Adsorption/Combustion-type Micro Gas Sensors: Typical VOC-sensing Properties and Material-design Approach for Highly Sensitive and Selective VOC Detection

Takeo HYODO[†] and Yasuhiro SHIMIZU

Graduate School of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan

Highly sensitive and selective detection of various volatile organic compounds (VOCs) has been most needed in a wide range of fields, such as medical diagnosis, health supervision, industry-process control, and environmental monitoring. Since a semiconductor-type gas sensor is a typical promising candidate among various portable VOC-sensing devices, many efforts on developing these gas sensors are introduced in this article for the first time. Through some development stages, it has been well known that the temperature-modulated operation of gas sensors is one of effective ways to improve the magnitude of VOC responses. On the other hand, catalytic combustion-type gas sensors operated with a mode of pulse-driven heating were developed in the early 2000s, and they are named as “adsorption/combustion-type gas sensors” after their gas-sensing mechanism, based on the combustion of VOC adsorbates on the sensing material. The representative VOC-sensing properties of the adsorption/combustion-type gas sensors and recent material-design approach to achieve highly sensitive and selective VOC detection are summarized in this article.

Keywords Adsorption/combustion-type gas sensors, temperature modulation, VOC, MEMS

(Received December 26, 2019; Accepted February 6, 2020; Advance Publication Released Online by J-STAGE February 14, 2020)

1 Introduction	401	4 Material Design of Adsorption/Combustion-type Gas Sensors and Clarification of the VOC-sensing Mechanism	404
2 Structure, Operation Mode, and Fundamental Gas-sensing Properties of Adsorption/Combustion-type Gas Sensors	403	5 Conclusion	409
3 Early Stage of Study on Adsorption/Combustion-type Gas Sensors—Possibility of Highly Sensitive and Selective Sensing to Various VOCs	403	6 Supporting Information	410
		7 References	410

1 Introduction

Volatile organic compounds (VOCs) are largely generated from new building materials, furniture, and household goods which are made of paints, resin, adhesives, and other petroleum

products. They are well known to be essential substances responsible for the sick-house and building syndrome comprising headaches, eye irritation, sore nose and throat, dizziness, fatigue, nausea, and various nonspecific symptoms.^{1,2} Many international institutes designate various gaseous organic chemicals such as formaldehyde, acetone, benzene, methylene chloride, and some

Takeo HYODO received his Doctor of Engineering Degree from Kyushu University, Fukuoka, Japan, in 1997. He has been an Associate Professor at the Graduate School of Engineering, Nagasaki University, since 2010. He received Young Researcher Award (Sano Award) of the Electrochemical Society of Japan (ECSJ) in 2002, Excellent Paper Awards of ECSJ with Prof. Shimizu in 2001 and 2005, and Seiyama Award of Japanese Association of Chemical Sensors in 2010.

Yasuhiro SHIMIZU received his Doctor of Engineering Degree from Kyushu University, Fukuoka, Japan, in 1987. Since 2005, he has been a full Professor first at the Faculty of Engineering, since 2011 at the Graduate School of Engineering, Nagasaki University. Currently, he has 170 full papers, 72 review papers and books, and 181 conference contributions, mainly in the field of ceramic gas sensors and electroceramics. He serves Co-Editor-in-Chief of Sensors and Actuators B: Chemical.

[†] To whom correspondence should be addressed.
E-mail: hyodo@nagasaki-u.ac.jp

kinds of alcohol as hazardous VOCs. In addition, microbial VOCs (MVOCs), which are a variety of compounds formed in the metabolism of bacteria and fungi, also seriously increased with a decrease in use of formaldehyde as a preservative and an antimicrobial.^{3,4} For example, acetone, 1-octen-3-ol, and benzyl cyanide are produced during primary metabolism, while 2-methyl-isoborneol, geosmin, and terpene are produced during secondary metabolism. They are also causative agents of the sick-house and building syndrome. On the other hand, there are a huge amount of VOCs in human exhaled breath, skin gas and farts, and their composition and components greatly depend on the physical conditions and states of internal organs and tissues in the human body. For example, acetone, isoprene or pentane, toluene or 1-nonanal, and methanethiol were reported to be specific biomarkers for diabetes, heart disease, lung cancer, and halitosis, respectively.⁵ Therefore, speedy and accurate analyses of these VOCs by low-cost, compact and simplified devices offer great potential for the diagnosis of specific diseases in a realistic medical setting and health supervision in personal use. On the basis of these situations, gas sensors are one of the promising candidates to detect these VOCs sensitively and selectively.⁶

A great deal of effort has been put into developing various types of VOC sensors (semiconductor gas sensors,⁷⁻¹⁶ solid-electrolyte gas sensors,¹⁷⁻²³ and others²⁴⁻²⁷). Most of them are generally operated under static conditions at constant temperature. In this case, the preconcentration of target VOCs in sample gas is one of the effective ways to detect quite small amounts of the target VOCs.²⁸⁻³⁰ After the target VOCs are adsorbed and then concentrated in large quantity on adsorbents with a large specific surface area (*e.g.*, zeolites, mesoporous materials, metal-organic frameworks (MOFs)) at lower temperatures (T_L), the adsorbed VOCs components instantaneously desorb from the surface during a short-period of heating at elevated temperatures (T_H). Therefore, the sensors can easily detect temporarily high-concentrated VOCs generated for a short time. We have also attempted to develop mesoporous adsorbents for the preconcentration of 2-pentylfuran.³¹ In these circumstances, Hiyama *et al.* have recently succeeded to develop prototype wearable devices capable of detecting small amounts of acetone generated from human skin (biomarker of fat burning in human body used for health management), which consist of semiconductor gas sensors and zeolite-based adsorbents.^{32,33}

Separately, a specific gas-sensing behavior of gas sensors operated with different kinds of temperature cycling and modulation (periodically driven with rectangular, sinusoidal, and/or pulse applied heating voltage) under various gaseous atmospheres was significant in the late 1980s and early 1990s. The effectiveness of these operating conditions was discussed to improve the gas-sensing properties of the TGS series of semiconductor-type gas sensors manufactured by Figaro Eng. Inc. (so-called TGS sensors; *e.g.*, #812 and #813) in most cases. Sears *et al.* reported that the dynamic resistance changes of TGS #812³⁴ and #813³⁵ sensors were largely dependent on the kinds and concentrations of gases and the values of T_L and T_H (time interval between two heating voltages: several – several ten seconds). They succeeded to distinguish the responses to target gases, such as propane, CO and H₂, both from each other and various VOCs. Lantto *et al.* discussed that the differences between equilibrium and non-equilibrium responses of semiconductor-type porous SnO₂ sensors to H₂S and the effects of water vapor on the CO response behavior of the TGS #812 sensor under rectangular heating-voltage modulation^{36,37} on the basis of detailed studies on active oxygen adsorbates (O⁻ species) frozen on the surface quickly cooled from T_H to T_L .³⁸

Wlodek *et al.* reported that the continuous resistance change of the TGS #813 sensor as a function of a monotonic increase in the operating temperature was represented as a linear combination of dynamic Gaussian-functioned signals to various gases.³⁹ Nakata and Yoshikawa *et al.* demonstrated that the nonlinear hysteresis resistance loop of the TGS #813 sensor was a function of the operating temperature with a sinusoidal heating voltage input in various VOCs and that the Fourier transformation analysis especially contributed to the achievement of a highly selective response.^{40,41} This fundamental technique also improved the gas-recognition properties of next-generation thick-film TGS sensors (*e.g.*, #2620), when used in combination with second-harmonic heating operation.⁴²⁻⁴⁴ At almost the same time, the dynamic response properties of semiconductor-type micro sensors based on the silicon-based platform, which were fabricated by micro-electro-mechanical system (MEMS) technology, to various anesthetic agents⁴⁵ and inorganic gases,⁴⁶ were also investigated with a sinusoidal modulation mode of the heating voltage. On the basis of these findings, many researchers analyzed the sensor-signal profiles to various VOCs, which largely depended on the dynamic change in temperature by employing various advanced computing technologies, such as principle component analysis (PCA) and linear discriminant analysis (LDA), along with a neural network.⁴⁷⁻⁵⁰ Our group also demonstrated that the Pt-loaded WO₃-based micro sensors showed quite large and selective dynamic responses to acetone under operation with sinusoidal heating-voltage modulation.⁵¹ Recently, high-performance semiconductor-type gas sensors operated under a pulse-driven temperature operation mode have been developed by two different groups, but the concepts of their sensor operation were completely different. Schütze and his colleagues effectively utilized large amounts of active oxygen adsorbates (O⁻ species), which were frozenly produced on the oxide surface after instantaneous cooling from T_H (*e.g.*, 450°C) to T_L (*e.g.*, 140°C),³⁸ and clarified that the reaction of various VOCs (benzene, ethanol, and so on) with the oxygen adsorbates at T_L showed specific and large transient responses of the semiconductor-type gas sensors,⁵²⁻⁵⁴ while Shimano and his colleagues developed high-performance toluene sensors operated with an abrupt pulse heating from T_L (RT, period of toluene adsorption) to T_H (*e.g.*, 250°C, period of toluene combustion).^{55,56}

