

Acetone-Sensing Properties of WO₃-Based Gas Sensors Operated in Dynamic Temperature Modulation Mode—Effects of Loading of Noble Metal and/or NiO onto WO₃—

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(Received April 27, 2016; accepted July 25, 2016)

Keywords: acetone, dynamic temperature modulation, semiconductor gas sensor, WO₃, hydrogen

Micro gas sensors fabricated with WO₃ loaded with and without a noble metal and/or NiO as a sensing material were operated in dynamic temperature modulation mode with sinusoidal modulation of Pt-heater voltage [low voltage: 0 V for RT, maximum voltage: 0.6 V (for 150 °C)–1.6 V (for 400 °C), period: 6 s], and their acetone-sensing properties were investigated in dry and wet air. The WO₃ sensor showed negligible dynamic responses to acetone and H₂, but the loading of a noble metal onto the WO₃ markedly improved the dynamic responses, particularly to acetone in dry air. Among all the 0.5 wt% noble-metal-loaded WO₃ (0.5N/WO₃, N: noble metal) sensors tested, the 0.5Pt/WO₃ sensor showed the largest dynamic response to acetone in dry air, while the dynamic response to acetone was largely decreased by the addition of moisture into the gaseous atmosphere. The loading of NiO onto WO₃ and 0.5Pt/WO₃ improved the dynamic response to acetone of the WO₃ and 0.5Pt/WO₃ sensors, and the 1.0 wt% NiO-loaded 0.5Pt/WO₃ sensor showed the largest dynamic acetone response and dynamic acetone selectivity against H₂. These acetone-sensing properties of the sensors operated in dynamic temperature modulation mode were superior to those of the ones operated in static constant temperature mode, possibly because of acetone and/or its partial oxidation products adsorbed on the oxide surface at low temperatures and their abrupt catalytic combustion with oxygen adsorbates at high temperatures.

1. Introduction

It is well known that human exhaled breath contains various types of gaseous species with high humidity, and that qualitative and quantitative analyses of the gases enable us to estimate health conditions and to diagnose various diseases. For example, the concentration of methane and hydrogen in exhaled breath increases with the growth of anaerobic bacteria in the large intestine,^(1–3) and thus their monitoring is useful for diagnosing the digestive and absorptive functions of carbohydrates. As volatile sulfur compounds such as methyl mercaptan and hydrogen sulfide are produced in the mouth by oral bacteria,^(4,5) the quantitative analysis of these compounds is helpful in diagnosing halitosis originating from periodontal disease in dental clinics. Relatively large amounts of ammonia,⁽⁶⁾ nitrogen monoxide,⁽⁷⁾ pentane,⁽⁸⁾ toluene,^(9,10) and 1-nonanal⁽¹¹⁾ are also known to be detected in the exhaled breath of patients with kidney disorder, asthma, heart disease, and lung

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cancer, respectively, and thus the development of breakthrough gas-sensing devices that can detect these gases sensitively and selectively has been expected for the early-stage detection of these diseases.

Acetone is produced in exhaled breath by the fat-burning process during weight-loss diet and exercise,⁽¹²⁾ and it is also one of the representative biomarkers contained in the exhaled breath of diabetic patients.⁽¹³⁾ Therefore, many researchers have attempted to develop highly sensitive and selective semiconductor-type acetone sensors by utilizing various types of metal oxides as acetone-sensing materials.^(10,14–23) For example, Righettoni *et al.* have reported that the loading of 10 mol% Si-based components onto WO₃ largely improved the acetone-sensing properties of the WO₃ sensor.^(15,16) Wang *et al.* have demonstrated that a 10 mol% Cr₂O₃-loaded WO₃ sensor showed a relatively large response to acetone, in comparison with responses to other gases such as ethanol, isoprene, and nitrogen monoxide.⁽¹⁷⁾ Xie *et al.* have clarified that the compositional and structural control of ZnO–CuO composite sensors effectively improved the acetone selectivity against toluene, ethanol, and methanol.⁽²³⁾ On the other hand, the operation of gas sensors in dynamic temperature modulation mode is quite effective in enhancing gas-sensing properties,^(24–34) particularly for volatile organic compounds (VOCs). Our group has actually demonstrated that catalytic combustion-type gas sensors that were operated in a mode of pulsed temperature heating (typical pulsed-heating period: 400 ms for 10 s), so-called adsorption/combustion-type gas sensors, showed large dynamic responses to various types of VOCs.^(35–40) In this work, we have attempted to improve the acetone-sensing properties of WO₃-based sensors, particularly in wet air, by the loading of noble metal and/or NiO onto the surface of WO₃, as well as by operation in dynamic temperature modulation mode.

