were confidently produced as reaction intermediates, and acetaldehyde and diethyl ether especially generated in the temperature range from ca. 120°C (i.e. \( T_{PO(CO₂)} \)) to ca. 300°C (i.e. \( T_{CP(CO₂)} \)). On the other hand, ethylene generated over the whole temperature range of more than 150°C, and the amount of ethylene was the largest around 400°C, even though ethanol was almost perfectly oxidized to produce CO₂. These catalytic reactions were generally given as follows [27,28].

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad \text{(dehydration)} \quad (1) \\
\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{CH}_3\text{CHO} + \text{H}_2 \quad \text{(dehydration)} \\
2\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{H}_2\text{O} \quad \text{(dehydration condensation)} \\
\end{align*}
\]

The ratio of each reaction to complete catalytic oxidation reaction of \( \text{C}_2\text{H}_5\text{OH} \),

\[
\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \quad (4)
\]

were largely dependent on the acid-base property and the catalytic oxidation/reduction activity on the surface [29–32]. At least, the generation of the large amounts of these reaction intermediates obviously
Figure 2. Catalytic combustion behavior of 923 ppm ethanol over γ-Al₂O₃, 1Pt/γ-Al₂O₃, 10MO/γ-Al₂O₃, and 1.0Pt/10MO/γ-Al₂O₃ in dry air (30 cm⁻³ min⁻¹, SV: 1664 h⁻¹).

shows that the oxidation activity of ethanol over γ-Al₂O₃ was quite low. Especially, the conversion ratio was ca. 14%, and the CO₂-production ratio was almost 0% at 150°C (Tᵣ in Figure 1), only with the generation of a little amount of diethyl ether. The mass–balance ratio (MBR) in this study is defined as

\[
MBR = \frac{2[\text{ethanol}_{\text{in}}] + 2[\text{CO}_2] + 2[\text{acetaldehyde}] + 4[\text{diethyl ether}]}{2[\text{ethanol}_{\text{in}}]}
\]

where [ethanol]ᵣ, [ethanol]ᵣ, [CO₂], [acetaldehyde], and [diethyl ether] are concentrations of inlet ethanol, outlet ethanol, outlet CO₂, outlet ethylene, outlet acetaldehyde, and outlet diethyl ether, respectively. The MBR is nearly 1.0 at 150°C, which means that unknown reaction intermediates were hardly produced on the γ-Al₂O₃ surface. On the other hand, both the ethanol-conversion ratio and the CO₂-production ratio were almost 100% at 450°C (Tᵣ in Figure 1), only with the generation of a little amount of ethylene (ca. 56 ppm).

The loading of 10 wt% MO (CeO₂ or Bi₂O₃) onto γ-Al₂O₃ slightly improved the conversion property over γ-Al₂O₃. Namely, all parameters on the ethanol-conversion ratio (Tₑ(E), Tₑ(E), and Tₑ(E)) and CO₂-production ratio (Tₑ(CO₂), Tₑ(CO₂), and Tₑ(CO₂)) were a little lower than those of γ-Al₂O₃. Especially according to the reduction in Tₑ(CO₂) of both the samples, their production onset temperature of acetaldehyde (Tₑ(AA)) substantially decreased from more than 150°C to ca. 50°C by the MO loading (the temperature at which the largest amount of acetaldehyde produced: ca. 180°C for both 10MO/mp-Al₂O₃ samples), and the total amount of acetaldehyde produced over 10Bi₂O₃/γ-Al₂O₃ and 10CeO₂/γ-Al₂O₃ became larger and smaller than that over γ-Al₂O₃, respectively. On the other hand, the amount of ethylene produced was drastically decreased by both the Bi₂O₃ and CeO₂ loading, and the Bi₂O₃ loading especially reduced the amount of ethylene produced in the high-temperature range of more than 270°C. In terms of diethyl ether, the CeO₂ loading lowered the production onset temperature (Tₑ(DE), less than 100°C) to exceed the amount of acetaldehyde produced at 150°C (Tᵣ), whereas the Bi₂O₃ loading raised the Tₑ(DE) to inhibit the production of diethyl ether at 150°C. The MBR of both 10MO/γ-Al₂O₃ samples at 150°C was also ca. 1, just like mp-Al₂O₃, even though the conversion ratio (ca. 50% for both 10MO/γ-Al₂O₃ samples) and the CO₂-production ratio (ca. 15% for 10CeO₂/γ-Al₂O₃ and ca. 37% for 10Bi₂O₃/γ-Al₂O₃) at 150°C were much larger than those of γ-Al₂O₃. These results indicate that the loading of Bi₂O₃ or CeO₂ hardly produced other reaction intermediates emitted leastwise to the gaseous atmosphere at 150°C. Considering these results on the catalytic combustion behavior of ethanol over the 10MO/γ-Al₂O₃ surfaces, the effects of the MO loading onto γ-Al₂O₃ at the operating temperature of 150°C can be explained by the following scenario. The CeO₂
loading enhanced the production reaction of acetaldehyde and diethyl ether produced through equations (2) and (3), respectively, on the surface at 150°C, and certain amounts of these intermediates were also oxidized to form CO₂. The Bi₂O₃ loading mainly enhanced the dehydrogenation of ethanol to acetaldehyde at 150°C, and the large part of acetaldehyde desorbed from the surface without further oxidation. On the other hand, both the conversion and CO₂ production ratio were nearly 100% at 450°C, with little production of reaction intermediates.

