

Effects of Flameless Catalytic Combustion of Hydrogen on the Parameters of Catalytic Sensors with Platinum-group Catalysts

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The response of catalytic hydrogen sensors with platinum-group catalysts (Pt + 3Pd, Pt, Pd, Ir, and Rh) in the room temperature range has been studied. It was demonstrated that a flameless catalytic hydrogen combustion reaction on the Pt and Pt + 3Pd catalysts occurs at 20 °C, which results in the heating of the sensing element of a catalytic sensor, and the microheater resistance increases. The microheater temperature was first measured, and it was shown that the temperature increases by 99 and 83 °C in the calibration gas mixture containing 0.96% vol. hydrogen for the Pt and Pt + 3Pd catalysts, respectively. A method has been provided for measuring hydrogen levels using a catalytic sensor without heating voltage input.

1. Introduction

Recently, hydrogen energy production has attracted increasing attention.^(1,2) Owing to the rapid development of hydrogen energy, there is an increased interest in producing hydrogen sensors, which are considered an important component of industrial safety.^(3–5) As for catalytic sensors of hydrogen, their main disadvantages include low selectivity to flammable gases and the need to heat the catalyst to temperatures exceeding 200 °C, which leads to the increased danger of using sensors in a hydrogen environment.⁽⁶⁾

The possibility of designing low-temperature catalytic hydrogen sensors is extremely attractive since it can significantly expand the areas of their industrial use, particularly where low-power sensors are required for long-term autonomous operation. Despite advances in their miniaturization, catalytic sensors, remain the most energy-consuming components of sensor nodes.^(7,8) Although applications of catalytic sensors with a power consumption of <10 mW have already been published⁽⁹⁾, the power consumption of industrial catalytic sensors exceeds 100 mW.^(10,11) The reduction in power consumption, which is realized simultaneously with the reduction in operating temperature, makes them suitable for applications requiring long-term autonomous operation, such as autonomous wireless sensor networks. Simultaneously, the

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operating temperature reduction increases the safe operation of sensors in a hydrogen–air environment.

Previously, a study was conducted on the temperature dependences of hydrogen sensors' responses with platinum-group catalysts, namely, the Pt + 3Pd and Ir catalysts at low and negative ambient temperatures.⁽¹²⁾ As a result, the temperature for the initiation of the catalytic hydrogen reaction was determined. In particular, it was found that for Pt + 3Pd catalyst sensors, the reaction initiation temperature of catalytic hydrogen combustion is in the range of 17–22 °C. For iridium-based catalysts, hydrogen combustion is induced at a temperature of about 190 °C.

The ability to burn hydrogen on a Pt + 3Pd catalyst at room temperature has made it possible to develop methods for the low-temperature measurement of hydrogen.⁽¹²⁾ In addition, it was demonstrated that decreasing the operating temperature of the sensor makes it possible to design selective hydrogen sensors capable of measuring hydrogen levels in mixtures of combustible gases, including hydrocarbons.⁽¹³⁾

The results are consistent with earlier studies of catalytic hydrogen combustion on platinum catalysts. Thus, for the Pd-based catalysts and a 30% vol. hydrogen concentration, the critical temperature of self-initiation (catalytic ignition temperature) was about 0 °C.⁽¹⁴⁾ A promising goal of the work is the development of a catalytic hydrogen sensor that can measure hydrogen in the room temperature range.

This research is aimed at studying the resistance and temperature of the sensing element of catalytic sensors with platinum-group catalysts during the flameless combustion of hydrogen in the pre-explosive concentration range. Particular attention is paid to measuring the parameters of catalytic sensors in the room temperature range. Notably, the ignition of hydrogen gas mixtures over the surface of platinum-group catalysts was previously studied.⁽¹⁵⁾ Along with that, no studies have been devoted to the assessment of the possibility of measuring the hydrogen concentration in air without forcedly heating the catalytic sensor.

2. Experiment Details

Each catalytic hydrogen sensor included working and reference sensing elements in the form of pellistors placed in a housing. The pellistors were made as a platinum microheater covered with a highly porous γ -Al₂O₃ layer. The working sensing element was impregnated with a catalyst. The sensors were manufactured by the Scientific and Technical Center of Measuring Gas Sensors, Lyubertsy, Russia.⁽¹⁶⁾ Their structure and manufacturing technology were described in detail in Ref. 17. In this work, sensors with platinum-group catalysts (Pt + 3Pd, Pt, Pd, Ir, and Rh) were studied.