2. Experimental Procedure

2.1 Preparation of WO₃ powders loaded with and without noble metal and/or NiO

HNO₃ aq. (0.10 mol dm⁻³, 10 cm³) was added dropwise into a Na₂WO₄ aqueous solution (0.15 mol/L, 100 cm³), and then the yellow resultant precipitate was calcined at 500 °C for 2 h in air. It was confirmed that the crystal structure of the prepared powder was monoclinic WO₃ (JCPDS No. 43-1035) by X-ray diffraction analysis (XRD; Rigaku Corp., RINT2200) using Cu K α radiation (40 kV, 36 mA). In addition, the specific surface area, which was measured by the general Brunauer–Emmett–Teller (BET) method using a N₂ adsorption isotherm (Micromeritics Inst. Corp., TriStar 3000), was ca. 11.6 m² g⁻¹. The WO₃ powder was impregnated with an appropriate amount of Ni(NO₃)₂ aqueous solution (0.07 mol/L), followed by calcination at 500 °C for 2 h in air. The obtained NiO-loaded WO₃ powders were denoted as *m*NiO/WO₃ [*m*: amount of NiO loading, 1.0, 5.0, and 10 (wt%)]. In addition, an appropriate amount of WO₃ or *m*NiO/WO₃ powder was added into RuCl₃ (8.5 × 10⁻³ mol dm⁻³), PtCl₄ (1.5 × 10⁻² mol dm⁻³), Pd(NO₃)₂ (2.1 × 10⁻² mol dm⁻³), or HAuCl₄ aq. (1.5 × 10⁻² mol dm⁻³) aqueous solution. After they were ultrasonicated at RT for 1 h, they were evaporated to dryness at 100 °C for 2 h in air. The resultant solids were heat-treated at 200 °C for 2 h in H₂, followed by calcination at 500 °C for 2 h in air. The obtained WO₃ and *m*NiO/WO₃ powders loaded with noble metal (*N*) were denoted as *nN*/WO₃ and *nN/m*NiO/WO₃ [*n*: amount of noble metal (*N*: Au, Pd, Pt, or Ru), 0.1, 0.5, and 1.0 (wt%)].

2.2 Fabrication of micro gas sensors and measurement of gas-sensing properties

Figure 1 shows a top view of a typical micro gas sensor fabricated by utilizing WO_3 as a gas-sensing material and a cross-sectional schematic drawing of micro gas sensors fabricated in this study. The paste containing the obtained powder and an appropriate amount of terpeneol were applied onto interdigitated Pt electrodes attached on a microsensor chip fabricated by a MEMS technique, by a drop coating technique employing an air-pulse fluid dispenser with a syringe of suitable size. Then, the microsensor chips were fired at $500\text{ }^\circ\text{C}$ for 3 h in air. The thickness of the oxide films was controlled to approximately $30\text{ }\mu\text{m}$. Hereafter, the sensor will be referred to, depending on the type of sensing material (namely, WO_3 , $m\text{NiO}/\text{WO}_3$, or $n\text{N}/m\text{NiO}/\text{WO}_3$).

The gas responses of these sensors were measured with 20 ppm acetone and 20 ppm H_2 balanced with air under dry and wet [relative humidity (RH): 50% at $30\text{ }^\circ\text{C}$] atmospheres at a flow rate of $100\text{ cm}^3\text{min}^{-1}$. These sensors were mainly operated in dynamic temperature modulation mode. The operating temperature was dynamically controlled by the sinusoidal modulation of heater voltage (V_h) with the amplitude of $0\text{--}V_{h,\text{max}}$ V [$V_{h,\text{max}}$: maximum of V_h , 0.6 V (for $150\text{ }^\circ\text{C}$)–1.6 V (for $400\text{ }^\circ\text{C}$)] and a period of 6 s, and the maximum temperature achieving $V_{h,\text{max}}$ in one period was denoted as T_{max} . Dynamic sensor response [$R_{\text{D(TG)}}$, target gas (TG): acetone (Ac) or H_2] was defined as the ratio of sensor resistance in 20 ppm acetone or 20 ppm H_2 balanced with air to that in air at each T_{max} . Dynamic acetone selectivity against H_2 (S_{D}) was defined as a ratio of $R_{\text{D(Ac)}}$ to $R_{\text{D(H}_2\text{)}}$. The sensors were operated during 10 cycles in the sinusoidal modulation mode, and the $R_{\text{D(TG)}}$ and S_{D} were calculated at the last cycle. The static sensing properties of some sensors to 20 ppm acetone

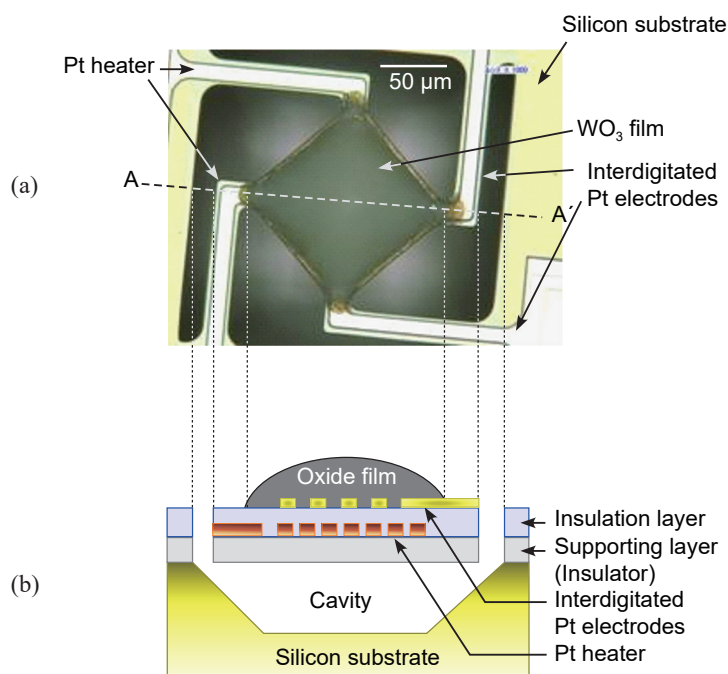


Fig. 1. (Color online) (a) Top view of typical micro gas sensor (gas-sensing material: WO_3) and (b) cross-sectional schematic drawing of region between A and A' of micro gas sensors fabricated in this study.

and H_2 were also measured at constant temperatures (150–400 °C). Static sensor response ($R_{S(TG)}$) was defined as the ratio of sensor resistance in 20 ppm acetone or H_2 balanced with air to that in air at each constant operating temperature, and static acetone selectivity against H_2 (S_S) was defined as the ratio of $R_{S(Ac)}$ to $R_{S(H_2)}$.