The loading of only 1 wt% Pt also enhanced the catalytic activity of γ-Al₂O₃, and the effect of the Pt loading was larger than that of the MO loading. T_{CO(E)} of 1Pt/γ-Al₂O₃ (ca. 30°C) was lower than those of 10MO/γ-Al₂O₃ even though T_{CC(E)} of 1Pt/γ-Al₂O₃ (ca. 230°C) was comparable to those of 10MO/γ-Al₂O₃. Thus, T_{50(E)} of the 1Pt/γ-Al₂O₃ (ca. 121°C) was lower than those of 10MO/γ-Al₂O₃. On the other hand, T_{PO(CO₂)} and T_{CP1(CO₂)} of 1Pt/γ-Al₂O₃ was slightly higher than those of 10MO/γ-Al₂O₃, whereas T_{50(CO₂)} of 1Pt/γ-Al₂O₃ (ca. 152°C) was lower than those of 10MO/γ-Al₂O₃. The Pt loading largely decreased the amounts of ethylene and diethyl ether produced over γ-Al₂O₃, and drastically reduced the T_{PO(α)} with a decrease in temperature at which the largest amount of acetaldehyde was produced (ca. 180°C), as is the case with the loading of 10 wt% MO. The MBR of 1Pt/γ-Al₂O₃ at 150°C (ca. 0.8) was smaller than those of γ-Al₂O₃ and 10MO/mp-Al₂O₃. Otherwise, the conversion ratio (ca. 88%) and the CO₂ production ratio (ca. 51%) at 150°C were much larger than those of 10MO/γ-Al₂O₃. These results indicate that other reaction intermediates adsorbing on the surface and/or desorbing to the gaseous atmosphere (not detected by GC-MS), which were different from either ethylene, acetaldehyde, or diethyl ether, were produced by the Pt loading onto the γ-Al₂O₃ surface.

The co-loading of Pt with MO quite further enhanced the catalytic oxidation activity of ethanol over γ-Al₂O₃. Namely, the co-loading of Pt with MO was quite effective in improving the ethanol conversion of γ-Al₂O₃, whereas the loading of only Pt or MO, and the 1Pt/10CeO₂/γ-Al₂O₃ especially showed the most excellent ethanol conversion property (the lowest T_{50(E)}, ca. 68°C). The co-loading of Pt with CeO₂ effectively improved the complete oxidation activity as well, and reduced the amounts of three reaction intermediates produced. T_{50(CO₂)} and T_{PO(CO₂)} of the 1Pt/10CeO₂/γ-Al₂O₃ (ca. 145°C and <30°C, respectively) were the lowest among those of all samples. T_{PO(α)} was quite low (less than 30°C), and the largest amount of acetaldehyde was intermittently produced at lower temperatures (30–270°C). The production of diethyl ether was hardly confirmed in the whole temperature range, while the small amount of ethylene produced at around 210°C.

The conversion ratio at 150°C (ca. 100%) and ca. 90% for 1Pt/10CeO₂/γ-Al₂O₃ and 1Pt/10Bi₂O₃/γ-Al₂O₃, respectively) was quite large in comparison with that of other samples. However, CO₂ production ratio of 1Pt/10CeO₂/γ-Al₂O₃ at 150°C was not so much large (ca. 53%), while that of 1Pt/10Bi₂O₃/γ-Al₂O₃ was extremely small (ca. 23%), which was much larger than that of γ-Al₂O₃ but smaller than those of 10MO/mp-Al₂O₃. Thus, the MBRs at 150°C of 1Pt/10CeO₂/γ-Al₂O₃ and 1Pt/10Bi₂O₃/γ-Al₂O₃ were ca. 0.7 and ca. 0.2, respectively. There was no doubt that the co-loading of Pt with MO enhanced the oxidation activity of ethanol, and thus their relatively enhanced oxidation activity probably induced to produce the large amounts of other reaction intermediates which were not detected, by the synergistic effect of Pt with MO. The high-molecular-weight and/or highly polarized intermediates (e.g. with carboxylic, aldehyde, and/or ester group) is strongly expected to be produced especially on the surface of 1Pt/10Bi₂O₃/γ-

| Sample name | T_{50(E)/°C} | T_{CO(E)/°C} | T_{CC(E)/°C} | T_{50(CO₂)/°C} | T_{PO(CO₂)/°C} | MBR at 150°C |
|-------------|--------------|--------------|--------------|----------------|----------------|--------------|
| γ-Al₂O₃     | 170          | 120          | 280          | 235            | 120            | 300          | 1.0          |
| 1Pt/γ-Al₂O₃ | 141          | 120          | 280          | 152            | 235            | 120          | 300          | 1.0          |
| 10CeO₂/γ-Al₂O₃ | 141     | 120          | 280          | 191            | 120            | 300          | 1.0          |
| 1Pt/10CeO₂/γ-Al₂O₃ | 68    | <30          | 130          | 145            | 30             | 210          | 0.7          |
| 10Bi₂O₃/γ-Al₂O₃ | 148     | 90           | 230          | 186            | 90             | 210          | 1.0          |
| 1Pt/10Bi₂O₃/γ-Al₂O₃ | 93     | 40           | 220          | 205            | 50             | 270          | 2.0          |
Al₂O₃, and thus we have been attempting to get the evidence on the production on the surface and/or in the gaseous atmosphere.

### 3.3. TPD and TPO properties

TPD and TPO profiles generally show temperature dependences of desorption behavior of the target gas adsorbed and/or chemical species produced on the surface, in an inactive gas (helium in this study) and in gas containing oxygen (21% oxygen in this study, i.e. dry air), respectively. When the adsorption/combustion-type gas sensors operate at a mode of pulse-driven heating, the amounts and kinds of adsorbates derived from the target gas are greatly dependent on the concentration of oxygen (i.e. the amounts of oxygen adsorbates and lattice oxygen at the surface of the sensing and reference materials). Therefore, the comparative characterization of TPD and TPO profiles offers significant findings to clarify the gas-sensing characteristics of the sensors. However, we should discuss these data carefully, because the rate of temperature rise in TPD and TPO profiles (ca. 3°C min⁻¹) are drastically different from that of the pulse-driven heating for the adsorption/combustion-type gas sensors (ca. 6 x 10⁴°C min⁻¹, which was roughly estimated).