To measure the current–voltage characteristics and response of catalytic sensors in a hydrogen–air environment, a Wheatstone bridge circuit was used. The working (R_{act}) and reference (R_{ref}) sensing elements were located in one branch, whereas precision resistors (R) with a nominal value of 10 k Ω were placed in the other branch [Fig. 1(a)]. To perform measurements, a heating voltage in the range from 0 to 3 V with an increment of 0.1 V was applied to the Wheatstone bridge circuit. A more detailed description of the measuring circuit is given in Ref. 12. A calibration gas mixture (CGM) containing 0.96% vol. hydrogen in air and

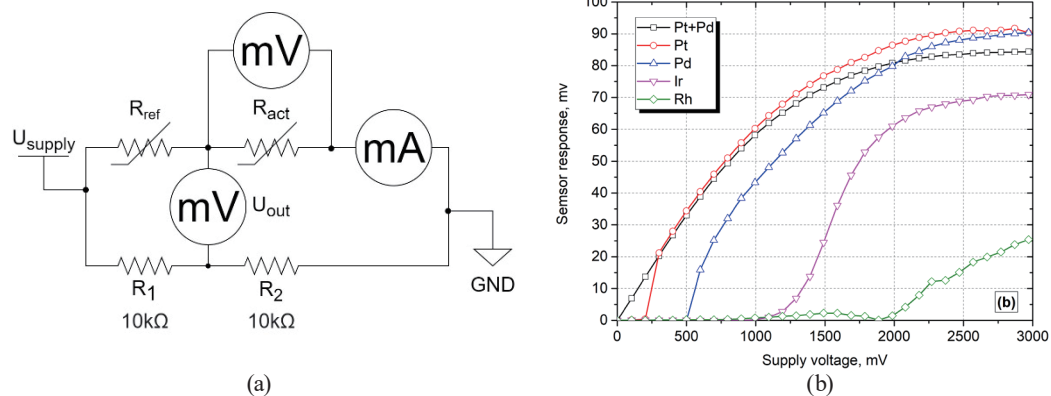


Fig. 1. (Color online) (a) Bridge measuring circuit and (b) dependence of catalytic sensor response on applied heating voltage for 0.96% vol. hydrogen with the Pt + 3Pd, Pt, Pd, Ir, and Rh catalysts.

mixtures containing 0.24 and 0.48% vol. hydrogen were used as hydrogen sources. A CGM of methane with a concentration of 1.01% vol. was used as a reference gas.

To measure the resistance of the working sensing element without applying a heating voltage, a measuring circuit was used where the catalytic sensor was powered down, and a multimeter operating in the resistance mode was connected to the outputs of the working sensing element. In addition to the working sensing element, the reference element was also measured.

A flow chamber with an embedded sensor, and a volume of 0.125 L, and equipped with gas supplying and discharging holes was used for experiments. The time to fill the chamber with the gas mixture was 5 min. The gas consumption rate was measured using a rotameter and was set at 2.52 L/h. This facilitated the control of the gas volume in the chamber at constant levels. The chamber was ventilated before the new gas was introduced.

3. Results and Discussion

The dependence of the catalytic sensor response (U_{out}) with the Pt + 3Pd, Pt, Pd, Ir, and Rh catalysts on the applied heating voltage (U_{supply}) in a CGM containing 0.96% vol. hydrogen is shown in Fig. 1(b). It can be seen that the Pt + 3Pd catalyst sensor response begins at room temperature, increases rapidly with heating voltage, and reaches saturation at about 2000 mV. A shift to the right was observed for similar dependences for sensors with the Pt, Pd, Ir, and Rh catalysts by 0.2, 0.5, 1.2, and 1.9 V, respectively. To associate the applied voltage and heater temperature, the dependence of platinum heater temperature on the applied voltage in air is shown in Fig. 2(a). Thus, one can conclude that the catalytic hydrogen combustion on the Pt + 3Pd and Pt catalysts occurs at room temperature. To activate Pd, slight heating is required. Whereas for the Ir and Rh catalysts, the level of heating should be considerable. An increase in microheater temperature as a result of hydrogen combustion leads to an increase in resistance that can be measured.

