Adsorption/combustion-type micro gas sensors: Typical VOC-sensing properties and material-design approach for highly sensitive and selective VOC detection

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Abstract

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, environmental monitoring, and so on. Since the kind of semiconductor-type gas sensor is a typical promising candidate among various portable VOC-sensing devices, many efforts on developing these gas sensors are firstly introduced in this article. Through some development stages, it has been well known that temperature-modulated operation of the 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
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 as essential substances responsible for sick house and building syndrome comprising headache, irritation of eyes, nose and throat, dizziness, fatigue, nausea, and various nonspecific symptoms.\textsuperscript{1,2} Many international institutes designate various gaseous organic chemicals such as formaldehyde, acetone, benzene, methylene chloride, and some 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.\textsuperscript{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 sick house and building syndrome. On the other hand, there are a huge amount of VOCs in human exhaled breath, skin gas and fart, and their composition and components greatly depend on the physical conditions and states of internal organs and tissues in human body. For example, acetone, isoprene or pentane, toluene or 1-nonanal, and methanethiol were reported as specific biomarkers for diabetes, heart disease, lung cancer, and halitosis, respectively.\textsuperscript{5} Therefore, speedy and accurate analyses of these VOCs by low cost, compact and simplified devices offer great potential for diagnosis of specific diseases in realistic medical setting and health supervision in personal use. On the basis of these situations, gas sensors are one of promising candidates to detect these VOCs sensitively and selectively.\textsuperscript{6}

A great deal of effort has been put to develop various types of VOC sensors (semiconductor gas sensors\textsuperscript{7-16}, solid-electrolyte gas sensors\textsuperscript{17-23}, and others\textsuperscript{24-27}). 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 effective ways in detecting a quite small amount of the target
VOCs. After the target VOCs are adsorbed and then concentrated in large quantity on the 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 the temporarily high-concentrated VOCs generated for a short time. We have also attempted to develop mesoporous adsorbents for the preconcentration of 2-pentylfuran. In these circumstances, Hiyama et al. have recently succeeded to develop prototype wearable devices capable of detecting a small amount 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.

Separately, 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 TAS sensors; e.g., #812 and #813) in most cases. Sears et al. reported that the dynamic resistance changes of TGS #812 and #813 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 H\(_2\) both from each other and various VOCs. Lantto et al. discussed that the differences between equilibrium and non-equilibrium responses of semiconductor-type porous SnO\(_2\) sensors to H\(_2\)S and effects of water vapor on CO response behavior of the TGS #812 sensor under rectangular heating-voltage modulation on the basis of detailed studies on active oxygen adsorbates (O\(^-\) species) frozen on the surface quickly cooled from \( T_H \) to \( T_L \). Wlodek et al. reported that the continuous resistance change of the TGS #813...
sensor as a function of a monotonic increase in operating temperature was represented as a linear combination of dynamic Gaussian-functioned signals to various gases. Nakata and Yoshikawa et al. demonstrated that the nonlinear hysteresis resistance loop of the TGS #813 sensor as a function of operating temperature with a sinusoidal heating voltage input in various VOCs and the Fourier transformation analysis especially contributed to the achievement of the highly selective response. This fundamental technique improved also the gas-recognition properties of the next-generation thick film TGS sensors (e.g., #2620), when used in combination with second-harmonic heating operation. At almost the same time, 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 agents and inorganic gases 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 dynamic change in temperature by employing various advanced computing technologies such as principle component analysis (PCA) and linear discriminant analysis (LDA) along with neural network. Our group also demonstrated that the Pt-loaded WO₃-based micro sensors showed quite large and selective dynamic responses to acetone under an operation with sinusoidal heating-voltage modulation. Recently, high performance semiconductor-type gas sensors operated under pulse-driven temperature operation mode have been developed by different two groups, but the concepts of their sensor operation were completely different. Schütze and his colleagues effectively utilized the large amount of active oxygen adsorbates (O⁻ species) which were frozenly produced on the oxide surface after instantaneous cooling from $T_{HI}$ (e.g., 450°C) to $T_L$ (e.g., 140°C) 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, while Shimanoe 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).\textsuperscript{55,56}