Figure 3. TPD profiles of ethanol, ethylene, acetaldehyde, diethyl ether, and CO₂ from all samples in helium (30 cm³ min⁻¹, SV: 1664 h⁻¹), after pre-treatment at 150°C for 1 h in 923 ppm ethanol balanced with dry air (30 cm³ min⁻¹).

Figure 4. TPO profiles of ethanol, ethylene, acetaldehyde, diethyl ether, and CO₂ from all samples in dry air (30 cm³ min⁻¹, SV: 1664 h⁻¹), after pre-treatment at 150°C for 1 h in 923 ppm ethanol balanced with dry air (30 cm³ min⁻¹).
The TPD and TPO profiles were shown in Figures 3 and 4, respectively.

3.3.1. γ-Al₂O₃
3.3.1.1. TPD profiles. The temperature at which ethanol (target gas) started to desorb (onset temperature) was around 100°C, and the desorption amount of ethanol abruptly increased with an increase in temperature. A large amount of ethanol intermittently desorbed, especially in a temperature range of 150–320°C (the largest concentration: ca. 200 ppm at 180°C), probably due to the direct adsorption on various adsorption sites on the surface, and then the desorption ended at ca. 300°C (offset temperature). Diethyl ether also started to desorb at around 100°C. However, the amount of diethyl ether desorbed at less than low-power heating (ethanol adsorption) temperature, \( T_L \) (i.e., 150°C), was extremely small, and it abruptly increased with an increase in temperature and it reached the maximum value (ca. 380 ppm) at 215°C. The offset temperature of diethyl ether was also ca. 300°C. Considering that diethyl ether was catalytically produced in the similar temperature range (120–300°C) under steady-state condition (see Figure 2) and that the offset temperature of ethanol was also ca. 300°C in the TPD profile, it is expected that both the forward (dehydration condensation) reaction and reverse (hydrolysis) reaction in the following equation simultaneously proceeded in the temperature range [33].

\[
2C_2H_5OH + O^n^- (\text{oxygen species on surface}) + (2-n)e^- \\
\rightarrow C_2H_4O_2C_2H_5 + 2OH^-
\]  

(6)

Ethylene and acetaldehyde started to desorb at much higher temperatures (ca. 180°C and ca. 190°C, respectively), and the maximum amounts of ethylene and acetaldehyde generated was ca. 1950 ppm and ca. 220 ppm, respectively, at ca. 250°C. The offset temperature of both gases was ca. 320°C. Namely, the temperature range in which these gases were generated was relatively higher than that in which ethanol and diethyl ether were generated. Therefore, ethanol and the related adsorbates, which strongly adsorbed on the oxide surface, probably reacted with oxygen species on the γ-Al₂O₃ surface to produce these gases, according to the following equations, because the catalytic activity of oxygen species (oxygen adsorbates and lattice oxygen) on the γ-Al₂O₃ surface is quite poor.

\[
C_2H_5OH + O^n^- (\text{oxygen species on surface}) + (2-n)e^- \\
\rightarrow C_2H_4 + 2OH^- 
\]  

(7)

\[
C_2H_5OH + 2O^n^- (\text{oxygen species on surface}) \\
\rightarrow CH_3CHO + 2OH^- + 2(n-1)e^- 
\]  

(8)

Besides, these reactions must be severely restricted on the TPD condition, because the oxygen species hardly increase due to the lack of oxygen in the flow gas (impurity oxygen may be slightly immixed from ambient air). Thus, the relative amount of acetaldehyde adsors on the γ-Al₂O₃ surface through equation (8) during the pretreatment at 150°C in ethanol balanced with dry air, and then it desorbs in the temperature range of more than 150°C. The fact that acetaldehyde was hardly produced at 150°C in dry air in the catalytic combustion behavior of ethanol (see Figure 2(c)) strongly supports the above process of acetaldehyde desorption. Ethylene cannot originally adsorb on the γ-Al₂O₃ surface at 150°C.

On the other hand, the TPD profile (Figure 3(e)) showed a little amount of CO₂ (several ten ppm) intermittently desorbed only in the temperature range of more than 300°C. This onset temperature is close to offset temperatures of three reaction intermediates. This is probably because the small number of relatively high-molecular-weight components \((C_6H_{12}O_6)\) which were produced by the polycondensation of ethanol, reacted with the oxygen species on the γ-Al₂O₃ surface to form CO₂ at the higher temperatures, according to the following equation.

\[
C_6H_{12}O_6 + vO^n^- \rightarrow xCO_2 + (v+z-2x)OH^- \\
+ (nv-v-z+2x)e^- 
\]  

(9)

3.3.1.2. TPO profiles. The amounts of ethanol and diethyl ether observed in the TPO profiles were extremely reduced due to the mixing of oxygen into the carrier gas (He). Onset and offset temperatures of ethanol generated were ca. 210°C and ca. 300°C, respectively, and the largest concentration was ca. 9.5 ppm at 270°C. The existence of oxygen in the carrier gas smoothly increases oxygen adsorbates (e.g., \(O_2^-\), \(O^-\), \(O^{2-}\)) and lattice oxygen at various temperatures.

\[
O_2 + ne^- \rightarrow \text{oxygen species} 
\]  

(10)

In the equation above, \( n \) is dependent on the kind of oxygen adsorbates (e.g., \(O_2^-\), \(O^-\), \(O^{2-}\)) and lattice oxygen. Therefore, adsorbed ethanol and the related compounds can react with the oxygen species even during the TPO process at lower temperatures to form other reaction intermediates (actually, the large amounts of acetaldehyde and ethylene generated at higher temperatures, as shown in Figure 4) and unknown higher-molecular-weight reaction intermediates adsorbed on the γ-Al₂O₃ surface.