To determine the resistance of the sensor microheater, the dependences of $I = f(U_{supply})$ in the air and hydrogen CGM were measured [Figs. 2(b)–2(f)]. Figure 2(b) shows that the dependence

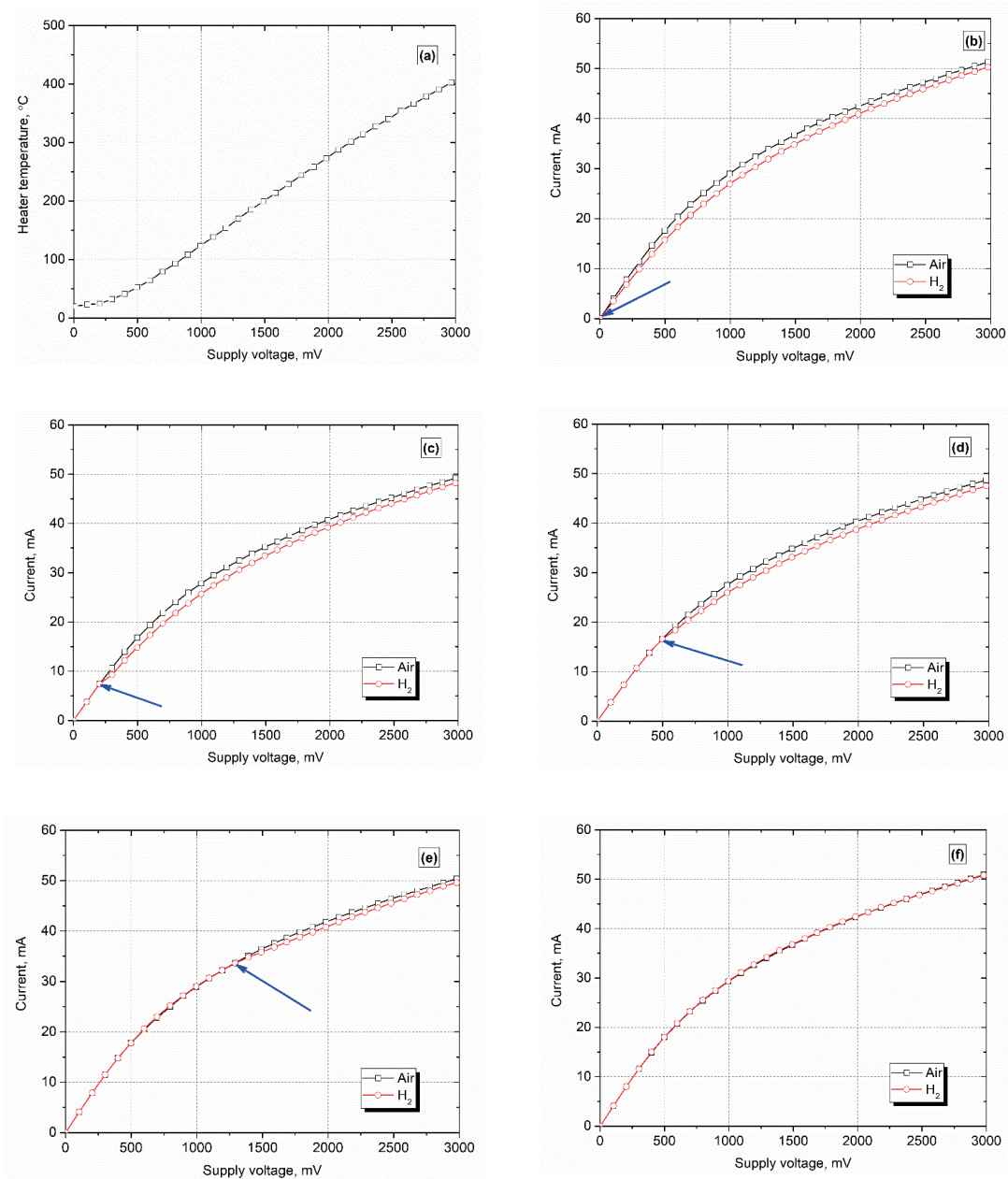


Fig. 2. (Color online) Dependences of (a) platinum microheater temperature on heated voltage (U_{supply}) in air and (b) of $I = f(U_{supply})$ in hydrogen CGM and air for sensors with (b) Pt + 3Pd, (c) Pt, (d) Pd, (e) Ir, and (f) Rh catalysts.

of $I = f(U_{supply})$ Pt + 3Pd in the hydrogen CGM is lower than that in the air, as well as they have different slopes near-zero voltage values. This can be explained by further increase in microheater resistance as a result of catalytic hydrogen combustion.