On the other hand, there was little report 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 adsorption, desorption, and combustion processes of target gases on the sensor surface. As 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 don’t have sufficient responses to quite low concentration of target gases (generally, less than 1 ppm). In such development situations of these sensors, Lerchner et al. demonstrated that adsorption and desorption behavior of some kinds of alcohols on specific polymer layer coated on MEMS sensor platform was able to be used as a source of sensor-signal output.\textsuperscript{57} By contrast, Sasahara and his groups optimized the microstructure of catalytic combustion-type gas sensors to adsorb various kinds of VOCs largely on the sensor surface at lower temperatures ($T_L$) and operated the sensors with a mode of pulse-driven heating at elevated temperatures ($T_H$).\textsuperscript{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.\textsuperscript{60}

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 general MEMS technique, but the design and size of the sensors gradually varied across the ages. A couple of platinum micro-heaters was formed on a Si(100) wafer covered with three insulating layers consisting of SiO$_2$, Si$_3$N$_4$ and HfO$_2$, and 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
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 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 shown in Section S1 and Fig. S1 of the 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 (TH: 450°C for 0.4 s, TL: RT for 9.6 s).58,59 This sensor shows the ordinary (static) sensor-signal profiles to H2 and CH4 as a conventional catalytic/combustion-type sensor, which simply increases to reach their steady-state values by ca. 40 ms after the abrupt rising in temperature by 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, and they 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 right after the 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 dynamic response is largely dependent on the period of low temperature (LT). In this case, the magnitude of dynamic response is already saturated, as 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 general response (ΔVMAX) for LT period of 0.6 s (ca. 1.25 V) is about half of that for LT period of 9.6 s (ca. 2.30 V).59

This type of sensor shows dynamic sensor-signal profiles which are specific also to other VOCs (e.g., various kinds of alcohols,58–62 formaldehyde62,63, acetaldehyde,62 acetone,58,59,62
diethyl carbonate, acetic acid, \( n \)-hexane, some kinds of aromatic compounds, total VOCs, 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 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 \( 15\text{Pd}/\gamma\text{-Al}_2\text{O}_3 \) sensor to eight kinds of alcohols with pulse-driven heating (\( T_H: 350°C \) for 0.2 s, \( T_L: \text{RT} \) for 9.8 s) are shown in Fig. 3(a). 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 (\( \Delta V_{\text{MAX}} \)) to all alcohols are observed within about 40 ms after heater-on. These differences probably result from differences of adsorption state and 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), and the behavior is simply explained in Section S2 of 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, 2-propanol and 2-butanol, resembles each other, though the first two sharp peaks are at clearly different positions. And third, the differential sensor-signal profiles to methanol, 2-propanol, 2-butanol, isobutanol and \textit{tert}-butanol exhibited a similarly shaped peak at 16–20 ms, which may be ascribed to combustion of methyl groups. Reasons for these features are not well recognized yet, but these differential sensor-signal profiles depending on the kinds of VOCs.
alcohols probably reflect the difference in molecular structure among these alcohols. Anyway, these results indicate that the kind of these alcohols can be easily discriminated by accurate analysis of the differential profiles of this sensor.