Onset and offset temperatures of diethyl ether generated were ca. 155°C and ca. 300°C, respectively, and both the values were almost coincident with those of its TPD profile. Besides, the concentration of diethyl ether generated was quite low. Thus, the small amount of diethyl ether in the TPO profile is expected to desorb
from the γ-Al2O3 surface by the same mechanism as that of TPD.

The amount of ethylene observed in the TPO profile, which was also smaller than that desorbed in the TPD profile, was much larger than that of diethyl ether. On the contrary, the amount of acetaldehyde in the TPO profile was about three times larger than that in the TPD profile. These results indicate that the dehydration processes (equations (7) and (6)) retracted and the dehydrogenation (equation (8)) proceeded with an increase in the amount of oxygen in the flow gas. Namely, the dehydrogenation is relatively dominant on the γ-Al2O3 surface in an oxygen-rich gaseous atmosphere at elevated temperatures, since some kinds of oxygen species can effectively adsorb on the surface (equation (10)).

The TPO profile in Figure 4(e) also showed that CO2 intermittingly desorbed in the temperature range of more than ca. 190°C, and the onset temperature of CO2 in the TPO profile is lower than that in the TPD profile. Besides, ca. 700 ppm and ca. 400 ppm of CO2 were produced at ca. 250°C and ca. 430°C, respectively. Considering that the amount of CO2 produced in the TPO profile is much larger than that in the TPD profile, it is expected that various ethanol and the related compounds adsorbed during the pretreatment were converted and/or transformed to various high-molecular-weight reaction intermediates on the γ-Al2O3 surface, and thus they were all oxidized at commensurate temperatures in the range of ca. 190–500°C. However, the amount of CO2 generated from γ-Al2O3 was much smaller than that from Pt and/or MO-loaded γ-Al2O3 samples as shown below, which means that the amounts of ethanol and the related compounds adsorbed on the γ-Al2O3 surface during the pretreatment at 150°C was quite smaller than those adsorbed on the Pt and/or MO-loaded γ-Al2O3 surfaces.

3.3.2. 10MO/γ-Al2O3

The amounts of ethanol, ethylene, and diethyl ether generated were drastically reduced by the MO loading in the TPO profiles. However, the generation behavior of acetaldehyde was different from that of others. Namely, both the CeO2 and Bi2O3 loading slightly lowered the temperature at which the maximum amount of acetaldehyde was generated. Besides, the CeO2 loading increased the maximum amount of acetaldehyde generated at ca. 215°C, while the Bi2O3 loading decreased the maximum amount of acetaldehyde generated at ca. 235°C. On the other hand, ethanol and three kinds of reaction intermediates were hardly generated in the whole temperature range in the TPO profiles.

Contrary to our expectations, both the TPD and TPO profiles of CO2 were unique. In these TPD profiles, CO2 started to be generated at a lower temperature than pretreatment temperature (less than 100°C), and the amount of CO2 increased with a rise in temperature. The amount of CO2 generated from 10CeO2/γ-Al2O3 was larger than that from 10Bi2O3/γ-Al2O3 at less than 350°C. However, the amount of CO2 generated from 10Bi2O3/γ-Al2O3 abruptly increased with a rise in temperature, and the amount of CO2 generated from 10Bi2O3/γ-Al2O3 was larger than that from 10CeO2/γ-Al2O3 at more than ca. 350°C. On the other hand, the onset temperature of CO2 generated from both the 10MO/γ-Al2O3 samples in the TPO profiles was comparable to that in the TPD profiles, and the amounts of CO2 generated from both the 10MO/γ-Al2O3 in the TPO profiles were much larger than those in the TPD profiles. Especially, the CeO2 loading intermittingly produced a quite large amount of CO2 (more than 6000 ppm) at 150–250°C, which was overwhelmingly larger than that from 10Bi2O3/γ-Al2O3. The amount of CO2 generated from both the 10MO/γ-Al2O3 samples shifted to decrease with a further rise in temperature, and then CO2 was hardly produced by 10CeO2/γ-Al2O3 and 10Bi2O3/γ-Al2O3 at more than 400°C and 460°C, respectively. Considering that the amount of CO2 increased at lower temperatures with an increase in oxygen concentration in the flow gas, the MO loading promoted the production reaction of high-molecular-weight components (C6H12O6) during the pretreatment to adsorb them on the 10MO/γ-Al2O3 surface. In the TPO process, they were oxidized with oxygen adsorbates and/or lattice oxygen, which was quantitively limited on the surface, due to the lack of oxygen in the flow gas. The number of active oxygen adsorbates at lower temperatures was originally small, and thus only a small amount of CO2 was generated at the lower temperatures. By contrast, many inactive oxygen adsorbates and/or lattice oxygen which originally existed became active at higher temperatures, and thus they oxidized the C6H12O6 species, to produce the large amount of CO2 despite no oxygen in the flow gas. On the other hand, in the TPO process, the active oxygen adsorbates at lower temperatures were constantly supplied from the flow gas, which seems to be the most important factor to generate the large amount of CO2 only at lower temperatures. The mixture of oxygen in the flow gas increased the number of active oxygen adsorbates and/or lattice oxygen at various temperatures on the 10MO/γ-Al2O3 surface, too, and thus the C6H12O6 species had hardly remained after most of them reacted with the active oxygen adsorbates at lower temperatures.