Similar dependences were obtained for the Pt, Pd, Ir, and Rh catalyst sensors. As shown in Figs. 2(c)–(f), the dependences of $I = f(U_{supply})$ in the air and hydrogen CGM coincide up to the voltage at which hydrogen combustion is induced (arrows indicate the voltage U_{supply} at which

there is still no hydrogen combustion). With further increase in the voltage U_{supply} , the dependence of $I = f(U_{supply})$ in a hydrogen environment is below $I = f(U_{supply})$ in air. On the basis of the obtained dependences, the dependences of the platinum microheater temperature on the heating voltage applied to the sensor in air and hydrogen CGM were calculated.

The temperature (T_h) of the platinum microheater was calculated as

$$R = R_0 (1 + \alpha (T_h - T_0)), \quad (1)$$

where R_0 is the platinum microheater resistance at $T_0 = 20$ °C and α is the resistance temperature coefficient of the platinum wire that is equal to 0.0035 1/K.

The dependences of the platinum microheater temperature on the applied voltage in the air and hydrogen CGM for sensors with the Pt + 3Pd, Pt, Pd, Ir, and Rh catalysts were calculated using Eq. (1). The obtained dependences are given in Fig. 3.

Figure 3(a) shows that for the Pt + 3Pd catalyst sensor at an ambient temperature of 20 °C, the appearance of hydrogen in the air results in a spontaneous increase in microheater temperature by 83 °C. This is a consequence of catalytic hydrogen combustion. Thus, the sensing element temperature increases spontaneously and reaches 103 °C without applying a heating voltage (U_{supply}). The obtained result can be explained as follows. With hydrogen appearance in the air, an exothermic reaction of the oxidation (combustion) of hydrogen takes place on the catalyst surface, i.e., $2H_2 + O_2 \rightarrow 2H_2O + Q\uparrow$. In this reaction, $Q = 230$ kJ/mol of heat is emitted. In this case, the catalyst surface is spontaneously heated to some quasi-equilibrium temperature. The heated surface also heats the γ -Al₂O₃ layer and the platinum microheater. It is apparent that the surface temperature of the sensing element in the steady-state combustion mode should be slightly different from that of the microheater.

When the heating voltage (U_{supply}) is applied to the bridge measuring circuit, the operating sensor temperature in the hydrogen CGM remains higher than that in the air. However, the difference in temperature decreases from 83 °C at zero U_{supply} to 50 °C at $U_{supply} = 3$ V [Fig. 3(a)]. This finding can easily be explained by emission from a heated surface. The power emitting from the surface of the heated body is proportional to $(T - T_0)^4$. Since the surface temperature of the sensing element in hydrogen is higher, more power is emitted from its surface. Therefore, the difference between the temperatures of the sensitive elements in the air and hydrogen–air environment (ΔT) will decrease with increasing heating voltage (U_{supply}).

A similar result is observed for Pt catalyst sensors [Fig. 3(b)]. The sensor temperature increases by 99 °C and reaches 119 °C without applying the heating voltage. When the heating voltage (U_{supply}) is applied, the temperature of the platinum microheater in the hydrogen CGM remains higher than that in the air. However, the temperature difference (ΔT) decreases with increasing heating voltage (U_{supply}).

The microheater resistance and temperature of sensors with the Pd, Ir, and Rh catalysts do not change at 20 °C [Figs. 3(c)–3(f)]. Resistance and temperature changes in the microheater begin after the onset of hydrogen combustion.

To further confirm that the observed increase in the temperature of the operating sensor micro-heater was caused by hydrogen combustion, both the working and reference sensing