The $^{15}$Pd/$\gamma$-Al$_2$O$_3$ sensor can also sensitively detect a quite low concentration of toluene (10 ppb at least) and show a linear relationship between logarithmic $\Delta V_{\text{MAX}}$ and 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. The important factors for the large response are to set the $T_L$ at higher temperature (RT $\rightarrow$ 200°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 the large number of toluene molecules on the $^{15}$Pd/$\gamma$-Al$_2$O$_3$ surface. In addition, indoor field tests of the $^{15}$Pd/$\gamma$-Al$_2$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). 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 gas chromatograph/mass spectrometer (GC/MS) and gas chromatograph/flame ion detector (GC/FID) for comparison. The obtained results show that the operation of the $^{15}$Pd/$\gamma$-Al$_2$O$_3$ sensor with a pulse-driven heating ($T_{\text{Hi}}$: 450°C for 0.4 s, $T_L$: 200°C for 17.6 s) allows the determination 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 $\gamma$-Al$_2$O$_3$ and the adoption of double-step pulse heating (1st $T_H$ (combustion stage): 200°C for 0.4 s, 2nd $T_{\text{Hi}}$ (heat-cleaning stage): 400°C for a few seconds, $T_L$: 200°C for 20 s) effectively enhanced the magnitude of formaldehyde response. The $^{15}$Pt/$\gamma$-Al$_2$O$_3$ sensor showed relatively large dynamic response to formaldehyde and little dynamic response to both toluene and styrene at $T_{\text{Hi}}$ of 200°C, while the sensor-signal behavior
indicated that three VOCs burned out on the \( \text{Pt}/\gamma\text{-Al}_{2}\text{O}_3 \) surface at \( T_H \) of 400°C. Thus, 1st \( T_H \) as a combustion stage and 2nd \( T_H \) as a heat-cleaning stage are determined to be 200°C and 400°C, respectively, and this temperature-modulation setting largely improved the formaldehyde selectivity against toluene and styrene and the magnitude of formaldehyde response (detection limit: below 40 ppb, which was half of the guideline for indoor air quality in Japan). On the other hand, Ozawa et al. attempted to detect VOCs decomposed from an early stage fire by the \( \text{Pd}/\gamma\text{-Al}_{2}\text{O}_3 \) sensor, and then they showed that the sensor was able to largely detect furfural and 5-methyl-2-furaldehyde, which had an aldehyde group in their molecular structures, under pulse-heating operation (\( T_H: 400^\circ\text{C} \) for 0.4 s, \( T_L: \text{RT} \) for 9.6 s).\(^{64,65}\) As mentioned above, the adsorption/combustion-type gas sensors have a great potential to detect various kinds of VOCs sensitively and selectively, and thus they can be practically applied in various fields which require ultratrace VOC detection.

4. Material design of adsorption/combustion-type gas sensors and clarification of VOC-sensing mechanism

Various advantages and characteristics of adsorption/combustion-type gas sensors were discussed in the last section, by using the representative \( \text{Pd}/\gamma\text{-Al}_{2}\text{O}_3 \) sensor (\( \text{Pt}/\gamma\text{-Al}_{2}\text{O}_3 \) 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 specific surface area (SSA) of the support material of catalysts for the sensing film is quite important in increasing the amount of adsorbed VOCs at \( T_L \) as well as enhancing catalytic oxidation activity of VOCs at \( T_H \). \( \gamma\text{-Al}_{2}\text{O}_3 \) 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 \( \gamma\text{-Al}_{2}\text{O}_3 \), because of their quite large SSA. 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 they investigated the effects of their SSAs on the magnitude of toluene responses of $15\text{Pt/}mp\text{-SiO}_2$ sensors, together with that of the $15\text{Pd/}\gamma\text{-Al}_2\text{O}_3$ sensor (SSA of common $15\text{Pd/}\gamma\text{-Al}_2\text{O}_3$ powder we used: $146 \text{ m}^2 \text{ g}^{-1}$). Actually, they succeeded to prepare three kinds of $15\text{Pt/}mp\text{-SiO}_2$ 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 ($\text{IDR}$) to 100 ppm toluene monotonically increased with an increase in SSA ($T_H: 400^\circ \text{C for 0.4 s, } T_L: \text{RT for 9.6 s}$). Unfortunately, the toluene sensitivity (the slope of the relationship between logarithmic IDR and logarithmic toluene concentration, in this case) of these $15\text{Pt/}mp\text{-SiO}_2$ sensors was lower than that of the $15\text{Pd/}\gamma\text{-Al}_2\text{O}_3$ sensor. This is probably because of the relatively low thermal conductivity, and thus it seems to be a bit difficult for these $15\text{Pt/}mp\text{-SiO}_2$ sensors to detect the quite low concentration of toluene (e.g., $< 1 \text{ ppb}$). However, we presently have great expectation that the utilization of mp-SiO$_2$ powders as only adsorbents of VOCs to the sensing material have a vital role in improving the VOC-sensing properties, since the large amount of VOCs can adsorb on the surface of mp-SiO$_2$ powders.