3.3.3. 1Pt/γ-Al2O3

The Pt loading onto γ-Al2O3 also drastically reduced the amounts of all reaction intermediates and perfectly
eliminated the desorption of ethanol in the TPD profile. Besides, the generation temperature of these reaction intermediates from 1Pt/γ-Al2O3 (the temperature at which the largest amounts of ethylene, acetaldehyde, and diethyl ether: ca. 310°C, ca. 400°C, and ca. 365°C, respectively) was hardly coincident with that of these reaction intermediates from 10MO/γ-Al2O3, which means that the adsorption/desorption properties of 1Pt/γ-Al2O3, as well as the catalytic combustion behavior, were largely different from those of 10MO/γ-Al2O3. The fact that MBR of 1Pt/γ-Al2O3 at 150°C (0.8) is smaller than that of 10MO/γ-Al2O3 (1.0) in their catalytic combustion behavior (see Table 1) promises more efficient production of higher-molecular-weight components on the 1Pt/γ-Al2O3 surface at Tl (150°C) than that on 10MO/γ-Al2O3, which might increase the generation temperatures of the reaction intermediates on the 1Pt/γ-Al2O3 surface. On the other hand, the TPO profiles showed that ethanol and three kinds of reaction intermediates were hardly generated in the whole temperature range.

The Pt loading onto γ-Al2O3 also increased the amounts of CO2 generated in the TPD and TPO profiles. The amount of CO2 intermittently generated from 1Pt/γ-Al2O3 was smaller than that from 10MO/γ-Al2O3 in the TPD profile, and the largest amount of CO2 generated from 1Pt/γ-Al2O3 in the temperature range of 300–370°C. On the other hand, the amount of CO2 in the TPO profile was comparable to that in the TPD profile at low temperatures (less than 230°C), but it abruptly increased with a rise in temperatures at more than 230°C and reached the maximum (ca. 7000 ppm) at around 320°C. Namely, there is a large difference in the amount of CO2 generated between TPD and TPO, even though there is little difference in the temperature dependence of CO2-generation behavior between TPD and TPO. This indicates that the larger number of high-molecular-weight components produced at Tl (150°C) and adsorbed on the surface was oxidized under oxygen-richer gas flowing, but the quality of the reaction sites for catalytic combustion was not so much dependent on oxygen concentration in the flow gas at the slow rate of temperature rise (3°C min⁻¹). A certain number of active reaction sites was formed on the surface of Pt and/or the boundary between Pt and γ-Al2O3, even under the oxygen-free gas flowing (i.e. under the TPD process) and the increase in the oxygen concentration in the flow gas probably incremented the number of active reaction sites on the 1Pt/γ-Al2O3 surface.

### 3.3.4. 1Pt/10MO/γ-Al2O3

The co-loading of Pt with MO onto γ-Al2O3 had a great influence on the TPD and TPO profiles of 1Pt/γ-Al2O3 as well as 10MO/γ-Al2O3. The generation of ethanol, acetaldehyde, and diethyl ether from 1Pt/10CeO2/γ-Al2O3 was hardly confirmed in the TPD profile. Ethylene was only generated from 1Pt/10CeO2/γ-Al2O3 at around 300°C, which is almost the same temperature as that for 1Pt/γ-Al2O3. The amount of ethylene generated (up to 200 ppm) was a little larger than that from 1Pt/γ-Al2O3, whereas it was much smaller than that from γ-Al2O3. On the other hand, the amounts of acetaldehyde and diethyl ether from 1Pt/10Bi2O3/γ-Al2O3 (ca. 125 ppm at 375°C and ca. 220 ppm at 330°C, respectively) were larger than those from 1Pt/γ-Al2O3 in the TPD profile. The generation temperature range was comparable to that from 1Pt/γ-Al2O3, which was higher than that from γ-Al2O3. Furthermore, the small amount of ethanol (ca. 30 ppm at 170°C) also desorbed in the lower temperature range (less than 220°C). Ethylene was hardly generated from 1Pt/10Bi2O3/γ-Al2O3. These results indicate that the reaction intermediates adsorbed on the 1Pt/10Bi2O3/γ-Al2O3 surface were quite different from those of the 1Pt/10CeO2/γ-Al2O3 surface. The CeO2 loading probably enhanced the production and desorption of high-molecular-weight components on the 1Pt/γ-Al2O3 surface at pretreatment at Tl (150°C), which were decomposed to form ethylene mainly at elevated temperatures. The Bi2O3 loading seemed to enhance the production and desorption of high-molecular-weight components of the 1Pt/γ-Al2O3 surface during pretreatment at Tl (150°C), which was decomposed only to form both acetaldehyde and diethyl ether at elevated temperatures. Nevertheless, the generation of ethylene, as well as three kinds of reaction intermediates from both 10MO/γ-Al2O3 surfaces, was hardly confirmed in the TPO profiles, which means that these specific high-molecular-weight components adsorbed on the surfaces were totally oxidized under the oxygen-rich gas flowing (TPO process).