3. Results and Discussion

Figure 2 shows the typical dynamic sensor-signal profiles of representative (WO_3 and 0.5Pt/ WO_3) sensors in dry air and in 20 ppm acetone balanced with dry air, together with modulated heater voltage (V_h , 0–0.8 V) and operating temperature (T , RT–200 °C). The resistances of these sensors decreased with increasing V_h (namely, with a rise in T), and the resistances became the smallest at $V_{h,max}$ (0.8 V, T_{max} : 200 °C). The resistance of the WO_3 sensor in 20 ppm acetone balanced with dry air was smaller than that in air over the entire range of V_h (T), but the difference between the resistance in dry air and that in 20 ppm acetone balanced with dry air was much smaller than we had expected. The loading of Pt onto the WO_3 increased the sensor resistance in dry air and markedly decreased the sensor resistance in 20 ppm acetone balanced with dry air, especially in the temperature range of ca. 100–200 °C. This indicates that the dynamic sensor response to acetone ($R_{D(Ac)}$) of the 0.5Pt/ WO_3 sensor was much larger than that of the WO_3 sensor in dry air. However, the resistance of the 0.5Pt/ WO_3 sensor in 20 ppm acetone balanced with dry air was comparable to that in dry air in the low temperature range (near RT), because the sensor resistance was in such a very high range that we could not exactly measure the difference in sensor resistances between in air, and in 20 ppm acetone balanced with dry air.

Figure 3 shows the T_{max} dependences of responses to 20 ppm acetone and 20 ppm H_2 ($R_{D(Ac)}$ and $R_{D(H_2)}$, respectively) of WO_3 and 0.5Pt/ WO_3 sensors in dry and wet air under dynamic temperature operation. The WO_3 sensor had little response to acetone and H_2 over the entire T_{max} range, regardless of whether moisture was added to the gaseous atmosphere. The Au loading onto the

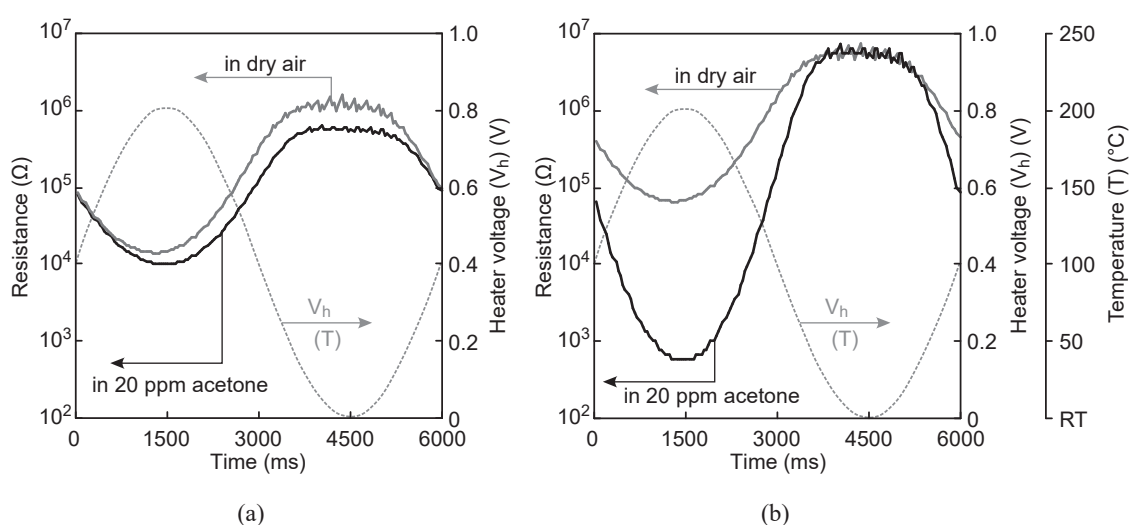


Fig. 2. Typical dynamic sensor-signal profiles of representative sensors in dry air and in 20 ppm acetone balanced with dry air, together with V_h and T . (a) WO_3 sensor. (b) 0.5Pt/ WO_3 sensor.