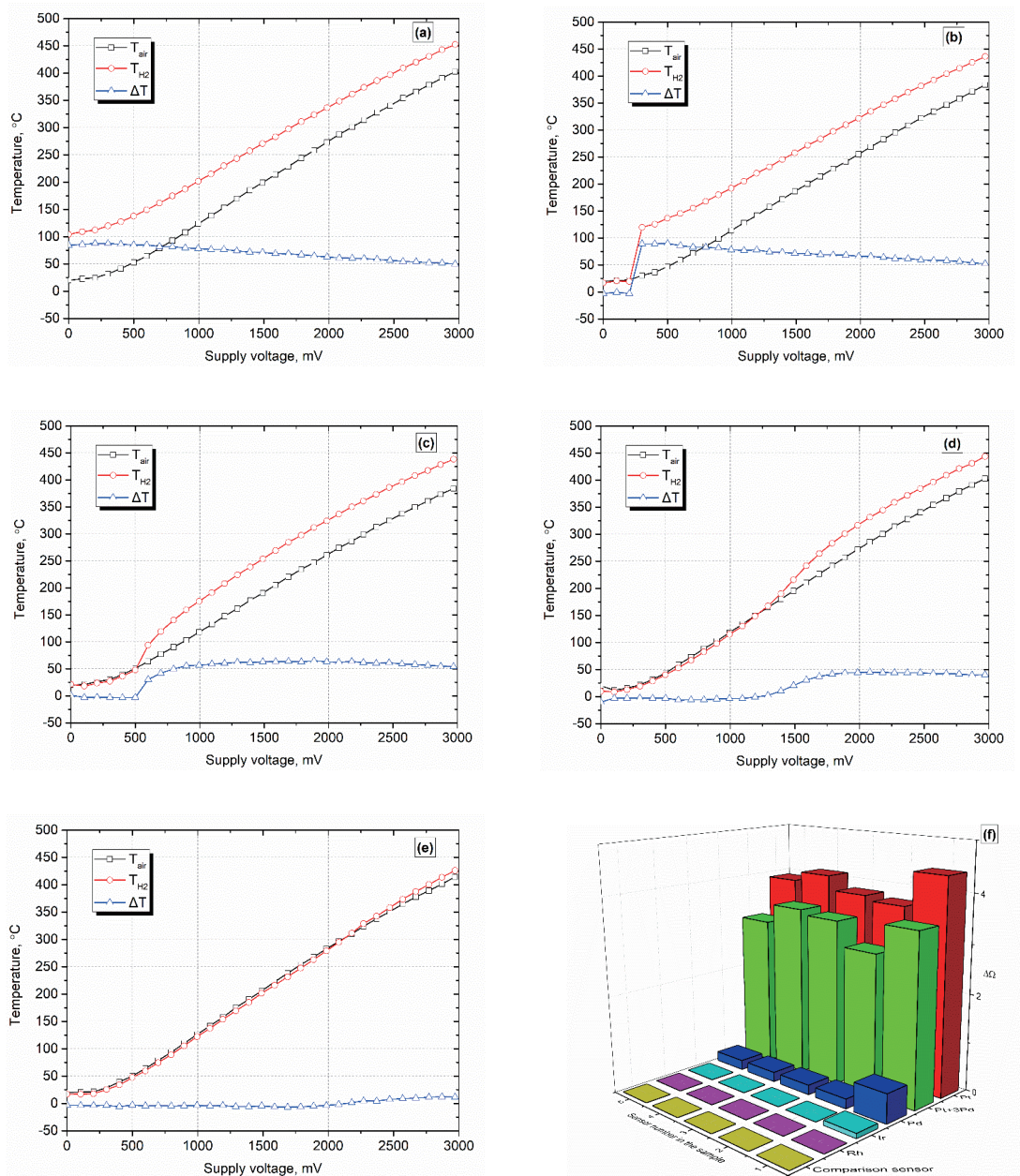


Fig. 3. (Color online) Dependences of platinum microheater temperature on supply voltage in air and hydrogen CGM, for sensors with (a) Pt + 3Pd, (b) Pt, (c) Pd, (d) Ir, and (e) Rh catalysts, and (f) diagram of platinum microwire resistance change for five catalytic hydrogen sensors with different types of platinum-group catalysts.

elements were tested in methane (1.01% vol.). According to Table 1, the microheater temperature and resistance do not change in these tests.

Table 1

Measured resistance and temperature values for microheater of catalytic sensor with platinum-group catalysts in hydrogen and methane media.

Catalyst	Sensor resistance (Ω) at					Temperature ($^{\circ}\text{C}$) at			
	0	0.24	0.48	0.96	1.01	0.24	0.48	0.96	1.01
	% vol. H_2	% vol. H_2	% vol. H_2	% vol. H_2	% vol. CH_2	% vol. H_2	% vol. H_2	% vol. H_2	% vol. CH_2
Pt + 3Pd	12.1	12.4	13.7	15.6	12.1	27	58	103	20
Pt	12.7	13.8	15	17.1	12.7	45	72	119	20
Pd	12.8	12.8	12.9	13	12.8	21	22	24	20
Ir	11.8	11.8	11.8	11.8	11.8	20	20	20	20
Rh	10.8	10.8	10.8	10.8	10.8	20	20	20	20
Reference sensing elements	12.2	12.2	12.2	12.2	12.2	20	20	20	20

4. Novel Approach to Hydrogen Measurement by Catalytic Sensor

The unexpectedly high level of spontaneous heating of the catalytic sensor sensing element with the Pt + 3Pd and Pt catalysts in the hydrogen–air mixture at room temperature (i.e., without forced sensor heating) opens up the potential for a fundamentally novel approach to hydrogen detection based on catalytic sensors.