The co-loading of Pt with MO onto γ-Al2O3 also increased the amounts of CO2 generated from γ-Al2O3 in the TPD profile. The CO2-generation behavior from 1Pt/10Bi2O3/γ-Al2O3 was comparable to that from 1Pt/γ-Al2O3, and the amount of CO2 intermittingly generated at elevated temperatures was slightly larger than that from 1Pt/γ-Al2O3. The co-loading of Pt with CeO2 reduced the CO2 onset temperature and increased the amount of CO2 generated in the temperature range of less than ca. 320°C (the largest amount of CO2 generated: ca. 1000 ppm). However, the amounts of CO2 generated from 1Pt/10MO/γ-Al2O3 were much smaller than those from 10MO/γ-Al2O3, especially at lower temperatures (less than ca. 220°C) and higher temperatures (more than ca. 330°C). In the TPO profiles, on the other hand, the co-loading of Pt with MO reduced the CO2 onset temperatures and decreased the amount of CO2 generated from 1Pt/γ-Al2O3. The co-loading of Pt with CeO2 was slightly effective in decreasing the CO2 onset temperature than the co-loading of Pt with Bi2O3, while the amount
of CO₂ generated from 1Pt/10CeO₂/γ-Al₂O₃ was smaller than that from 1Pt/10Bi₂O₃/γ-Al₂O₃. Nevertheless, the CO₂ onset temperatures of 1Pt/10MO/γ-Al₂O₃ were higher than those of 10MO/γ-Al₂O₃, and the amounts of CO₂ from 1Pt/10MO/γ-Al₂O₃ were much smaller than those of 10MO/γ-Al₂O₃. The co-loading of 1Pt with 10CeO₂ obviously enhanced the catalytic oxidation activity of 1Pt/γ-Al₂O₃ and 10CeO₂/γ-Al₂O₃, but the co-loading of Pt with MO lowered their MBR at 150°C (ca. 0.7 for 1Pt/10CeO₂/γ-Al₂O₃ and ca. 0.2 for 1Pt/10Bi₂O₃/γ-Al₂O₃ (ca. 0.2), as shown in Figure 2 and Table 1. The TPO profiles show that the number of the high-molecular-weight reaction intermediates adsorbed during the pretreatment at Tₜ (150°C) on the 1Pt/10MO/γ-Al₂O₃ surfaces was smaller than that on the surfaces of 10MO/γ-Al₂O₃ (especially, 10CeO₂/γ-Al₂O₃). Besides, the loading of only Pt and the co-loading of Pt with Bi₂O₃ largely increased the amount of CO₂ generated at around 300 and 330°C, respectively, but the co-loading of Pt with CeO₂ only slightly enhanced the amount of CO₂ generated in lower temperature range, with a decrease in the oxygen concentration in the flow gas. These results indicate that the co-loading of Pt with CeO₂ is quite effective in totally oxidizing the high-molecular-weight reaction intermediates on the surface, even under the oxygen-poor gas flowing.

### 3.4. Effects of catalytic combustion behavior and adsorption/desorption properties on ethanol-sensing characteristics of adsorption/combustion-type micro VOC sensors

Based on the catalytic combustion behavior and TPD and TPO properties of all samples in sections 3.2 and 3.3, the ethanol-sensing characteristics of adsorption/combustion-type gas sensors are discussed in this section, along with the role of each of the sensing materials.

### 3.4.1. Validity of γ-Al₂O₃ as a reference material

The catalytic activity of the γ-Al₂O₃ surface was so low at Tₜ (150°C) that only diethyl ether was slightly produced as a reaction intermediate, through dehydration condensation without the production of CO₂. Ethanol and diethyl ether were adsorbed at 150°C and they were directly desorbed with a rise in temperature. Ethanol may be slightly oxidized to form high-molecular-weight intermediates, but their amounts can be vanishingly low, because the MBR at 150°C was almost 1.0. Besides, the rise in temperature of up to ca. 300°C generated ethylene and acetaldehyde with low active oxygen adsorbates on the γ-Al₂O₃ surface and totally oxidized them (and/or the related adsorbates) to produce a small amount of CO₂ according to TPD and TPO spectra. These results indicate that ethanol, diethyl ether, and the related adsorbates were not effectively oxidized on the γ-Al₂O₃ surface at the initial stage of the pulse-driven heating from 150°C to 450°C (i.e. ca. several tens of milliseconds for the dynamic response). Namely, it is expected that endothermic process such as just desorption of the adsorbates is superior to exothermic process such as oxidation at the stage. Based on these discussions, γ-Al₂O₃ is quite suitable as a reference material of adsorption/combustion-type gas sensors operable at 150°C as Tₜ. On the other hand, the CO₂ production ratio was almost 100% on the γ-Al₂O₃ surface at higher than 300°C. Ethanol was totally oxidized at 450°C, which is a temperature value over an almost entire period of pulse-driven heating, whereas the adsorption/combustion-type gas sensors employing γ-Al₂O₃ as a reference material showed ethanol responses appropriate for the catalytic materials used (see Figure 1). Namely, the γ-Al₂O₃ sufficiently worked as a reference material. We would like to discuss the differences in catalytic combustion behavior and adsorption/desorption (i.e. TPD and TPO) properties between γ-Al₂O₃ and catalytic gas-sensing materials (Pt and/or MO-loaded γ-Al₂O₃) in the following sections.