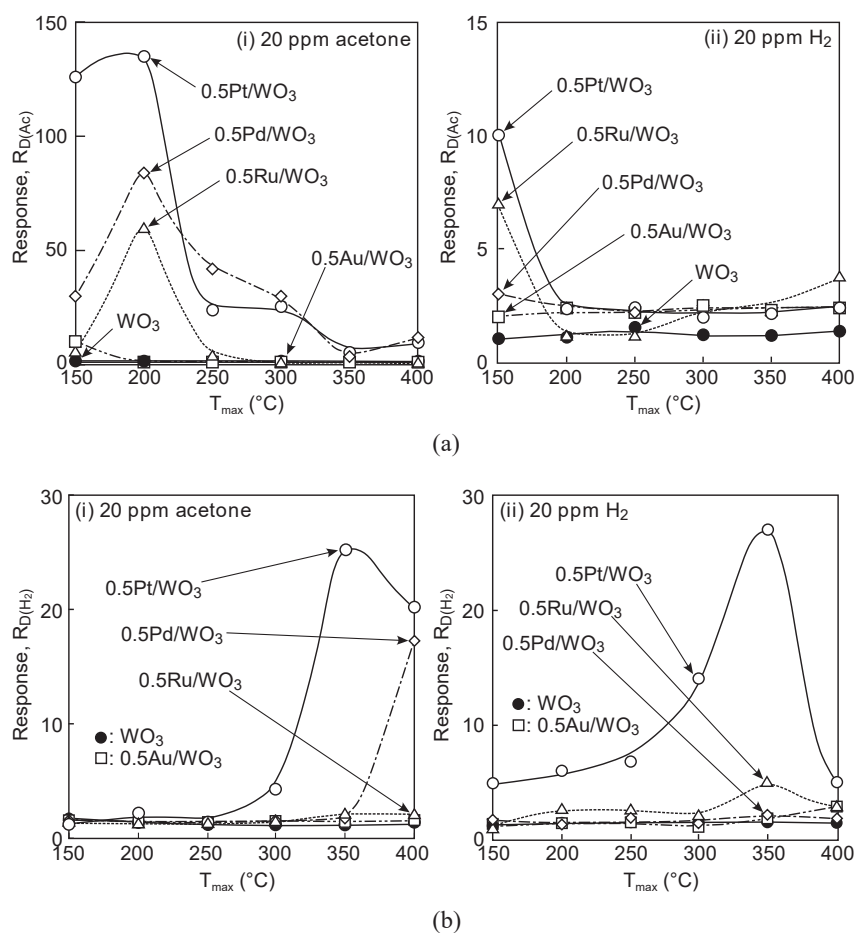


Fig. 3. Variations in responses of WO₃ and 0.5M/WO₃ sensors to 20 ppm acetone and 20 ppm H₂ in dry and wet air, with maximum temperature (T_{\max}) under dynamic temperature operation. (a) In dry air. (b) In wet air.

WO₃ hardly improved $R_{D(\text{Ac})}$ and $R_{D(\text{H}_2)}$ of the WO₃ sensor, but the loading of Pd, Pt, or Ru onto the WO₃ was effective in enhancing both responses. The 0.5N/WO₃ sensors (N: Pd, Pt, and Ru) showed relatively large acetone responses at low temperatures (especially at 200 °C) in dry air, but the addition of moisture into the gaseous atmosphere markedly reduced their $R_{D(\text{Ac})}$ at low temperatures and enhanced their $R_{D(\text{Ac})}$ in the temperature range of ca. 350–400 °C. On the other hand, the loading of Pd, Pt, or Ru onto WO₃ also tended to increase the $R_{D(\text{H}_2)}$ of these sensors in dry air at the lowest T_{\max} (150 °C), while the addition of moisture into the gaseous atmosphere decreased the $R_{D(\text{H}_2)}$ at 150 °C and increased the $R_{D(\text{H}_2)}$ at 350 °C. The shift in T_{\max} of the largest $R_{D(\text{Ac})}$ and $R_{D(\text{H}_2)}$ from low temperature (200 °C) to high temperature (350–400 °C) by the addition of moisture into the gaseous atmosphere probably originates from the reduction in the catalytic combustion activities of acetone and H₂ over the gas-sensing materials (0.5M/WO₃, N: Pd, Pt, and Ru) by the adsorption of water molecules on the oxide surface. Among all the 0.5M/WO₃ sensors, the 0.5Pt/WO₃ sensor showed the largest $R_{D(\text{Ac})}$ and $R_{D(\text{H}_2)}$, which were quite dependent on humidity in the gaseous atmosphere. Therefore, the excellent acetone selectivity of the 0.5Pt/WO₃ sensor against H₂ (S_D) at 200 °C in dry air (ca. 58) dropped to ca. 0.38 with the addition of moisture into the gaseous atmosphere, since

$R_{D(\text{Ac})}$ (ca. 2.3) was smaller than $R_{D(\text{H}_2)}$ (ca. 6.0) at 200 °C in wet air. In addition, the relatively large $R_{D(\text{Ac})}$ and $R_{D(\text{H}_2)}$ of the 0.5Pt/WO₃ sensor at 350 °C in wet air were not helpful in improving the S_D .

As mentioned above, the loading of the noble metal enhanced the magnitude of the acetone response of the WO₃ sensor, but it was not effective in reducing the effect of humidity on the acetone selectivity against H₂. Kim *et al.* have demonstrated that the humidity dependence of CO-sensing properties of SnO₂-based sensors is reduced to a negligible level by NiO loading onto the SnO₂ surface.⁽⁴¹⁾ Therefore, NiO was dispersively loaded onto the WO₃ powder by impregnation employing Ni(NO₃)₂ to improve the acetone-sensing properties of the WO₃-based sensor in wet air. Figure 4 shows the T_{max} dependences of $R_{D(\text{Ac})}$ and $R_{D(\text{H}_2)}$ of $m\text{NiO}/\text{WO}_3$ sensors ($m = 1.0, 5.0,$ and 10) in dry and wet air, under dynamic temperature operation, together with those of the WO₃ sensor. The $R_{D(\text{Ac})}$ in dry air gradually increased with an increase in the amount of NiO loading, especially at 300 and 400 °C, and the $R_{D(\text{Ac})}$ of all $m\text{NiO}/\text{WO}_3$ sensors was apparently larger than $R_{D(\text{H}_2)}$ only at 400 °C in dry air. On the other hand, the loading of 1.0 wt% NiO onto WO₃ was quite effective in improving the $R_{D(\text{Ac})}$ of the WO₃ sensor in wet air, but the further increase in the amount of NiO loading reduced the positive impact of the NiO loading on the $R_{D(\text{Ac})}$ in wet air. As the $R_{D(\text{H}_2)}$ of all $m\text{NiO}/\text{WO}_3$ sensors in wet air was comparable to that of the WO₃ sensor, the 1.0NiO/WO₃