The microstructure of $\gamma\text{-Al}_2\text{O}_3$ 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. After attempting to prepare $\gamma\text{-Al}_2\text{O}_3$ 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 ($\text{Al(}sec\text{-OC}_4\text{H}_9\text{)}_3$) as an Al source and behenic acid ($\text{C}_{21}\text{H}_{43}\text{COOH}$) as a template are firstly mixed with 1-ropanol. After a given amount of pure water is added to the solution, it is stirred at RT for 45 h to hydrolyze $\text{Al(}sec\text{-OC}_4\text{H}_9\text{)}_3$. After the solution is treated at $110^\circ \text{C for 1 h by a solvothermal method, white precipitates obtained are centrifuged at 2500 rpm for 10 min, washed with ethanol and then fired at } 700^\circ \text{C for 2 h in air. The SSA of the } \gamma\text{-Al}_2\text{O}_3 \text{ powder obtained is quite large}$. 

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(typically, 230–260 m² g⁻¹), and the mesoporous structure (estimated pore size: 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-Al₂O₃ powder obtained in this method (hereafter, referred to as
“mp-Al₂O₃ 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-Al₂O₃ (6Pd/mp-Al₂O₃) sensor
shows larger dynamic ethanol response than that of the 15Pd/γ-Al₂O₃ sensor, even though the
amount of Pd loaded onto the mp-Al₂O₃ surface was smaller than that onto the γ-Al₂O₃ 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
n₁ wt% Pd and n₂ wt% Au co-loaded mp-Al₂O₃ (n₁Pd-n₂Au/mp-Al₂O₃, n₁ + n₂ = 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 n₁Pd-n₂Au/mp-Al₂O₃ powders with the amount of Au loaded (n₂: 10 –
n₁ [wt%]).⁶⁹ The Pd and Au nanoparticles were loaded by general impregnation technique, followed
by annealing at 350°C for 1 h under hydrogen atmosphere. The ΔV_MAX to 1000 ppm ethanol is
dramatically 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-Al₂O₃ 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. Now, we understand that this tendency originates from their
synergistic effects. In addition, a given amount of the Pd and Au loaded on the as-prepared
n₁Pd-n₂Au/mp-Al₂O₃ powder was alloyed at various ratios, just after annealing at 350°C for 1 h
under hydrogen atmosphere, while most of the Pd component was oxidized and dispersive loaded on the mp-Al₂O₃ 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). These microstructural features should have a great impact on the oxidation activity of ethanol over the n₁Pd·n₂Au/mp-Al₂O₃ powders and their thermal conductivity. The effect of the mixing of thermally conductive material with δPd·2Au/mp-Al₂O₃ powder on the magnitude of dynamic ethanol response was also investigated as shown in Fig. 4(b). Here, α-Al₂O₃ was selected as the thermally conductive material, because α-Al₂O₃, which is thermally stable, shows high crystallinity, large crystallite size, and 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 δPd·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 