### 3.4.2. Effects of MO loading on ethanol-sensing properties

The MO loading onto γ-Al₂O₃ certainly activated the catalytic activity of ethanol. On the other hand, the TPD profiles of 10MO/γ-Al₂O₃ indicated that even the rate of temperature rise of 3°C min⁻¹ was too fast to completely oxidize the high-molecular-weight components adsorbed on the surface, only with oxygen adsorbates formed during the pretreatment. Namely, further enhanced oxidation activities over these oxide surfaces were essential in proceeding with the complete oxidation. The increase in oxygen concentration in the flow gas drastically reduced the generation temperature of the large amount of CO₂, according to the TPO profile. This result also indicates that the complete-oxidation rate of the high-molecular-weight components on the 10MO/γ-Al₂O₃ surface was quite slow. The intermitting CO₂ generation in the wide temperature range shows that various types of high-molecular-weight components are largely produced and subsequently adsorbed on the surface. In the case of static catalytic combustion of ethanol over the 10MO/γ-Al₂O₃ surface (see Figure 2); therefore, Tₜ (E) and Tₜ(CO₂) of 10MO/γ-Al₂O₃ were quite high and the MBR at 150°C was about 1.0, while the high-molecular-weight components on the surface were decomposed to desorb as each of three kinds of reaction intermediates as well as CO₂. On the other hand, the rate of abrupt temperature rise of adsorption/combustion-type gas sensors at pulse-driven heating (flash combustion) was roughly ca.
6 × 10⁴°C min⁻¹. The MO loading improved the oxidation activity of γ-Al₂O₃, but the rate of complete oxidation of ethanol over 10MO/γ-Al₂O₃ cannot follow the abrupt temperature rising. This is the main reason why the MO loading onto γ-Al₂O₃ did not contribute to enhancing the dynamic oxidation of ethanol and the 10MO/γ-Al₂O₃ sensor showed an extremely small dynamic response to ethanol. In addition, these sensor-signal profiles negatively shifted to a lower concentration of ethanol immediately after the dynamic response. The thermal conductivity of ceramic materials generally decreases with an increase in the mass of the constituent metal (M), lattice defects, grain boundaries, impurities, and so on [34]. Therefore, the MO loading is likely to cause the reduction in thermal conductivity of the sensing γ-Al₂O₃ film. The balance between the thermal conductivity and the catalytic oxidation activity of 10MO/γ-Al₂O₃ (gas-sensing material) and γ-Al₂O₃ (reference) are quite important for determining the shift direction of the sensor-signal profiles.

These 10MO/γ-Al₂O₃ sensors also showed a quite small static response to ethanol. This is probably because the rate of catalytic combustion of ethanol at 450°C directly influenced the magnitude of ethanol response. Namely, the rate of catalytic combustion of ethanol over 10MO/γ-Al₂O₃ was only slightly faster than that over γ-Al₂O₃, considering that only ethylene generated over 10MO/γ-Al₂O₃ was smaller than that over γ-Al₂O₃ at 450°C. This slight difference in rates of catalytic combustion between 10MO/γ-Al₂O₃ and γ-Al₂O₃ determined the magnitude of static ethanol response.

### 3.4.3. Effects of Pt loading and Pt/MO co-loading on ethanol-sensing properties

The Pt loading onto γ-Al₂O₃ largely improved the CO₂-production ratio as well as ethanol conversion, and thus both $T_{50}(E)$ and $T_{50}(CO₂)$ shifted to lower temperatures. Therefore, the amounts of various adsorbates on the 1Pt/γ-Al₂O₃ surface were relatively small, in comparison with that of on the 10MO/γ-Al₂O₃ surface. However, the activity of the reaction sites for catalytic combustion was not so much dependent on oxygen concentration in the flow gas, because the 1Pt/γ-Al₂O₃ has active oxygen species on the surface, which can effectively oxidize the relatively small amounts of ethanol, reaction intermediates, and high-molecular-weight components adsorbed at 150°C, even under the oxygen-poor TPD conditions. These highly qualified catalytic combustion properties of the 1Pt/γ-Al₂O₃ surface were the main reason why the magnitude of the dynamic response of the 1Pt/γ-Al₂O₃ sensor was much larger than that of the 10MO/γ-Al₂O₃ sensors. Besides, the 1Pt/γ-Al₂O₃ sensor naturally shows a quite large static response, in comparison with that of the 10MO/γ-Al₂O₃ sensors, because the catalytic combustion rate of ethanol over 1Pt/γ-Al₂O₃ at 450°C was much larger than that over 10MO/γ-Al₂O₃.

Furthermore, the co-loading of Pt with MO onto γ-Al₂O₃ modified the catalytic combustion behavior and adsorption/desorption properties of ethanol over 1Pt/γ-Al₂O₃ and 10MO/γ-Al₂O₃, and then it made an important impact on their dynamic responses to ethanol. The co-loading of Pt with Bi₂O₃ onto γ-Al₂O₃ produced and then adsorbed the large amounts of relatively high-molecular-weight components on the surface at 150°C, in comparison with those produced on the surface of other samples, as expected from the small MBR (ca. 0.2, see Figure 2). Therefore, it is difficult to efficiently oxidize them on the 1Pt/10Bi₂O₃/γ-Al₂O₃ surface at the initial stage of the pulse-driven heating from 150°C to 450°C. This is the reason why the 1Pt/10Bi₂O₃/γ-Al₂O₃ sensor showed a relatively small and slow dynamic response to ethanol (see Figure 1). On the other hand, the co-loading of Pt with CeO₂ onto γ-Al₂O₃ showed the largest catalytic combustion properties, with relatively large MBR at 150°C (ca. 0.7, see Figure 2) and the small amounts of reaction intermediates. Besides, the TPD and TPO profiles (Figure 3(e) and 4(e)) show that the high-molecular-weight components adsorbed on the 1Pt/10CeO₂/γ-Al₂O₃ surface, which probably had relatively small molecular weight, are efficiently oxidized to form CO₂ at low temperatures in comparison with those on the 1Pt/γ-Al₂O₃ and 1Pt/10Bi₂O₃/γ-Al₂O₃ surfaces. In addition, CeO₂ has a large oxygen storage/release capacity [35–39]. The considerable amounts of oxygen components are liberated from the bulk of CeO₂ with a rise in temperature, especially under oxygen-poor gaseous atmosphere, and thus they promoted the oxidation of various adsorbates on the surface, even at the quite fast flash heating (ca. 6 × 10⁴°C min⁻¹). They are the reasons why the 1Pt/10CeO₂/γ-Al₂O₃ sensor showed a quite large dynamic response.

On the other hand, the magnitude of static responses of the 1Pt/10CeO₂/γ-Al₂O₃ sensor was quite comparable with those of the 1Pt/γ-Al₂O₃ and 1Pt/10Bi₂O₃/γ-Al₂O₃ sensors. The catalytic combustion behavior, as well as TPD and TPO profiles at 450°C, were quite similar between 1Pt/γ-Al₂O₃, 1Pt/10Bi₂O₃/γ-Al₂O₃, and 1Pt/10CeO₂/γ-Al₂O₃. These results strongly show that the rate of catalytic combustion of ethanol over their surfaces determines the total amount of heat on their surface at 450°C, which directly reflects the magnitude of static response.