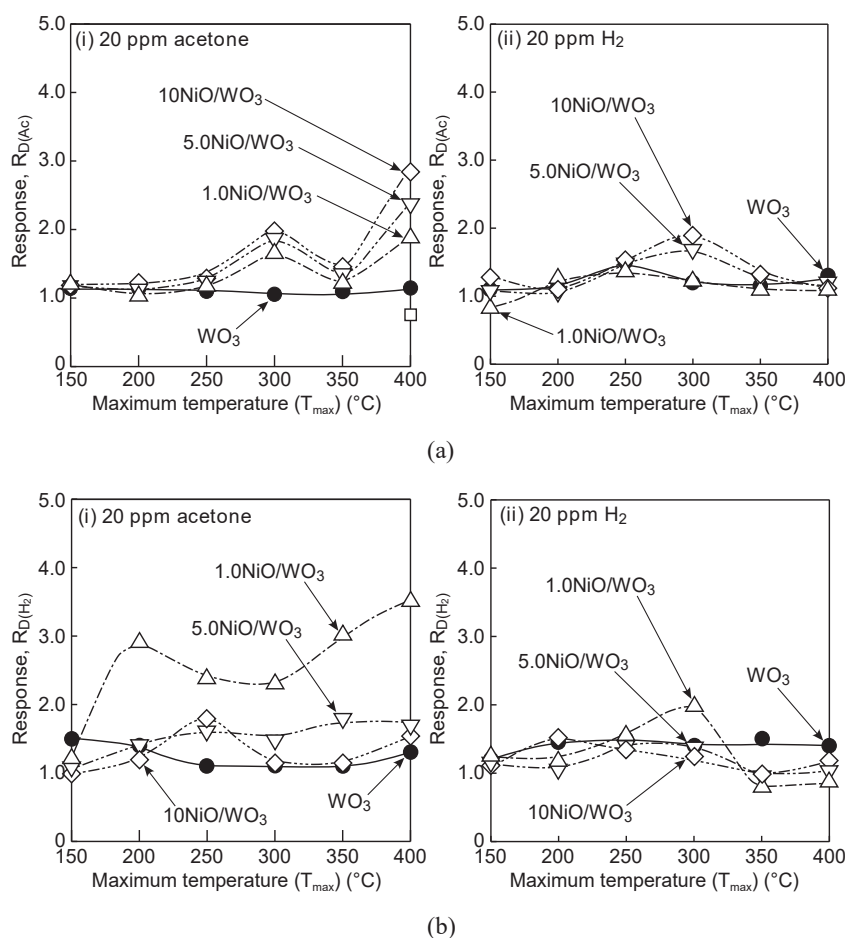


Fig. 4. Variations in response of WO₃ and $m\text{NiO}/\text{WO}_3$ sensors to 20 ppm acetone and 20 ppm H₂ in dry and wet air, with maximum temperature (T_{max}) under dynamic temperature operation. (a) In dry air. (b) In wet air.

sensor showed a relatively large S_D in the temperature range between 200 and 400 °C, among all the $m\text{NiO}/\text{WO}_3$ sensors.

We attempted to improve the acetone-sensing properties of the $1.0\text{NiO}/\text{WO}_3$ sensor, which showed the largest $R_{D(\text{Ac})}$ and S_D in wet air among all the $m\text{NiO}/\text{WO}_3$ sensors, by the loading of Pt onto the $1.0\text{NiO}/\text{WO}_3$. Figure 5 shows the T_{max} dependences of $R_{D(\text{Ac})}$ and $R_{D(\text{H}_2)}$ of $n\text{Pt}/1.0\text{NiO}/\text{WO}_3$ sensors ($n = 0.1, 0.5, \text{ and } 1.0$) in dry and wet air under dynamic temperature operation. The $R_{D(\text{Ac})}$ of the $n\text{Pt}/1.0\text{NiO}/\text{WO}_3$ sensors both in dry and wet air tended to be smaller than that of the $0.5\text{Pt}/\text{WO}_3$ sensor (see Fig. 3), but the loading of Pt apparently enhanced both $R_{D(\text{Ac})}$ and $R_{D(\text{H}_2)}$ of the $1.0\text{NiO}/\text{WO}_3$ sensor (see Fig. 4). The $0.5\text{Pt}/1.0\text{NiO}/\text{WO}_3$ sensor showed the largest $R_{D(\text{Ac})}$ both in dry and wet air among all $n\text{Pt}/1.0\text{NiO}/\text{WO}_3$ sensors, probably because the larger amount of Pt loading (e.g., 1 wt%) onto WO_3 excessively enhanced the catalytic combustion properties of acetone over $n\text{Pt}/1.0\text{NiO}/\text{WO}_3$ and thus the concentration of acetone at the bottom of $1.0\text{Pt}/1.0\text{NiO}/\text{WO}_3$ films near interdigitated Pt electrodes of the sensor was lower than that of the $0.5\text{Pt}/1.0\text{NiO}/\text{WO}_3$ film. On the other hand, the loading of Pt also enhanced the $R_{D(\text{H}_2)}$ of the $1.0\text{NiO}/\text{WO}_3$ sensor (see Fig. 4), and the $R_{D(\text{H}_2)}$ of the $n\text{Pt}/1.0\text{NiO}/\text{WO}_3$ sensors both in dry and wet air increased with increasing the amount of Pt loading, probably because the amount of H_2 oxidized on the surface of $n\text{Pt}/1.0\text{NiO}/$