On the other hand, there was only a few reports on calorimetric gas sensors and catalytic combustion-type gas sensors under dynamic temperature modulation. These sensors were operated by utilizing exothermal and/or endothermal energy generated through the adsorption, desorption, and combustion processes of target gases on the sensor surface. Because these types of sensors have a good linear relationship between the sensor response and the concentration of target gases, they have been utilized in various application fields. However, they do not have sufficient responses to quite low concentrations of target gases (generally, less than 1 ppm). In such development situations of these sensors, Lerchner *et al.* demonstrated that adsorption and desorption behaviors of some kinds of alcohols on a specific polymer layer coated on the MEMS sensor platform were able to be used as a source of sensor-signal output.⁵⁷ In contrast, Sasahara and his groups optimized the microstructure of catalytic combustion-type gas sensors to adsorb various kinds of VOCs mainly on the sensor surface at lower temperatures (T_L) and operated the sensors with a mode of pulse-driven heating at elevated temperatures (T_H).⁵⁸⁻⁷⁶ They named the series of these sensors “adsorption/combustion-type gas sensors” after the gas-sensing mechanism based on the combustion of VOCs adsorbates on the sensing film.⁶⁰

Fig. 1 Schematic drawing of typical adsorption/combustion-type gas sensor. Reproduced with permission from Ref. 71.

2 Structure, Operation Mode, and Fundamental Gas-sensing Properties of Adsorption/Combustion-type Gas Sensors

Figure 1 shows a typical schematic drawing of an adsorption/combustion-type gas sensor. The silicon-based sensor platform was fabricated by a general MEMS technique, but the design and size of the sensors gradually varied over time. A couple of platinum micro-heaters was formed on a Si(100) wafer covered with three insulating layers consisting of SiO₂, Si₃N₄ and HfO₂. The back portions of the silicon substrate underneath the micro-heaters were only removed by anisotropic etching with 25 wt% tetramethylammonium hydroxide aqueous solution, to form the diaphragm structure. The paste containing a VOC-sensing material (e.g., γ -Al₂O₃ powder loaded with noble-metal nanoparticles) and another paste containing a reference material (e.g., unloaded γ -Al₂O₃ powder) were applied on the Pt electrodes (micro heaters), respectively, by a drop coating technique employing an air-pulse fluid dispenser, and then the microsensor chips attached with these films were fired at 700°C for 1 h in ambient air. Hereafter, the sensors obtained are referred to as the kind of the VOC-sensing materials. The operating conditions of the sensors with a mode of pulsed temperature heating, typical sensor-signal profile, and definition of their responses are precisely described in Sect. S1 and Fig. S1 concerning electronic Supporting Information.

Figure 2 shows representative sensor-signal profiles of the 15 wt% Pd-loaded γ -Al₂O₃ (15Pd/ γ -Al₂O₃) sensor to 1000 ppm ethanol (C₂H₅OH), H₂, and CH₄ with pulse-driven heating (T_H : 450°C for 0.4 s; T_L : RT for 9.6 s).^{58,59} This sensor shows ordinary (static) sensor-signal profiles to H₂ and CH₄ as a conventional catalytic/combustion-type sensor, which simply

Fig. 2 Sensor-signal profiles of 15Pd/ γ -Al₂O₃ sensor to 1000 ppm ethanol, H₂, and CH₄ with pulse-driven heating (T_H , 450°C for 0.4 s; T_L , RT for 9.6 s). Reproduced with permission from Ref. 59.

increases to reach their steady-state values by *ca.* 40 ms after an abrupt rising in the temperature due to the pulse-driven heating. Namely, these gases do not adsorb on the surface of both 15Pd/ γ -Al₂O₃ (sensing material) and unloaded γ -Al₂O₃ (reference material) at RT for 9.6 s, but just catalytically burn, especially on the sensing 15Pd/ γ -Al₂O₃ film at 450°C. On the other hand, this sensor shows a large specific (dynamic) sensor-signal profile to ethanol within *ca.* 100 ms just after pulse-driven heating, because a large number of ethanol molecules adsorb on the 15Pd/ γ -Al₂O₃ surface at RT, and thus they burn all at once. In addition, the magnitude of the dynamic response is largely dependent on the period of low temperature (LT). In this case, the magnitude of the dynamic response is already saturated, since the LT period (9.6 s) is sufficiently spent to adsorb a number of ethanol molecules on the 15Pd/ γ -Al₂O₃ surface, but the magnitude of the general response (ΔV_{MAX}) for an LT period of 0.6 s (*ca.* 1.25 V) is about half of that for an LT period of 9.6 s (*ca.* 2.30 V).⁵⁹

This type of sensor shows dynamic sensor-signal profiles that are also specific to other VOCs (e.g., various kinds of alcohols,⁵⁸⁻⁶² formaldehyde,^{62,63} acetaldehyde,⁶² acetone,^{58,59,62} diethyl carbonate,^{58,59} acetic acid,^{58,59} *n*-hexane,⁶² some kinds of aromatic compounds,^{58,59,64,65} total VOCs,⁶² and so on), and this sensing behavior is the origin of highly sensitive responses to VOCs.

3 Early Stage of Study on Adsorption/Combustion-type Gas Sensors—Possibility of Highly Sensitive and Selective Sensing to Various VOCs

The shape of the dynamic sensor-signal profiles of the adsorption/combustion-type gas sensors is considerably dependent on the kinds of VOCs. The sensor-signal profiles of the 15Pd/ γ -Al₂O₃ sensor to eight kinds of alcohols with pulse-driven heating (T_H , 350°C for 0.2 s; T_L , RT for 9.8 s) are shown in Fig. 3(a).⁶¹ It is obvious that the dynamic profiles, especially the specific rising behavior just after the pulse heating, are quite different from each other, though the maximum peaks (ΔV_{MAX}) to all alcohols are observed within about 40 ms after heater-on. These differences probably result from differences of the adsorption state and the catalytic oxidation behavior of these alcohols on the catalyst surface. The differentiation of these dynamic sensor-signal profiles with respect of the pulse heating time makes the different characteristics clearer, as shown in Fig. 3(b),⁶¹ and the behavior is simply explained in Sect. S2 of

Fig. 3 (a) General and (b) differential sensor-signal profiles of $15\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ sensor to 8 kinds of alcohol with pulse-driven heating (T_{H} , 350°C for 0.2 s; T_{L} , RT for 9.8 s). Reproduced with permission from Ref. 61.

the electronic Supporting Information. Some features in these differential sensor-signal profiles to alcohol are summarized as below. First, the $15\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ sensor shows significantly different profiles to all the primary alcohols. Except for methanol, the differential peaks appeared later with an increase in the number of carbon atoms involved in their molecules. Second, the shape of differential sensor-signal profiles to secondary alcohols, 2propanol and 2butanol, resembles each other, though the first two sharp peaks are at clearly different positions. And third, the differential sensor-signal profiles to methanol, 2propanol, 2butanol, isobutanol and *tert*-butanol exhibited a similarly shaped peak at 16 – 20 ms, which may be ascribed to the combustion of methyl groups. The reasons for these features are not well recognized yet, but these differential sensor-signal profiles, depending on the kinds of alcohols, probably reflect the difference in the molecular structure among these alcohols. In any case, these results indicate that the kinds of these alcohols can be easily discriminated by accurate analysis of the differential profiles of this sensor.