δPd·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 ΔVₘₐₓ 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 ΔVₘₐₓ 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) (n₁Pd/n₂Au) nanoparticles by sonochemical reduction technique, and loaded them on the mp-Al₂O₃ surface, to further improve the VOC-sensing properties. The important key to synthesis of the monodispersed n₁Pd/n₂Au nanoparticles is to irradiate strong ultrasonic wave (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. As 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 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 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 \( n_1 \)Pd/\( n_2 \)Au nanoparticles on the mp-Al2O3 surface (zeta potential of \( n_1 \)Pd/\( n_2 \)Au and mp-Al2O3: ca. +28 mV and ca. −8 mV, respectively, at pH 4). The obtained powders were denoted as \( n_1 \)Pd/\( n_2 \)Au/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, and the detailed explanation is shown in Section S3 of the electronic supporting information. On the basis of the discussion, the highly-dispersive loading of Pd-based ultra-nanoparticles 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 the
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%). When these sensors were pulse-heated to 450°C, the 8Pd-2Au/mp-Al2O3 sensor showed the largest \(\Delta V_{\text{MAX}}\) to ethanol among them and the response speed of the 8Pd-2Au/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, the \(\Delta V_{\text{MAX}}\) 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 \(\Delta V_{\text{MAX}}\) 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 the large ethanol response even at 350°C, and thus the \(\Delta V_{\text{MAX}}\) 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 \(\Delta V_{\text{MAX}}\) of all the sensors was extremely low at the pulse-heating temperature of 250°C, but only the 0.8Pd/0.2Au/mp-Al2O3 sensor showed relatively large response enough to detect 1000 ppm ethanol. Figure 7(a) shows 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 \(\Delta V_{\text{MAX}}\) to these VOCs decreased and the shape of 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 \(\Delta V_{\text{MAX}}\) 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
The slope of the relationship between logarithmic $\Delta V_{\text{MAX}}$ 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 $0.4\text{Pd}/0.1\text{Au/mp-}\text{Al}_2\text{O}_3$ sensor. In addition, the $\Delta V_{\text{MAX}}$ of the $0.4\text{Pd}/0.1\text{Au/mp-}\text{Al}_2\text{O}_3$ sensor to these VOCs were larger than that of the $0.4\text{Pd}-0.1\text{Au/mp-}\text{Al}_2\text{O}_3$ sensor. These results also indicated that the highly dispersive loading of Pt and Au on the mp-\text{Al}_2\text{O}_3 powder showed excellent sensitivity as well as large response to these target gases, in comparison with those of the $0.4\text{Pd}-0.1\text{Au/mp-}\text{Al}_2\text{O}_3$ sensor.