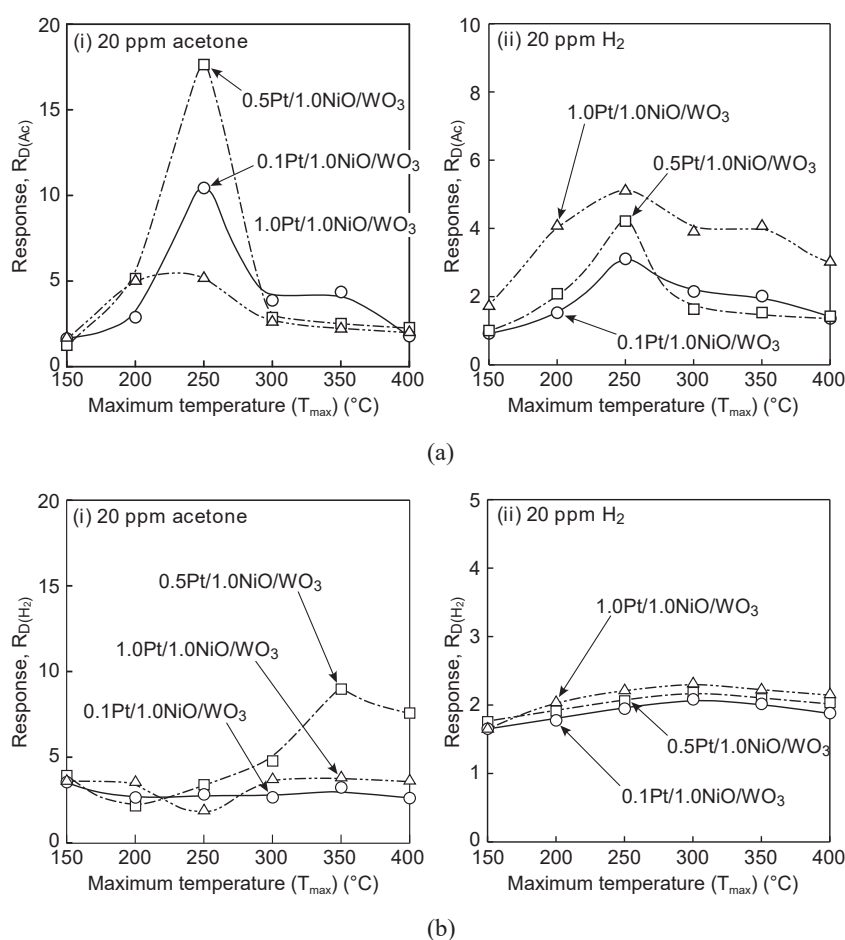


Fig. 5. Variations in response of $n\text{Pt}/1.0\text{NiO}/\text{WO}_3$ sensors to 20 ppm acetone and 20 ppm H_2 in dry and wet air, with maximum temperature (T_{max}) under dynamic temperature operation. (a) In dry air. (b) In wet air.

WO₃ films was much smaller than that of acetone and thus the amount of H₂ that reacted with oxygen adsorbates on the *n*Pt/1.0NiO/WO₃ surface at the bottom side of the films was dependent on the amount of Pt loading. In addition, all the *n*Pt/1.0NiO/WO₃ sensors showed the largest $R_{D(Ac)}$ and $R_{D(H_2)}$ at lower T_{max} (250 °C) in dry air, but the addition of moisture into the gaseous atmosphere shifted T_{max} of the largest $R_{D(Ac)}$ and $R_{D(H_2)}$ from low temperature (200 °C) to high temperature (350–400 °C), as is the case with the 0.5Pt/WO₃ sensor. In addition, the 0.5Pt/1.0NiO/WO₃ sensor showed the most excellent S_D (e.g., ca. 4.1 at 250 °C in dry air and ca. 5.2 at 350 °C in wet air) among all the *m*NiO/WO₃ sensors.

Representative (WO₃, 0.5Pt/WO₃, and 0.5Pt/1.0NiO/WO₃) sensors were statically operated at constant temperatures, and the static responses of these sensors to 20 ppm acetone and 20 ppm H₂ in dry and wet air were investigated, in comparison with the dynamic responses of these sensors operated in dynamic temperature modulation mode. Figure 6 shows the operating temperature dependence of static responses to 20 ppm acetone ($R_{S(Ac)}$) and 20 ppm H₂ ($R_{S(H_2)}$) of these sensors in dry and wet air. The WO₃ sensor had little $R_{S(Ac)}$ and $R_{S(H_2)}$ at all operating temperatures both in dry and wet air. The loading of 0.5 wt% Pt apparently enhanced the $R_{S(Ac)}$ in dry air, in comparison with the $R_{S(H_2)}$, but the effect of the Pt loading on the $R_{S(Ac)}$ in dry air was much smaller than that of the