The $15\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ sensor can also sensitively detect a quite low concentration of toluene (10 ppb at least) and show a linear

relationship between logarithmic ΔV_{MAX} and the toluene concentration in the range of 10 – 1000 ppb, when the sensor is operated with pulse-driven heating (T_{H} , 450°C for 0.4 s) after maintaining at a low temperature (T_{L}) of 200°C for 17.6 s.⁶² The important factors for the large response are to set T_{L} at higher temperature (RT $\rightarrow 200^\circ\text{C}$) in order to reduce the number of water molecules adsorbed on the catalyst surface and to enlarge the T_{L} -temperature period (9.6 s $\rightarrow$ 17.6 s) in order to sufficiently adsorb a large number of toluene molecules on the $15\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ surface. In addition, indoor field tests of the $15\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ sensor were conducted in new residential houses, at which there were 44 kinds of VOCs (e.g., aromatic series (benzene, toluene, xylene, and so on), hydrocarbons (hexane, heptane, and so on), some kinds of ketones, aldehydes, and so on).⁶² All gaseous components in indoor air were trapped on an active carbon adsorbent, and then the thermally desorbed VOCs, as shown above, were qualitatively and quantitatively analyzed also by a gas chromatograph/mass spectrometer (GC/MS) and a gas chromatograph/flame ion detector (GC/FID) for a comparison. The obtained results show that the operation of the $15\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ sensor with pulse-driven heating (T_{H} , 450°C for 0.4 s; T_{L} , 200°C for 17.6 s) allows for determinations of the total amount of all the VOCs, which were generally comparable to those quantitated by GC/MS and GC/FID.

The loading of Pt nanoparticles onto the $\gamma\text{-Al}_2\text{O}_3$ and the adoption of double-step pulse heating (1st T_{H} (combustion stage), 200°C for 0.4 s; 2nd T_{H} (heat-cleaning stage), 400°C for a few seconds; T_{L} , 200°C for 20 s) effectively enhanced the magnitude of the formaldehyde response.⁶³ The $15\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ sensor showed a relatively large dynamic response to formaldehyde and a small dynamic response to both toluene and styrene at T_{H} of 200°C , while the sensor-signal behavior indicated that three VOCs burned out on the $15\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ surface at T_{H} of 400°C . Thus, 1st T_{H} as a combustion stage and 2nd T_{H} as a heat-cleaning stage were determined to be 200 and 400°C , respectively, and this temperature-modulation setting largely improved the formaldehyde selectivity against toluene and styrene and the magnitude of the formaldehyde response (detection limit of below 40 ppb, which was half of the guideline for the indoor air quality in Japan). On the other hand, Ozawa *et al.* attempted to detect VOCs decomposed from an early stage fire by the $15\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ sensor; and then they showed that the sensor was able to largely detect furfural and 5methyl-2-furaldehyde, which had an aldehyde group in their molecular structures, under pulse-heating operation (T_{H} , 400°C for 0.4 s; T_{L} , RT for 9.6 s).^{64,65} As mentioned above, the adsorption/combustion-type gas sensors have great potential to detect various kinds of VOCs sensitively and selectively, and thus they can be practically applied in various fields that require ultratrace VOC detection.

4 Material Design of Adsorption/Combustion-type Gas Sensors and Clarification of the VOC-sensing Mechanism

Various advantages and characteristics of adsorption/combustion-type gas sensors were discussed in the last section, by using the representative $15\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ sensor ($15\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ sensor only for formaldehyde detection), while our recent design trends of the sensor materials to improve their VOC-sensing properties are mentioned in this section.

The increase in the specific surface area (SSA) of the support material of catalysts for the sensing film is quite important for increasing the amount of adsorbed VOCs at T_{L} as well as

enhancing the catalytic oxidation activity of VOCs at T_H . γ - Al_2O_3 is thus commonly used as a support material of catalysts for the sensing film, but mesoporous silicas (mp- SiO_2) were also attractive as alternatives of γ - Al_2O_3 , because of their quite large SSAs. Sasahara *et al.* prepared the mp- SiO_2 powders from tetraethyl orthosilicate (TEOS) by utilizing a self-assembly of *n*-cetylpyridinium chloride as a mesopore template, and also investigated the effects of their SSAs on the magnitude of the toluene responses of 15Pt/mp- SiO_2 sensors, together with that of the 15Pd/ γ - Al_2O_3 sensor (SSA of common 15Pd/ γ - Al_2O_3 powder we used: $146 \text{ m}^2 \text{ g}^{-1}$).⁶⁷ Actually, they succeeded to prepare three kinds of 15Pt/mp- SiO_2 powders (SSA: 673 – 897 $\text{m}^2 \text{ g}^{-1}$, depending on the preparation condition) and clarified that the amount of toluene adsorbed and the magnitude of integrated dynamic response (IDR) to 100 ppm toluene monotonically increased with an increase in SSA (T_H , 400°C for 0.4 s; T_L , RT for 9.6 s). Unfortunately, the toluene sensitivity (the slope of the relationship between the logarithmic IDR and the logarithmic toluene concentration, in this case) of these 15Pt/mp- SiO_2 sensors was lower than that of the 15Pd/ γ - Al_2O_3 sensor. This is probably because of the relatively low thermal conductivity, and thus it seems to be a little difficult for these 15Pt/mp- SiO_2 sensors to detect the quite low concentration of toluene (*e.g.*, < 1 ppb). However, we presently have a great expectation that the utilization of mp- SiO_2 powders as only adsorbents of VOCs to the sensing material has a vital role in improving the VOC-sensing properties, since large amounts of VOCs can adsorb on the surfaces of mp- SiO_2 powders.

The microstructure of γ - Al_2O_3 powders as the sensing material was also optimized by choosing their source reagents (mainly, some kinds of aluminum alkoxides) and additives as a mesopore template (general surfactants, block copolymers, or long-chain saturated carboxylic acids) and controlling the preparation conditions.^{67,68} After attempting to prepare γ - Al_2O_3 powders by using a number of the materials under various conditions, we have presently adopted the following preparation procedure. An appropriate amount of aluminum secondary butoxide ($\text{Al}(\text{sec-OC}_4\text{H}_9)_3$) as an Al source and behenic acid ($\text{C}_{21}\text{H}_{43}\text{COOH}$) as a template are firstly mixed with 1-propanol. After a given amount of pure water is added to the solution, it is stirred at RT for 45 h to hydrolyze $\text{Al}(\text{sec-OC}_4\text{H}_9)_3$. After the solution is treated at 110°C for 1 h by a solvothermal method, white precipitates obtained are centrifuged at 2500 rpm for 10 min, washed with ethanol and then fired at 700°C for 2 h in air. The SSA of the γ - Al_2O_3 powder obtained is quite large (typically, 230 – 260 $\text{m}^2 \text{ g}^{-1}$), and the mesoporous structure (estimated pore size of *ca.* 6 nm) is well developed among small crystallites (4.0 – 4.5 nm in diameter, which are estimated by XRD and TEM).^{69,70} The most suitable γ - Al_2O_3 powder obtained in this method (hereafter, referred to as “mp- Al_2O_3 powder”), was used as a support material of catalysts for the sensing film, in the following overall discussion. Actually, the 6 wt% Pd-loaded mp- Al_2O_3 (6Pd/mp- Al_2O_3) sensor shows a larger dynamic ethanol response than that of the 15Pd/ γ - Al_2O_3 sensor, even though the amount of Pd loaded onto the mp- Al_2O_3 surface was smaller than that onto the γ - Al_2O_3 surface.⁶⁸