The loading of only a specific metal oxide (MO) on the mp-\text{Al}_2\text{O}_3 powder promotes the catalytic oxidation activity of VOCs over the mp-\text{Al}_2\text{O}_3 powder, but the effectiveness was extremely limited to have the excellent VOC-sensing properties of MO-loaded mp-\text{Al}_2\text{O}_3 sensor.\textsuperscript{75,76} However, co-loading of a noble metal with MO on the mp-\text{Al}_2\text{O}_3 powder effectively enhanced the VOC-sensing properties of noble metal-loaded mp-\text{Al}_2\text{O}_3 sensors.\textsuperscript{71-76} In the article, sensing properties of typical $n$ wt\% Pt and $m$ wt\% MO co-loaded mp-\text{Al}_2\text{O}_3 ($n\text{Pt}/m\text{MO/mp-}\text{Al}_2\text{O}_3$) sensors to VOCs are discussed. The $n\text{Pt}/m\text{MO/mp-}\text{Al}_2\text{O}_3$ powders were prepared through general loading of MO by impregnation technique using constituent metal nitrate aqueous solution and subsequent Pt loading by sonochemical reduction technique using chloroplatinic acid aqueous solution, and the high dispersibility of Pt and MO on the mp-\text{Al}_2\text{O}_3 surface was confirmed by TEM. Among all the powders tested, the co-loading of Pt with CeO$_2$ on the mp-\text{Al}_2\text{O}_3 powder was the most effective in improving the VOC-sensing properties. The sensor-signal profiles of the typical $1.0\text{Pt}/10\text{CeO}_2/mp-\text{Al}_2\text{O}_3$ sensor to 6 kinds of VOCs (ethanol, acetone, ethyl acetates, benzene, toluene, and $o$-xylene) with pulse-driven heating ($T_{\text{HI}}$: 450°C for 0.4 s, $T_{\text{L}}$: RT, 100°C, or 150°C for 9.6 s) are shown in Fig. 8. The magnitude of response to the VOCs and the shape of the sensor-signal profiles were largely dependent on the kind of VOCs. The $1.0\text{Pt}/10\text{CeO}_2/mp-\text{Al}_2\text{O}_3$ sensor showed the largest $\Delta V_{\text{MAX}}$ to ethanol among all the VOCs at every $T_{\text{L}}$. The shape of the sensor-signal profiles of the sensor to ethanol was almost independent
of $T_L$, but the magnitude of $\Delta V_{\text{MAX}}$ gradually decreased with an increase in $T_L$. The sensor showed relatively large $\Delta V_{\text{MAX}}$ even to acetone, but the magnitude of $\Delta V_{\text{MAX}}$ to acetone was less than half of that to ethanol at $T_L$ of RT. In addition, the rise in the $T_L$ from RT to 100°C largely reduced the $\Delta V_{\text{MAX}}$ to acetone almost by half and accelerated the dynamic response speed, but the magnitude of $\Delta V_{\text{MAX}}$ 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 so 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 not almost observed at $T_L$ of 100°C and 150°C. In addition, the magnitude of $\Delta V_{\text{MAX}}$ 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 behavior to benzene and toluene in their sensor-signal profiles was obscure at every $T_L$, as the dynamic response by the flash combustion was not sufficiently large in comparison with the static response by general catalytic combustion. Thus, the $\Delta V_{\text{MAX}}$ 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 $\Delta V_{\text{MAX}}$ to o-xylene obviously increased with a rise in at $T_L$, since both the dynamic and static responses increased with a rise in $T_L$. However, the enlarged broad dynamic response which was observed at $T_L$ of 100°C 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 $\Delta V_{\text{MAX}}$ 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 “$T_L [\text{RT}] \rightarrow T_L [450^\circ C] \rightarrow T_L [100^\circ C] \rightarrow T_L [450^\circ C] \rightarrow T_L [150^\circ C] \rightarrow T_L [450^\circ C] \rightarrow T_L [\text{RT}] \rightarrow \cdots$”, could perform with strictly controlling temperatures and accurately analyzing these sensor-signal profiles by adequate computing technique, we would believe that the enhancing selective VOC-sensing will be realized by the sensors. In addition, the differentiation of these sensor-signal profiles is also quite effective in improving the VOC selectivity. Figure S3 shows the differential sensor-signal profiles of the 1.0Pt/10CeO$_2$/mp-Al$_2$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 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 quite fast response speed and a broad differential dynamic response with slow response speed. The magnitude of the sharp differential dynamic response increased with an increase in the number of methyl group in these molecules, while the response speed of the broad differential dynamic response decelerated with an increase in the number of methyl group. We can clearly recognize the slight differences among the sensor-signal profiles to the kinds of VOCs, through the 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 drastically improve the VOC selectivity.