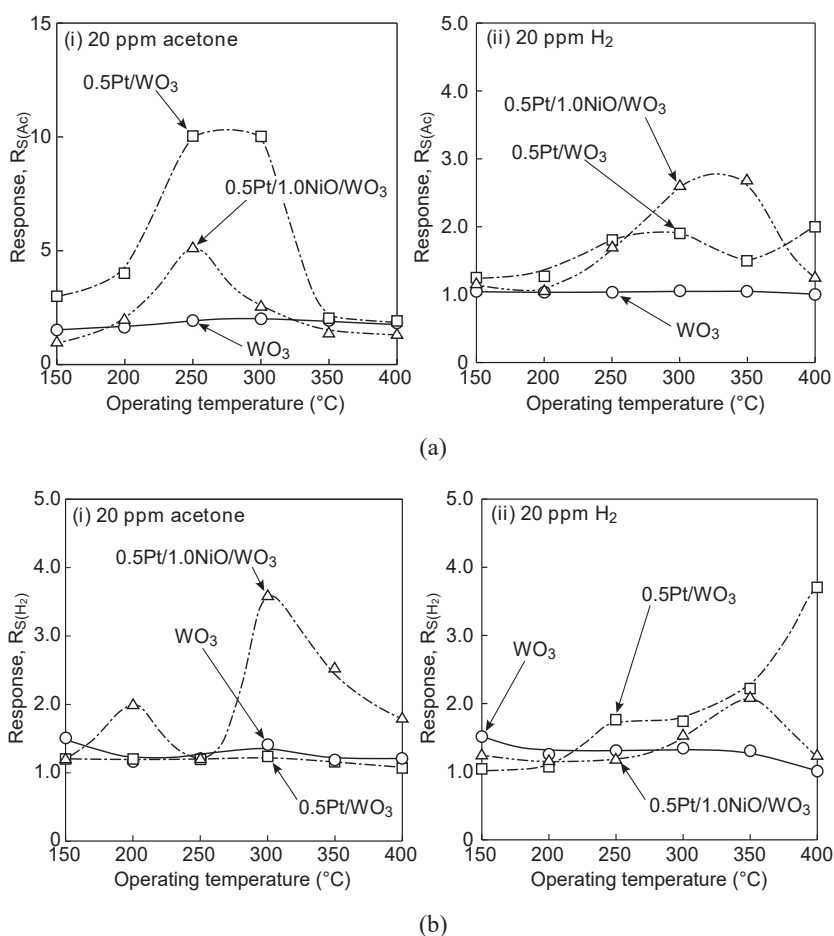


Fig. 6. Variations in response of WO₃, 0.5Pt/WO₃, and 0.5Pt/1.0NiO/WO₃ sensors to 20 ppm acetone and 20 ppm H₂ in dry and wet air, with operating temperature under static temperature operation. (a) In dry air. (b) In wet air.

dynamic response ($R_{D(Ac)}$) in dry air [see Fig. 3(a-i)]. In addition, the addition of moisture into the gaseous atmosphere markedly decreased the $R_{S(Ac)}$, as is the case with the $R_{D(Ac)}$. The $R_{S(H_2)}$ of the 0.5Pt/WO₃ sensor is also smaller than the $R_{D(H_2)}$, but the effect of humidity on the $R_{S(H_2)}$ seems to be limited in comparison with that on the $R_{D(H_2)}$. On the other hand, the $R_{S(Ac)}$ of the 0.5Pt/1.0NiO/WO₃ sensor was smaller than that of the 0.5Pt/WO₃ sensor and the $R_{D(Ac)}$ of the 0.5Pt/1.0NiO/WO₃ sensor in dry air [see Fig. 5(a-i)], while the effect of humidity on the $R_{S(Ac)}$ of the 0.5Pt/1.0NiO/WO₃ sensor (largest $R_{S(Ac)}$: ca. 5.1 at 250 °C in dry air, ca. 3.6 at 300 °C in wet air) was much smaller than that on the $R_{S(Ac)}$ of the 0.5Pt/WO₃ sensor. The $R_{S(H_2)}$ of the 0.5Pt/1.0NiO/WO₃ sensor was apparently larger than that of the 0.5Pt/WO₃ sensor only at 300 and 350 °C in dry air, but the addition of moisture into the gaseous atmosphere reduced the $R_{S(H_2)}$ at all the operating temperatures.

The temperature dependences of S_D and S_S of the WO₃, 0.5Pt/WO₃, and 0.5Pt/1.0NiO/WO₃ sensors under dynamic and static temperature operations, respectively, are summarized in Fig. 7. The 0.5Pt/WO₃ sensor showed the largest S_S under static temperature operation in dry air, but the S_S largely decreased with the addition of moisture into the gaseous atmosphere. The loading of NiO with Pt onto WO₃ decreased the S_S of the 0.5Pt/WO₃ sensor in dry air, but the S_S of the 0.5Pt/1.0NiO/WO₃ sensor was relatively larger than those of the WO₃ and 0.5Pt/WO₃ sensors