### 3.5. Effects of $T_s$ and $T_m$ on the ethanol-sensing properties of 1Pt/10CeO₂/γ-Al₂O₃ sensor

Based on these results and discussion, the effects of $T_s$ and $T_m$ on the ethanol-sensing properties of the adsorption-combustion-type gas sensors are discussed in this
section. Figure 5 shows the sensor-signal profiles of the 1Pt/10CeO$_2$/γ-Al$_2$O$_3$ sensor to ethanol under the operation with a mode of pulsed temperature heating of $T_H$ at 450°C after $T_L$-operation at RT, 100, and 150°C and ethanol-concentration dependences of the various responses. The reduction in $T_L$ naturally had an insignificant effect on the magnitude of static responses. However, it was surprisingly ineffective in improving the magnitude of dynamic responses, too. The magnitude of dynamic response to 1000 ppm ethanol slightly increased with a rise in $T_L$, while that to 100 ppm ethanol inversely decreased with a rise in $T_L$. The $T_L$ dependences of its $\Delta V_{\text{MAX}}$ and IDR of the sensor (Figure 5(b)) (i) and (ii) obviously shows that the amounts of ethanol and/or various adsorbates containing reaction intermediates and high-molecular-weight components adsorbed on the surface are the important key in exhibiting the large responses. Therefore, the amount and kind of adsorbed components are expected to largely depend on $T_L$, according to the catalytic combustion behavior (Figure 1). However, the actual amount of heat generated by the combustion of these adsorbates seems not to be much dependent on $T_L$. The fact indicates that the amounts of various adsorbates at 150°C on the 1Pt/10CeO$_2$/γ-Al$_2$O$_3$ surface were almost comparable to that at RT, from the viewpoint of their combustion heat. The operation of $T_L$ at 150°C is discouraged in terms of energy saving. However, the relatively high-temperature $T_L$ operation above 100°C is generally quite effective in reducing the influence of moisture on the magnitude of dynamic responses of the sensor.

On the other hand, $T_H$ had a large influence on the magnitude of both dynamic and static responses, as we had expected. Figure 6 shows the sensor-signal profiles of the 1Pt/10CeO$_2$/γ-Al$_2$O$_3$ sensor to ethanol under the operation with a mode of pulsed temperature heating of $T_H$ at 250, 350, and 450°C after $T_L$-operation at 150°C and ethanol-concentration dependences of the various responses. Firstly, the magnitude of static response reduced with a decrease in $T_H$. This behavior is similar to that of general catalytic combustion-type gas sensors. Thus, the magnitude of static responses had been quite small, even though both the ethanol conversion and the production ratio of CO$_2$ at 250°C nearly were 100%. This behavior means that the reaction rate was slow and the amount of heat generation was small at 250°C in comparison with those at elevated temperatures. In contrast, the magnitude of the dynamic response of the 1Pt/10CeO$_2$/γ-Al$_2$O$_3$ sensor also reduced with a decrease in $T_H$, but the sensor showed a relatively large dynamic response as low as 10 ppm ethanol, in comparison with the static response. This shows that a certain amount of various adsorbates at 150°C on the surface were efficiently
4. Conclusions

Catalytic combustion behavior and adsorption/desorption properties of ethanol over these materials of ethanol over γ-Al₂O₃ powders co-loaded with and without 1Pt and/or 10MO were investigated in detail and the ethanol-sensing characteristics of the adsorption/combustion-type gas sensors employing these gas-sensing materials were discussed in this study. γ-Al₂O₃ shows poor catalytic activity for ethanol oxidation, and thus three kinds of reaction intermediates (ethylene, acetaldehyde, and diethyl ether) were generated in large amounts. The MO loading slightly promoted the catalytic activity and reduced the amounts of reaction intermediates. However, it was not so effective in improving the rate of catalytic combustion of ethanol, and thus the 10MO/γ-Al₂O₃ sensors showed a quite small magnitude of ethanol responses. On the other hand, the Pt loading drastically improved the catalytic activity and then accelerated the rate of catalytic combustion of ethanol. Therefore, the ethanol response of 1Pt/γ-Al₂O₃ sensor was much larger than those of the 10MO/γ-Al₂O₃ sensors. The loading of Pt with Bi₂O₃ decreased MBR at 150°C and then the produced high-molecular-weight components on the surface are not easily oxidized at the initial stage of the pulse-driven heating. Therefore, the 1Pt/10Bi₂O₃/γ-Al₂O₃ sensor showed a relatively small and slow dynamic response to ethanol. 1Pt/10CeO₂/γ-Al₂O₃ showed the largest catalytic activity. The amounts of adsorbates on the surface were the smallest among all samples. However, they were efficiently oxidized on the surface to form CO₂, probably because of the large oxygen-release capacity.
of CeO₂ even at quite fast flash heating. They are the reasons why the 1Pt/10CeO₂/γ-Al₂O₃ sensor showed the largest dynamic response to ethanol. The magnitude of static responses of the 1Pt/γ-Al₂O₃ and 1Pt/10MO/γ-Al₂O₃ sensors is independent of the kind of loading species, because of their comparable catalytic activities at 450°C. The effects of Tᵢ and Tᵣ on the ethanol-sensing properties of the 1Pt/10CeO₂/γ-Al₂O₃ sensor were also explained well enough, on the basis of the catalytic activity for ethanol oxidation and TPD/TPO properties.

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Disclosure of potential conflicts of interest

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