The compositional and microstructural optimizations of noble-metal nanoparticles loaded on the alumina surface for the sensing film have significant impacts on the VOC-sensing properties of the adsorption/combustion-type gas sensors. Among some combinations of Pd with other noble metal, the co-loading of Pd with Au was the most effective in improving the dynamic response of the sensors.⁶⁸ Figure 4(a) shows variations in both the general dynamic response (ΔV_{MAX}) of the n_1 wt% Pd and n_2 wt% Au co-loaded mp- Al_2O_3 (n_1 Pd- n_2 Au/

Fig. 4 (a) Variations in ΔV_{MAX} of n_1 Pd- n_2 Au/mp- Al_2O_3 sensors ($n_1 + n_2 = 10$ [wt%]) to 1000 ppm ethanol and specific surface area (SSA) of n_1 Pd- n_2 Au/mp- Al_2O_3 powders with the amount of Au loaded, n_2 , and (b) variations in ΔV_{MAX} of 8Pd-2Au/mp- $\text{Al}_2\text{O}_3(x)/\alpha$ - $\text{Al}_2\text{O}_3(y)$ sensors to 100 ppm ethanol and SSA of 8Pd-2Au/mp- $\text{Al}_2\text{O}_3(x)/\alpha$ - $\text{Al}_2\text{O}_3(y)$ powders with the amount of α - Al_2O_3 mixing, y (T_H : 400°C for 0.4 s, T_L : RT for 9.6 s, as condition of pulse-driven heating). Reproduced with permission from Ref. 69.

mp- Al_2O_3 , $n_1 + n_2 = 10$ [wt%]) sensors to 1000 ppm ethanol, which were operated with pulse-driven heating (T_H , 400°C for 0.4 s; T_L , RT for 9.6 s), and SSA of n_1 Pd- n_2 Au/mp- Al_2O_3 powders with the amount of Au loaded.⁶⁹ The Pd and Au nanoparticles were loaded by a general impregnation technique, followed by annealing at 350°C for 1 h under a hydrogen atmosphere. The ΔV_{MAX} to 1000 ppm ethanol is drastically dependent on the ratio of Au to Pd, even though their SSAs are hardly dependent on the ratio of Au to Pd, and the 8Pd-2Au/mp- Al_2O_3 sensor showed the largest response among them. Generally, the catalytic activity decreases with an increase in the amount of Au, but recent experimental results show also that the small amount of Au loading may enhance the oxidation activity. On the other hand, the thermal conductivity of the film generally increases with an increase in the amount of Au. We now understand that this tendency originates from their synergistic effects. In addition, a given amount of the Pd and Au loaded on the as-prepared n_1 Pd- n_2 Au/mp- Al_2O_3 powder was alloyed at various ratios, just after annealing at 350°C for 1 h under a hydrogen atmosphere,⁶⁹ while most of the Pd component was oxidized and dispersively loaded on the mp- Al_2O_3 surface, and most of the Au component was agglomerated as a metal after firing at 700°C for 2 h (*i.e.*, after the sensor fabrication).⁷⁰ These microstructural features should have a great impact on the oxidation activity of ethanol over n_1 Pd- n_2 Au/mp- Al_2O_3 powders and their thermal conductivity. The effect of the mixing of a thermally conductive material with 8Pd-2Au/mp- Al_2O_3 powder on the magnitude of the dynamic ethanol response was also investigated, as shown in Fig. 4(b). Here, α - Al_2O_3 was selected as the thermally conductive material, because α - Al_2O_3 , which is

Fig. 5 TEM photograph of 0.8Pd/0.2Au nanoparticles prepared by utilizing a sonochemical reduction technique, together with their particle distribution measured by dynamic light scattering (inlet). Reproduced with permission from Ref. 70.

thermally stable, shows high crystallinity, a large crystallite size, and a small SSA (*ca.* 9 m² g⁻¹), compared with those of mp-(γ)-Al₂O₃. The α -Al₂O₃ powder was mixed with the mp-Al₂O₃ powder before loading Pd and Au on these powders by impregnation, and the sensors fabricated were denoted as 8Pd-2Au/mp-Al₂O₃(*x*)/ α -Al₂O₃(*y*) sensors (*x* and *y*: the mixing amount of mp-Al₂O₃ and α -Al₂O₃, respectively (wt%), *x* + *y* = 100). The 8Pd-2Au/mp-Al₂O₃(*x*)/ α -Al₂O₃(*y*) sensors showed the largest response to 100 ppm ethanol at *y* = 10 wt%, even though the SSA monotonically decreased with an increase in the amount of α -Al₂O₃ mixing. The increase in the ΔV_{MAX} at *y* ≤ 10 wt%, irrespective of the decrease in SSA, originates from the improvement of the thermal conductivity of the sensing film, due to the mixing of α -Al₂O₃, while the decrease in the ΔV_{MAX} at *y* ≥ 10 wt% is undoubtedly ascribed to the decrease in SSA and thus the reduction in the amount of ethanol adsorbed on the oxide surface.

On the basis of these findings, we synthesized monodispersed core(Au)/shell(Pd) (*n*₁Pd/*n*₂Au) nanoparticles by a sonochemical reduction technique, and loaded them on the mp-Al₂O₃ surface, to further improve the VOC-sensing properties.⁷⁰ The important key to the synthesis of monodispersed *n*₁Pd/*n*₂Au nanoparticles is to irradiate strong ultrasonic waves (200 kHz, 6 W cm⁻²) into the precursor aqueous solution containing an appropriate amount of PdCl₂, HAuCl₄, and polyethylene glycol monostearate (C₁₇H₃₅CO(CH₂CH₂O)₄₀OH) as a reductant, in a container filled with argon at 20°C. This treatment reduced Au³⁺ to produce Au nanoparticles at first, and Pd, which was subsequently reduced, was coated around the Au nanoparticles.⁷⁷ Figure 5 shows a TEM photograph and a particle distribution of 0.8Pd/0.2Au nanoparticles. The average particle size estimated from the TEM photograph was about 6.0 nm, while the particle size measured by dynamic light scattering (DLS) was about 12.7 nm. Since the 0.8Pd/0.2Au nanoparticles were covered with a large number of polyethylene glycol monostearate molecules in the aqueous solution, the particle size measured by DLS contained the size of these molecules. In addition, we confirmed that the ratio of Pd to Au (Pd:Au, wt%) in the 0.8Pd/0.2Au nanoparticles, which was measured by energy dispersive spectroscopy (EDS) equipped with TEM, 77:23, was comparable to that in the precursor solution (Pd:Au = 80:20 in wt%, composition ratio for preparation). Unfortunately, the core/shell structure of the nanoparticles cannot be confirmed by TEM, but no plasmon

Fig. 6 Sensor-signal profiles of 0.8Pd/0.2Au/mp-Al₂O₃ and 0.8Pd-0.2Au/mp-Al₂O₃ sensors (the total loading amount of Pd and Au: 1.0 wt%) to 1000 ppm ethanol in air at the pulse-driven heating (*T*_H, 250–450°C for 0.4 s; *T*_L, RT for 9.6 s), together with those of a 8Pd-2Au/mp-Al₂O₃ sensor (the total loading amount of Pd and Au: 10 wt%). Reproduced with permission from Ref. 70.

adsorption derived from Au (around 530 nm) was confirmed from the 0.8Pd/0.2Au nanoparticles. This result strongly indicated that Au nanoparticles were mostly covered with a Pd layer and thus the Pd layer only contributed to the light absorption and/or scattering (*i.e.*, 0.8Pd/0.2Au nanoparticles were successfully formed in the solution). The appropriate amount of the mp-Al₂O₃ powders obtained was added into the colloidal aqueous solution and the pH was adjusted to about 4, to adsorb *n*₁Pd/*n*₂Au nanoparticles on the mp-Al₂O₃ surface (zeta potential of *n*₁Pd/*n*₂Au and mp-Al₂O₃: *ca.* +28 mV and *ca.* −8 mV, respectively, at pH 4). The obtained powders were denoted as *n*₁Pd/*n*₂Au/mp-Al₂O₃ (*n*₁:*n*₂ = 4:1, *n*₁: 0.8 (wt%), *n*₂: 0.2 (wt%), mainly in this article).