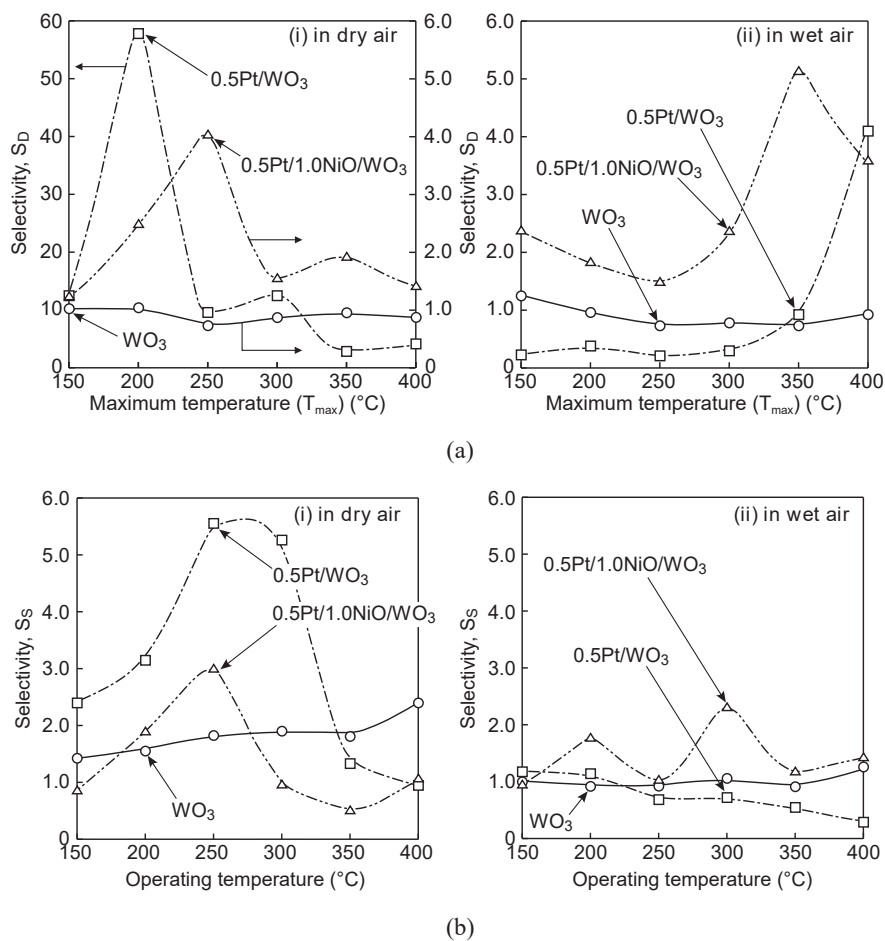


Fig. 7. Variations in acetone selectivity of WO₃, 0.5Pt/WO₃, and 0.5Pt/1.0NiO/WO₃ sensors against H₂ in dry and wet air, with T_{max} and operating temperature under dynamic and static temperature operations, respectively. (a) Dynamic operation (temperature modulation). (b) Static operation (constant temperature).

in wet air. This result indicates that the loading of NiO reduced the negative effect of moisture on the acetone selectivity against H_2 under static temperature operation. On the other hand, the S_D of the WO_3 sensor under dynamic temperature operation was smaller than its S_S under static temperature operation both in dry and wet air, while the S_D of the $0.5Pt/WO_3$ sensor in dry air was largely improved by the dynamic temperature modulation. However, the S_D of the $0.5Pt/WO_3$ sensor markedly decreased with the addition of moisture into the gaseous atmosphere. The S_D of the $0.5Pt/1.0NiO/WO_3$ sensor, which was much smaller than that of the $0.5Pt/WO_3$ sensor in dry air, increased at higher temperatures by the addition of moisture, and the $0.5Pt/1.0NiO/WO_3$ sensor showed the largest acetone selectivity against H_2 with a relatively large acetone response [see Fig. 5(b-i)] when it was operated in dynamic temperature-modulation mode with T_{max} of 350 °C. The large acetone selectivity against H_2 (S_D) and the large acetone response ($R_{D(Ac)}$) of the $0.5Pt/WO_3$ and $0.5Pt/1.0NiO/WO_3$ sensors in dynamic temperature-modulation mode in dry air probably result from the effective adsorption of a large amount of acetone and/or the partial oxidation products on the Pt-loaded WO_3 surface in the temperature range between RT and the medium temperature (e.g., one hundred and several tens of degrees Celsius) and subsequent abrupt catalytic combustion of these adsorbates in the temperature range between medium temperature and T_{max} . In addition, the loading of NiO on the WO_3 improved the S_D and $R_{D(Ac)}$ of the WO_3 and $0.5Pt/WO_3$ sensors in wet air. Kim *et al.* suggested that NiO-loaded SnO_2 sensors exhibit an excellent CO response that is independent of humidity (ca. 25%RH), because NiO loaded on the SnO_2 surface served as a strong humidity absorber and it protected the SnO_2 from being affected by water-derived species.⁽⁴¹⁾ According to the discussion, the relatively large S_D and $R_{D(Ac)}$ of the $0.5Pt/1.0NiO/WO_3$ sensor operated in dynamic temperature-modulation mode even in wet air may be associated with the selective adsorption of water molecules onto the NiO, which assisted the adsorption and subsequent catalytic combustion of acetone and/or its partial oxidation products onto active Pt/ WO_3 regions on the $0.5Pt/1.0NiO/WO_3$ sensor.

4. Conclusions

The acetone-sensing properties of WO_3 , $mNiO/WO_3$, and $nN/mNiO/WO_3$ sensors operated in dynamic temperature mode with sinusoidal modulation of V_h {amplitude: $0-V_{h,max}$ V [$V_{h,max}$: 0.6 V (for 150 °C)–1.6 V (for 400 °C)] and a period of 6 s} in dry and wet air have been investigated and the effects of the dynamic temperature operation and the co-loading of Pt and NiO onto WO_3 on acetone response and acetone selectivity against H_2 have been clarified in this study. The $R_{D(Ac)}$ and $R_{D(H_2)}$ of the WO_3 sensor was negligible, but the loading of a noble metal onto the WO_3 was effective in improving the $R_{D(Ac)}$ and $R_{D(H_2)}$. The $0.5Pt/WO_3$ sensor showed the largest $R_{D(Ac)}$ among all the $0.5N/WO_3$ sensors tested in dry air, but the addition of moisture into the gaseous atmosphere markedly reduced the $R_{D(Ac)}$ of the $0.5Pt/WO_3$ sensor. The loading of NiO improved the negative effect of moisture on the S_D as well as $R_{D(Ac)}$ of the WO_3 and $0.5Pt/WO_3$ sensors, and the $0.5Pt/1.0NiO/WO_3$ sensor showed the most excellent acetone-sensing properties in wet air. In addition, the operation of the sensors in dynamic temperature modulation mode effectively enhanced the acetone response and the acetone selectivity against H_2 in comparison with the operation in static constant temperature mode, probably because a large amount of acetone and/or the partial oxidation products adsorbed on the oxide surface at low temperatures and, subsequently, they reacted with oxygen adsorbates at high temperatures to decrease the resistance of the sensors.

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