Furthermore, the ratio of integrated dynamic response ($IDR$) and integrated static response ($ISR$) [$IDR/ISR$] is also largely dependent on the kinds of VOCs and their concentrations in target gas. Figure S4 shows sensor-signal profiles of the $1.0\text{Pt/mCeO}_2/\text{mp-Al}_2\text{O}_3$ 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 response largely reduced with a decrease in the VOC concentration in comparison 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 much great potential to detect a quite-low concentration of VOCs.

The absorbability and reactivity of VOCs on the surface of the sensor materials are the most important factor in determining the VOC-sensing properties of the adsorption/combustion-type gas sensors. Therefore, 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 $15\text{Pd/γ-Al}_2\text{O}_3$ 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°C under He flowing (10°C/min) probably due to the reaction of the adsorbed ethanol molecules with oxygen adsorbates on the surface. In addition, the amount of CO$_2$ generated in the TPD are comparatively correlated with the magnitude of dynamic responses (i.e., $\Delta V_{MAX}$ and $IDR$) of the sensor-signal profiles of the $15\text{Pd/γ-Al}_2\text{O}_3$ 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 in improving the magnitude of dynamic responses. Furthermore, TPO spectra of some kinds of VOCs (ethanol, 1-butanol, and 2-butanol) 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 increase in temperature under air flowing (2°C/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.\textsuperscript{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).\textsuperscript{71} On the basis of these findings, the catalytic oxidation properties of ethanol, ethyl acetate, and toluene over unloaded mp-Al$_2$O$_3$, $1.0\text{Pt}/\text{mp-Al}_2\text{O}_3$, $1.0\text{Pt}/10\text{MO}/\text{mp-Al}_2\text{O}_3$ (MO: CeO$_2$ or Bi$_2$O$_3$) were recently estimated in details, together with their TPD and TPO properties (pre-adsorption condition of these VOCs: 150°C for 1 h).\textsuperscript{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$_2$O$_3$) have been recently attempted, in order to improve their sensing properties to toluene\textsuperscript{75} and a series of alcohol.\textsuperscript{76}

4. 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 $15\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ sensor$^{62}$ and $15\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ sensor$^{63}$ 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, the co-loading of Pd and Au (esp., as core(Au)/shell(Pd) nanoparticles), 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 quite sensitively detect VOCs by controlling the sensing materials compositionally and microstructurally as well as by operating with specific dynamic temperature modulation, and other types of attractive VOC sensors have also been developed as a key device of leading electronic nose systems. In addition, the use of pre-concentrators of VOCs with semiconductor-type gas sensors also dramatically enhanced both the sensitivity and selectivity. Hereafter, it is indispensable in accelerating the development of the adsorption/combustion-type gas sensors capable of detecting a further small concentration (i.e., ppt or less) of VOCs, based on their VOC-sensing mechanism which is recently being elucidated. These achievements will provide the adsorption/combustion-type gas sensors with excellent VOC-sensing performance, which is far superior to other sensors.
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**Figure Captions**

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

Fig. 2. Sensor-signal profiles of \(15\)Pd/\(\gamma\)-Al\(_2\)O\(_3\) sensor to 1000 ppm ethanol, H\(_2\), and CH\(_4\) 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.

Fig. 3. (a) General and (b) differential sensor-signal profiles of \(15\)Pd/\(\gamma\)-Al\(_2\)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.

Fig. 4. (a) Variations in \(\Delta V_{MAX}\) of \(n_1\)Pd-\(n_2\)Au/mp-Al\(_2\)O\(_3\) sensors \((n_1 + n_2 = 10 \text{ wt\%})\) to 1000 ppm ethanol and specific surface area (SSA) of \(n_1\)Pd-\(n_2\)Au/mp-Al\(_2\)O\(_3\) powders with the amount of Au loaded, \(n_2\), and (b) variations in \(\Delta V_{MAX}\) of \(8\)Pd-2Au/mp-Al\(_2\)O\(_3\)(x)/\(\alpha\)-Al\(_2\)O\(_3\)(y) sensors to 100 ppm ethanol and SSA of \(8\)Pd-2Au/mp-Al\(_2\)O\(_3\)(x)/\(\alpha\)-Al\(_2\)O\(_3\)(y) powders with the amount of \(\alpha\)-Al\(_2\)O 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.

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

Fig. 6. Sensor-signal profiles of \(0.8\)Pd/\(0.2\)Au/mp-Al\(_2\)O\(_3\) and \(0.8\)Pd-0.2Au/mp-Al\(_2\)O\(_3\) 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 \(8\)Pd-2Au/mp-Al\(_2\)O\(_3\) sensor (the total loading amount of Pd and Au: 10 wt%). Reproduced with permission from Ref. 70.

Fig. 7. (a) Sensor-signal profiles of \(0.4\)Pd/\(0.1\)Au/mp-Al\(_2\)O\(_3\) 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 $\Delta V_{\text{MAX}}$ of both 0.4Pd/0.1Au/mp-Al$_2$O$_3$ and 0.4Pd-0.1Au/mp-Al$_2$O$_3$ 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.

Fig. 8. Sensor-signal profiles of 1.0Pt/10CeO$_2$/mp-Al$_2$O$_3$ 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.
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