TEM photographs and SSAs of 0.8Pd/0.2Au/mp-Al₂O₃ and 0.8Pd-0.2Au/mp-Al₂O₃ powders before and after firing at 700°C for 2 h in air are shown in Fig. S2 of the electronic Supporting Information, and the detailed explanation is given in Sect. S3 of the electronic supporting information. On the basis of the discussion, the highly-dispersive loading of Pd-based ultranano-particles and relatively large Au particles was confirmed on the 0.8Pd/0.2Au/mp-Al₂O₃ surface, which was really expected to improve the catalytic activity and thermal conductivity of the sensing film, respectively. Figure 6 shows sensor-signal profiles of 0.8Pd/0.2Au/mp-Al₂O₃ and 0.8Pd-0.2Au/mp-Al₂O₃ sensors (the total loading amount of Pd and Au: 1.0 wt%) to 1000 ppm

ethanol in air at the pulse-driven heating (T_H , 250–450°C for 0.4 s; T_L , RT for 9.6 s), together with those of a 8Pd2Au/mp-Al₂O₃ sensor (the total loading amount of Pd and Au: 10 wt%). When these sensors were pulse-heated to 450°C, the 8Pd-2Au/mp-Al₂O₃ sensor showed the largest ΔV_{MAX} to ethanol among them and the response speed of the 8Pd2Au/mp-Al₂O₃ sensor was much faster than those of other sensors, because the large amount of Au and Pd loaded on mp-Al₂O₃ effectively burned ethanol molecules adsorbed on the surface and the heat effectively conducted to the Pt electrode. In addition, ΔV_{MAX} and the response speed of the 0.8Pd/0.2Au/mp-Al₂O₃ sensor were comparable to those of the 0.8Pd-0.2Au/mp-Al₂O₃ sensor. However, the ΔV_{MAX} of the 0.8Pd-0.2Au/mp-Al₂O₃ and 8Pd-2Au/mp-Al₂O₃ sensors drastically decreased with a decrease in the pulse-heating temperatures, while the 0.8Pd/0.2Au/mp-Al₂O₃ sensor showed a large ethanol response even at 350°C, and thus the ΔV_{MAX} of the 0.8Pd/0.2Au/mp-Al₂O₃ sensor was much larger than those of the 0.8Pd-0.2Au/mp-Al₂O₃ and 8Pd-2Au/mp-Al₂O₃ sensors at 350°C. On the other hand, the ΔV_{MAX} of all the sensors was extremely low at a pulse-heating temperature of 250°C, but only the 0.8Pd/0.2Au/mp-Al₂O₃ sensor showed a relatively large response sufficient to detect 1000 ppm ethanol. Figure 7(a) gives the representative sensor-signal profiles of the 0.4Pd/0.1Au/mp-Al₂O₃ sensor (the total loading amount of Pd and Au: 0.5 wt%) to 10–1000 ppm ethanol, toluene and *n*-hexane in air with the pulse-driven heating (T_H , 450°C for 0.4 s; T_L , RT for 9.6 s). The ΔV_{MAX} to these VOCs decreased and the shape of the dynamic profiles broadened with a decrease in the concentration, but the sensor certainly detected 10 ppm target gases (ca. 35 mV for ethanol, ca. 22 mV for toluene, and ca. 11 mV for *n*-hexane), irrespective of the quite small amount of Pd and Au loaded. Variations in logarithmic ΔV_{MAX} to ethanol, toluene and *n*-hexane of both 0.4Pd/0.1Au/mp-Al₂O₃ and 0.4Pd-0.1Au/mp-Al₂O₃ sensors with concentration of the three target gases in air (T_H , 450°C for 0.4 s; T_L , RT for 9.6 s) are shown in Fig. 7(b). The sensitivity (the slope of the relationship between logarithmic ΔV_{MAX} and logarithmic concentration) to ethanol was comparable to that to toluene, and the sensitivities to these VOCs were much larger than that to *n*-hexane, as for the 0.4Pd/0.1Au/mp-Al₂O₃ sensor. In addition, the ΔV_{MAX} values of the 0.4Pd/0.1Au/mp-Al₂O₃ sensor to these VOCs were larger than that of the 0.4Pd-0.1Au/mp-Al₂O₃ sensor. These results also indicated that the highly dispersive loading of Pt and Au on the mp-Al₂O₃ powder showed excellent sensitivity as well as a large response to these target gases, in comparison with those of the 0.4Pd-0.1Au/mp-Al₂O₃ sensor.

The loading of only a specific metal oxide (MO) on the mp-Al₂O₃ powder promotes the catalytic oxidation activity of VOCs over the mp-Al₂O₃ powder, but the effectiveness was extremely limited to have the excellent VOCsensing properties of MOloaded mp-Al₂O₃ sensor.^{75,76} However, the co-loading of a noble metal with MO on the mp-Al₂O₃ powder effectively enhanced the VOC-sensing properties of noble metal-loaded mp-Al₂O₃ sensors.^{71–76} In the article, the sensing properties of typical *n* wt% Pt and *m* wt% MO co-loaded mp-Al₂O₃ (*n*Pt/*m*MO/mp-Al₂O₃) sensors to VOCs are discussed. The *n*Pt/*m*MO/mp-Al₂O₃ powders were prepared through the general loading of MO by an impregnation technique using a constituent metal nitrate aqueous solution and subsequent Pt loading by a sonochemical reduction technique using a chloroplatinic acid aqueous solution, and the high dispersibility of Pt and MO on the mp-Al₂O₃ surface was confirmed by TEM. Among all of the powders tested, the co-loading of Pt with CeO₂ on the mp-Al₂O₃ powder was the most effective in improving the VOC-sensing properties. The sensor-signal profiles of the typical

Fig. 7 (a) Sensor-signal profiles of 0.4Pd/0.1Au/mp-Al₂O₃ sensor (the total loading amount of Pd and Au: 0.5 wt%) to 10, 100 and 1000 ppm ethanol, toluene and *n*-hexane and (b) dependences of logarithmic ΔV_{MAX} of both 0.4Pd/0.1Au/mp-Al₂O₃ and 0.4Pd-0.1Au/mp-Al₂O₃ sensors on concentration of ethanol, toluene and *n*-hexane in air (T_H , 450°C for 0.4 s; T_L , RT for 9.6 s, as condition of pulse-driven heating). Reproduced with permission from Ref. 70.

1.0Pt/10CeO₂/mp-Al₂O₃ sensor to 6 kinds of VOCs (ethanol, acetone, ethyl acetates, benzene, toluene, and *o*-xylene) with pulse-driven heating (T_H , 450°C for 0.4 s; T_L , RT, 100°C, or 150°C for 9.6 s) are shown in Fig. 8. The magnitude of the response to the VOCs and the shape of the sensor-signal profiles were largely dependent on the kind of VOCs. The 1.0Pt/10CeO₂/mp-Al₂O₃ sensor showed the largest ΔV_{MAX} to ethanol among all of the VOCs at every T_L . The shape of the sensor-signal profiles of the sensor to ethanol was almost independent of T_L , but the magnitude of ΔV_{MAX} gradually decreased with an increase in T_L . The sensor showed a relatively large ΔV_{MAX} , even to acetone, but the magnitude of ΔV_{MAX} to acetone was less than half of that

Fig. 8 Sensor-signal profiles of 1.0Pt/10CeO₂/mp-Al₂O₃ sensor to 6 kinds of VOCs (1000 ppm) with pulse-driven heating (T_H , 450°C for 0.4 s; T_L , RT, 100°C, or 150°C for 9.6 s). Reproduced with permission from Ref. 71.

to ethanol at T_L of RT. In addition, the rise in T_L from RT to 100°C largely reduced the ΔV_{MAX} to acetone almost by half and accelerated the dynamic response speed; however, the magnitude of ΔV_{MAX} to acetone and the dynamic response speed at T_L of 100°C were comparable to those at T_L of 150°C. The response behavior to ethyl acetate was very complicated in comparison with those to ethanol and acetone, especially at lower T_L . Namely, the response to acetone at T_L of RT was abruptly negative-shifted as soon as the pulse heating started, and subsequently it was reversely positive-shifted within *ca.* 10 ms. The negative shift probably arises from endothermic reactions, such as hydrolysis and/or desorption of ethyl acetate, and the negative shift of the response was almost not observed at T_L of 100 and 150°C. In addition, the magnitude of ΔV_{MAX} to ethyl acetate increased with a rise in T_L , and the dynamic response peaks at T_L of RT and 150°C were quite broader than that at T_L of 100°C. These broad response peaks may arise from the intermittent adsorption and subsequent oxidation (exothermic processes at T_H) of those partially-decomposed species which were formed particularly at T_L .

On the other hand, the dynamic response behaviors to benzene and toluene in their sensor-signal profiles were obscure at every T_L , as the dynamic response by the flash combustion was not sufficiently large, compared with the static response by general

catalytic combustion. Thus, the ΔV_{MAX} to benzene and toluene was also largely dependent on the magnitude of the static response at each T_L . The dynamic response to *o*-xylene was also much smaller than the static response at T_L of RT, but its dynamic response time (*ca.* 12 ms) was quite short. The ΔV_{MAX} to *o*-xylene obviously increased with a rise in T_L , since both the dynamic and static responses increased with a rise in T_L . However, the enlarged broad dynamic response that was observed at T_L of 100 and 150°C (response time, around 100 ms) seems to be different from the small dynamic response, which was confirmed even at T_L of RT (response time, *ca.* 20 ms).

As mentioned above, the adsorption/combustion gas sensors showed that the magnitude of ΔV_{MAX} and the signal shapes were drastically dependent on the kinds of VOCs and T_L , *i.e.*, temperature for the adsorption as well as the partial decomposition of these VOCs. Therefore, if the pulse-driven heating with successively changing T_L , such as " T_L [RT] $\rightarrow$ T_L [450°C] $\rightarrow$ T_L [100°C] $\rightarrow$ T_L [450°C] $\rightarrow$ T_L [150°C] $\rightarrow$ T_L [450°C] $\rightarrow$ T_L [RT] $\rightarrow$...", could be performed with strictly controlling temperatures and accurately analyzing these sensor-signal profiles by an adequate computing technique, we would believe that enhanced selective VOC-sensing would be realized by the sensors. In addition, differentiation of these sensor-signal profiles is also quite effective in improving the VOC selectivity.

Figure S3 of the electronic Supporting Information shows the differential sensor-signal profiles of the $1.0\text{Pt}/10\text{CeO}_2/\text{mp-Al}_2\text{O}_3$ sensor to these VOCs at T_L of 100°C . For example, the differential sensor-signal profile to ethanol consists of first medium differential dynamic response with a quite fast differential dynamic response time (within *ca.* 10 ms) and subsequent large differential dynamic response with slightly-slower differential dynamic response time (after *ca.* 10 ms), while these differential dynamic responses to acetone are almost inseparable. The differential sensor-signal profile to ethyl acetate only shifted rapidly (within *ca.* 5 ms) to a negative direction just after the sensor was pulse-heated up to 450°C , probably due to endothermic reactions, such as hydrolysis and/or desorption of ethyl acetate-based adsorbates even at T_L of 100°C . The differential sensor-signal profiles of three aromatic compounds were mainly comprised of both a sharp differential dynamic response with a quite fast response speed and a broad differential dynamic response with a slow response speed. The magnitude of the sharp differential dynamic response increased with an increase in the number of methyl groups in these molecules, while the response speed of the broad differential dynamic response decelerated with an increase in the number of methyl groups. We can clearly recognize the slight differences among the sensor-signal profiles to the kinds of VOCs, through differentiation analysis by such a simple signal processing, and thus we now expect that the combination of successive pulse-driven heating with changing T_L and the differential signal processing will drastically improve the VOC selectivity.

Furthermore, the ratio of the integrated dynamic response (*IDR*) and the integrated static response (*ISR*) [*IDR/ISR*] is also largely dependent on the kinds of VOCs and their concentrations in the target gas. Figure S4 of the electronic Supporting Information shows sensor-signal profiles of the $1.0\text{Pt}/m\text{CeO}_2/\text{mp-Al}_2\text{O}_3$ sensors to three kinds of VOCs (ethanol, ethyl acetate and *o*-xylene, concentration: 10, 100 and 1000 ppm), together with their *IDR/ISR* values. These sensors showed large dynamic responses to these 1000 ppm VOCs, while their static responses to their 1000 ppm VOCs were also relatively large. Thus, their *IDR/ISR* values were very small. On the other hand, these static responses largely reduced with a decrease in the VOC concentration, compared with the dynamic response, and thus the *IDR/ISR* values to 10 ppm VOCs were much larger than those to 1000 ppm VOCs. Considering that the dynamic and static responses originate from the adsorption/combustion and the general catalytic combustion, respectively, these results also showed that the adsorption/combustion-type gas sensors have a very great potential to detect a quite-low concentration of VOCs.

The adsorbability and reactivity of VOCs on the surface of the sensor materials are the most important factors in determining the VOC-sensing properties of the adsorption/combustion-type gas sensors. Therefore, the catalytic oxidation behavior, temperature-programmed desorption (TPD) and oxidation (TPO), and adsorption breakthrough curves of various VOCs on the sensor-material surface were estimated in conjunction with measuring their sensor-signal profiles to their VOCs. TPD spectra of ethanol pre-adsorbed on the $15\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ surface at RT for 30 min showed that the relatively large amount of CO_2 generated during an increase in temperature over the wide range of $100 - 500^\circ\text{C}$ under He flowing ($10^\circ\text{C}/\text{min}$), probably due to the reaction of the adsorbed ethanol molecules with oxygen adsorbates on the surface.⁵⁹ In addition, the amount of CO_2 molecules generated in the TPD is comparatively correlated with the magnitude of dynamic responses (*i.e.*, ΔV_{MAX} and *IDR*) of the sensor-signal profiles of the $15\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ sensor to ethanol with pulse-driven heating (T_H , 450°C for 0.4 s; T_L , RT

for 9.6 s). This result provides a significant finding that both increasing the amount of ethanol adsorbed and enhancing the catalytic activity of ethanol on the sensor materials are indispensable for improving the magnitude of the dynamic responses. Furthermore, the TPO spectra of some kinds of VOCs (ethanol, 1butanol, and 2butanol) pre-adsorbed on $15\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ powders at RT for 1 h showed that the amount of CO_2 generated with an increase in temperature under air flowing ($2^\circ\text{C}/\text{min}$) tended to increase the number of carbon atoms involved in their molecules, and the responses of the $15\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ sensor to these gases with pulse-driven heating (T_H , 450°C for 0.4 s; T_L , RT for 9.6 s) are also roughly dependent on the amount of CO_2 generated in the TPO.⁷² On the other hand, the amount of VOCs (ethanol, acetone, ethyl acetates, benzene, toluene, and *o*-xylene) adsorbed on the $1.0\text{Pt}/10\text{CeO}_2/\text{mp-Al}_2\text{O}_3$ surface was actually estimated by measuring the adsorption breakthrough curves of these VOCs at RT, and the *IDR* values of the $1.0\text{Pt}/10\text{CeO}_2/\text{mp-Al}_2\text{O}_3$ sensor to these VOCs were largely dependent on the amount of VOCs adsorbed on the surface, compared with their magnitude of static response (*i.e.*, *ISR* values).⁷¹ On the basis of these findings, the catalytic oxidation properties of ethanol, ethyl acetate, and toluene over unloaded $\text{mp-Al}_2\text{O}_3$, $1.0\text{Pt}/\text{mp-Al}_2\text{O}_3$, $10\text{MO}/\text{mp-Al}_2\text{O}_3$, $1.0\text{Pt}/10\text{MO}/\text{mp-Al}_2\text{O}_3$ (MO: CeO_2 or Bi_2O_3) were recently estimated in detail, together with their TPD and TPO properties (pre-adsorption condition of these VOCs: 150°C for 1 h).^{73,74} Their results indicate quite considerable findings that the amount of these VOCs and the related intermediates adsorbed (and desorbed), the rate of reaction of these VOCs with oxygen adsorbates, and thermal conductivity of the sensor materials have a great impact on the sensor-signal profiles of the $1.0\text{Pt}/10\text{MO}/\text{mp-Al}_2\text{O}_3$ sensors. On the basis of these findings, the compositional and microstructural controls of the $n\text{Pt}/m\text{MO}/\text{mp-Al}_2\text{O}_3$ sensors (mainly, MO: CeO_2 or Bi_2O_3) have been recently attempted, in order to improve their sensing properties to toluene⁷⁵ and a series of alcohol.⁷⁶

5 Conclusion

Adsorption/combustion-type gas sensors, which are dynamically operated with a mode of pulse-driven temperature modulation, are a quite powerful candidate to detect various kinds of VOCs sensitively and selectively, as mentioned above. These sensors can certainly detect 10 ppb toluene and 40 ppb formaldehyde by optimizing the dynamic temperature-modulation conditions of $15\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ ⁶² and $15\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ sensor⁶³ sensors, respectively. In addition, some material-design approach to obtain excellent VOC-sensing materials for the sensors, the use of mesoporous silicas as a support of the sensing material,⁶⁶ the co-loading of Pd and Au (*esp.*, as core(Au)/shell(Pd) nanoparticles),⁶⁸⁻⁷⁰ and the co-loading of a metal oxide with a noble metal on the oxide surface,^{71,73-76} was quite effective in improving the VOC-sensitivity and selectivity. On the other hand, recent semiconductor-type gas sensors can sensitively detect VOCs by controlling the sensing materials both compositionally and microstructurally⁷⁻¹⁶ as well as by operating with specific dynamic temperature modulation.⁵²⁻⁵⁶ Further, other types of attractive VOC sensors have also been developed as devices for leading electronic nose systems.¹⁷⁻²⁷ In addition, the use of preconcentrators of VOCs with gas sensors also enhanced both the sensitivity and selectivity.²⁸⁻³³ Hereafter, it is indispensable for accelerating the development of adsorption/combustion-type gas sensors capable of detecting further small concentrations (*i.e.*, ppt or less) of VOCs, based on their VOC-sensing

mechanism, which is recently being elucidated.⁷²⁻⁷⁴ These achievements will provide adsorption/combustion-type gas sensors with excellent VOC-sensing performance that are far superior to other sensors.

6 Supporting Information

This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

7 References

1. B. Guieysse, C. Hort, V. Platel, R. Munoz, M. Ondarts, and S. Revah, *Biotechnol. Adv.*, **2008**, 26, 398.
2. T. Petry, D. Vitale, F. J. Joachim, B. Smith, L. Cruse, R. Mascarenhas, S. Schneider, and M. Singal, *Regul. Toxicol. Pharmacol.*, **2014**, 69, 55.
3. K. S. Ramirez, C. L. Lauber, and H. Fierer, *Biogeochemistry*, **2010**, 99, 97.
4. A. Araki, T. Kawai, Y. Eitaki, A. Kanazawa, K. Morimoto, K. Nakayama, E. Shibata, M. Tanaka, T. Takigawa, T. Yoshimura, H. Chikara, Y. Saijo, and R. Kishi, *Sci. Total Environ.*, **2010**, 408, 2208.
5. Y. Broza and H. Haick, *Nanomedicine*, **2013**, 8, 785.
6. G. W. Hunter, R. A. Dweik, D. B. Makel, C. C. Grigsby, R. S. Mayes, and C. E. Davis, *Electrochem. Soc. Interface*, **2016**, 25, 63.
7. T.-H. Kim, S.-Y. Jeong, Y.-K. Moon, and J.-H. Lee, *Sens. Actuators, B*, **2019**, 301, 127104.
8. B.-Y. Kim, J.-W. Yoon, J.-K. Kim, Y.-C. Kang, and J.-H. Lee, *ACS Appl. Mater. Interfaces*, **2018**, 10, 16605.
9. J.-W. Yoon, Y. J. Hong, G. D. Park, S.-J. Hwang, F. Abdel-Hady, A. A. Wazzan, Y. C. Kang, and J.-H. Lee, *ACS Appl. Mater. Interfaces*, **2015**, 7, 7717.
10. A. T. Günter, N. A. Sievi, S. J. Theodore, T. Gulich, M. Kohler, and S. E. Pratsinis, *Anal. Chem.*, **2017**, 89, 10578.
11. K. Nakamura, Y. Hosokawa, Y. Morita, M. Nishitani, and Y. Sadaoka, *ECS Trans.*, **2016**, 75, 83.
12. I.-D. Kim, S.-J. Choi, S.-J. Kim, and J.-S. Jang, in “*Smart Sensors for Health and Environment Monitoring*”, ed. C.-M. Kyung, **2015**, Springer, Dordrecht, 19.
13. T. Itoh, D. Lee, T. Goto, T. Akamatsu, N. Izu, W. Shin, and T. Kusaga, *Sens. Mater.*, **2016**, 28, 1165.
14. Y. Masuda, T. Itoh, W. Shin, and K. Kato, *Sci. Rep.*, **2015**, 5, 10122.
15. Y. Shimizu, S. Kai, Y. Takao, T. Hyodo, and M. Egashira, *Sens. Actuators, B*, **2000**, 65, 349.
16. T. Ueda, T. Maeda, Z. Huang, K. Higuchi, K. Izawa, K. Kamada, T. Hyodo, and Y. Shimizu, *Sens. Actuators, B*, **2018**, 252, 268.
17. X. Hao, B. Wang, C. Mas, F. Liu, X. Yang, T. Liu, X. Liang, C. Yang, H. Zhu, and G. Lu, *Sens. Actuators, B*, **2018**, 255, 1173.
18. T. Ueda, H. Abe, K. Kamada, S. R. Bishop, H. L. Tuller, T. Hyodo, and Y. Shimizu, *Sens. Actuators, B*, **2017**, 252, 268.
19. Y. Tanaka, T. Sato, H. Ikeda, and N. Miura, *Sens. Actuators, B*, **2014**, 203, 899.
20. M. Mori, H. Nishimura, Y. Itagaki, Y. Sadaoka, and E. Traversa, *Sens. Actuators, B*, **2009**, 143, 56.
21. T. Sato, V. V. Plashnitsa, M. Utiyama, and N. Miura, *J. Electrochem. Soc.*, **2011**, 158, J175.
22. M. Mori, Y. Itagaki, Y. Sadaoka, S. Nakagawa, M. Kida, and T. Kojima, *Sens. Actuators, B*, **2014**, 191, 351.
23. N. Miura, Y. Yan, G. Lu, and N. Yamazoe, *Sens. Actuators, B*, **1996**, 34, 367.
24. K. Shiba, R. Tamura, T. Sugiyama, Y. Kameyama, K. Koda, E. Sakon, K. Minami, H. T. Ngo, G. Imamura, K. Tsuda, and G. Yoshikawa, *ACS Sens.*, **2018**, 3, 1592.
25. I. Osica, G. Imamura, K. Shiba, Q. Ji, L. K. Shrestha, J. P. Hill, K. J. Kurzydłowski, and G. Yoshikawa, *ACS Appl. Mater. Interfaces*, **2017**, 9, 9945.
26. K. Iitani, Y. Hayakawa, K. Toma, T. Arakawa, and K. Mitsubayashi, *Talanta*, **2019**, 197, 249.
27. M. Ye, P.-J. Chien, K. Toma, T. Arakawa, and K. Mitsubayashi, *Biosens. Bioelectron.*, **2015**, 73, 208.
28. M. Leidinger, M. Rieger, T. Sauerwald, C. Alépée, and A. Schütze, *Sens. Actuators, B*, **2016**, 236, 988.
29. H. Lahlow, X. Vilanova, and X. Correig, *Sens. Actuators, B*, **2013**, 176, 198.
30. K. Song and S.-K. Lee, *Sens. Actuators, B*, **2007**, 125, 173.
31. N. Oide, T. Ueda, K. Kamada, T. Hyodo, and Y. Shimizu, Abstracts of 55th Kyushu Area Joint Meeting of the Chemistry-Related Societies, Kitakyushu, Japan, **2018**, Abstract PC-1-043.
32. Y. Yamada, S. Hiyama, and T. Toyooka, *NTT DOCOMO Tech. J.*, **2015**, 17, 77.
33. Y. Yamada, S. Hiyama, T. Toyooka, S. Takeuchi, K. Itabashi, T. Okubo, and H. Tabata, *Anal. Chem.*, **2015**, 87, 7588.
34. W. M. Sears, K. Colbow, and F. Consadori, *Sens. Actuators*, **1989**, 19, 333.
35. W. M. Sears, K. Colbow, R. Slamka, and F. Consadori, *Sens. Actuators, B*, **1990**, 1, 62.
36. P. Romppainen, V. Lantto, and S. Leppävuori, *Sens. Actuators, B*, **1990**, 1, 73.
37. V. Lantto, P. Romppainen, T. S. Rantala, and S. Leppävuori, *Sens. Actuators, B*, **1991**, 4, 451.
38. V. Lantto and P. Romppainen, *Surf. Sci.*, **1987**, 192, 243.
39. S. Wlodek, K. Colvow, and F. Consadori, *Sens. Actuators, B*, **1991**, 3, 62.
40. S. Nakata, H. Nakamura, and K. Yoshikawa, *Sens. Actuators, B*, **1992**, 8, 187.
41. S. Nakata, S. Akakabe, M. Nakasuji, and K. Yoshikawa, *Anal. Chem.*, **1996**, 68, 2067.
42. Y. Kato, K. Yoshikawa, and M. Kitora, *Sens. Actuators, B*, **1997**, 40, 33.
43. K. Kato, Y. Kato, K. Takamatsu, T. Ueda, T. Nakahara, Y. Matsuura, and K. Yoshikawa, *Sens. Actuators, B*, **2000**, 71, 192.
44. S. Nakata, H. Okunishi, and Y. Nakashima, *Sens. Actuators, B*, **2006**, 119, 556.
45. Q. Wu and W. H. Ko, *Sens. Actuators, B*, **1990**, 1, 183.
46. A. Heilig, N. Bârsan, U. Weimar, M. Schweizer-Berberich, J. W. Gardner, and W. Göpel, *Sens. Actuators, B*, **1997**, 43, 45.
47. K. An Ngo, P. Lauque, and K. Aguir, *Sens. Actuators, B*, **2007**, 124, 209.
48. E. Martinelli, D. Polese, A. Catinei, and A. D’Amico, C. Di Natale, *Sens. Actuators, B*, **2012**, 161, 534.
49. R. Gosangi and R. Gutierrez-Osuna, *Sens. Actuators, B*, **2013**, 185, 201.
50. F. Herrero-Carrón, D. J. Yáñez, F. de Borja Rodríguez, and P. Varona, *Sens. Actuators, B*, **2015**, 206, 555.
51. T. Hyodo, T. Kaino, T. Ueda, K. Izawa, and Y. Shimizu, *Sens. Mater.*, **2016**, 28, 1179.
52. T. Baur, A. Schütze, and T. Sauerwald, *Tech. Mess.*, **2015**, 82, 187.

53. C. Schultealbert, T. Baur, A. Schütze, S. Böttcher, and T. Sauerwald, *Sens. Actuators, B*, **2017**, 239, 390.
54. T. Sauerwald, T. Baur, M. Leidinger, W. Reimringer, L. Spinelle, M. Gerboles, G. Kok, and A. Schütze, *J. Sens. Sens. Syst.*, **2018**, 7, 235.
55. K. Suematsu, Y. Shin, N. Ma, T. Oyama, M. Sasaki, M. Yuasa, T. Kida, and K. Shimanoe, *Anal. Chem.*, **2015**, 87, 8407.
56. K. Suematsu, W. Harano, T. Oyama, Y. Shin, K. Watanabe, and K. Shimanoe, *Anal. Chem.*, **2018**, 90, 11219.
57. J. Lerchner, D. Caspary, and G. Wolf, *Sens. Actuators, B*, **2000**, 70, 57.
58. T. Sasahara, H. Ishihara, K. Toyoda, T. Sunayama, S. Uematsu, T. Ozawa, K. Ogino, and M. Egashira, *Chem. Sens.*, **2002**, 18(B), 157.
59. T. Sasahara, H. Ishihara, K. Toyoda, T. Sunayama, S. Uematsu, T. Ozawa, K. Ogino, and M. Egashira, *Electrochemistry*, **2003**, 71, 457.
60. A. Kido, T. Sasahara, T. Sunayama, and M. Egashira, *Chem. Sens.*, **2003**, 19(B), 178.
61. T. Sasahara, A. Kido, T. Sunayama, S. Uematsu, and M. Egashira, *Sens. Actuators, B*, **2004**, 99, 532.
62. T. Sasahara, H. Kato, A. Saito, M. Nishimura, and M. Egashira, *Sens. Actuators, B*, **2007**, 126, 536.
63. T. Sasahara, N. Takahashi, and M. Egashira, *IEEE Trans. Sens. Micromachines*, **2008**, 128, 149.
64. T. Sasahara, A. Kido, H. Ishihara, T. Sunayama, and M. Egashira, Technical Digest of the 10th International Meeting on Chemical Sensors, Tsukuba, Japan, July 11 – 14, **2004**, 60 – 61.
65. T. Ozawa, Y. Ishiguro, K. Toyoda, M. Nishimura, T. Sasahara, and T. Doi, *Sens. Actuators, B*, **2005**, 108, 478.
66. T. Sasahara, A. Kido, H. Ishihara, T. Sunayama, and M. Egashira, *Sens. Actuators, B*, **2005**, 108, 478.
67. K. Sakamoto, T. Hyodo, T. Sasahara, Y. Shimizu, and M. Egashira, Abstract of the 18th Fall Meeting of The Ceramic Society of Japan, Osaka, Japan, Sep. 27 – 29, **2005**, 403.
68. T. Hyodo, K. Hieda, T. Sasahara, Y. Shimizu, and M. Egashira, *Chem. Sens.*, **2008**, 24(B), 67.
69. Y. Yuzuriha, T. Hyodo, T. Sasahara, Y. Shimizu, and M. Egashira, *Sens. Lett.*, **2011**, 9, 409.
70. T. Hyodo, Y. Yuzuriha, O. Nakagoe, T. Sasahara, S. Tanabe, and Y. Shimizu, *Sens. Actuators, B*, **2014**, 202, 748.
71. T. Hyodo, T. Hashimoto, T. Ueda, O. Nakagoe, K. Kamada, T. Sasahara, S. Tanabe, and Y. Shimizu, *Sens. Actuators, B*, **2015**, 220, 1091.
72. H. Shibata, T. Hyodo, T. Sasahara, Y. Shimizu, and M. Egashira, *Chem. Sens.*, **2006**, 21(B), 139.
73. T. Hyodo, T. Hiura, K. Nagae, K. Kamada, T. Ueda, and Y. Shimizu, *Chem. Sens.*, **2018**, 34(B), 94.
74. T. Hyodo, T. Hiura, K. Nagae, K. Kamada, T. Ueda, and Y. Shimizu, *Chem. Sens.*, **2019**, 35(A), 88.
75. K. Nagae, T. Ueda, T. Sasahara, O. Nakagoe, S. Tanabe, T. Hyodo, and Y. Shimizu, *ECS Trans.*, **2016**, 75, 23.
76. T. Hyodo, K. Nagae, T. Sasahara, K. Kamada, T. Ueda, and Y. Shimizu, *Chem. Sens.*, **2017**, 33(B), 31.
77. Y. Mizukoshi, K. Okitsu, Y. Maeda, Y. A. Yamamoto, R. Oshima, and Y. Nagata, *J. Phys. Chem. B*, **2005**, 101, 249.