In the traditional approach to gas concentration measurements, the measured quantity is the response of a catalytic sensor (usually, a voltage) included in a Wheatstone bridge or voltage divider circuit. A current must flow through the sensor to heat the catalyst to the operating temperature at which hydrogen combustion begins. One of the main problems of catalytic sensors is their high power consumption, which limits their use in stand-alone gas detectors. Avoiding heating the sensing element of a catalytic sensor can significantly expand their application area and simplify or reduce the price of hydrogen sensors.

In cases where catalytic combustion takes place at room temperature, hydrogen detection can be performed using the mode of microheater resistance measurement due to the spontaneous increase in its temperature as a result of hydrogen flameless combustion on the catalyst.

This approach to measuring hydrogen levels has been tested. A diagram displaying the measurement of the sensing element resistance with various platinum-group catalysts at room temperature is given in Fig. 3(f). Each group included five sensors with catalysts based on Pt + 3Pd, Pt, Pd, Ir, and Rh.⁽¹⁷⁾ In addition, the resistances of five reference sensing elements were measured.

The measurement results show that on the Pt and Pt + 3Pd catalysts, a spontaneous catalytic hydrogen combustion reaction takes place at 20 $^{\circ}\text{C}$. A very low grade reaction occurs on the Pd catalyst. Sensors with the Ir- or Rh-based catalysts and reference sensors demonstrate no activity to hydrogen at room temperature. The arithmetic means of the calculated temperatures are presented in the column “0.96 % vol. H_2 ” in Table 1.

It is important to note that the heater resistance changes for the Pt + 3Pd and Pt catalysts are 3.5 and 4.4 Ohm, respectively. This is a significant change in resistance for 0.96% vol. hydrogen. Therefore, in the range of pre-explosive concentrations (0 to 4% vol. hydrogen), instead of

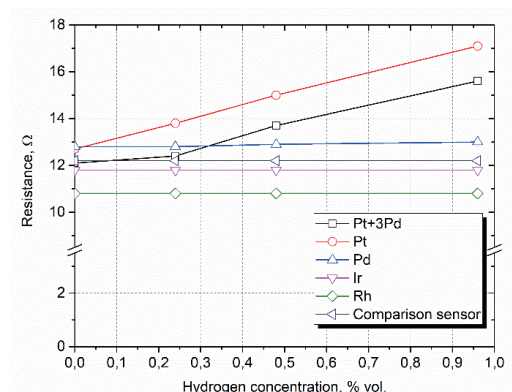


Fig. 4. (Color online) Change in catalytic sensor microheater resistance with different platinum-group catalysts as a function of hydrogen concentration.

measuring the response voltage in the full bridge circuit, one may measure the sensor microheater resistance at room temperature. Importantly, the absence of the need to apply a heating voltage to the catalytic sensor reduces the power consumption of the sensor to virtually zero. Moreover, the safety of measurements in hydrogen-containing media is improved.

The dependences of resistance changes of the catalytic sensor microheater with platinum-group catalysts on hydrogen concentration are given in Fig. 4. As shown, the Pt-catalyst-equipped sensor has a linear dependence. The resistance of sensors with the Pd or Pt + 3Pd catalyst varies nonlinearly when the hydrogen concentration is low. This may be due to the inaccuracy of resistance measurement in the area of low hydrogen concentration, as well as to the junction resistance interference. The resistances of the reference and working sensors do not change with the Ir- or Rh-based catalyst.

This experiment facilitated the evaluation of changes in sensor microheater resistance depending on the gas concentration when using different catalysts. The results of the temperature calculation of the sensing elements of sensors are summarized in Table 1.

5. Conclusions

The effect of initiating the reaction of the flameless hydrogen combustion on platinum-group catalysts in catalytic sensors was studied. It was demonstrated that for the Pt- and Pt + 3Pd-based catalysts, catalytic ignition occurs at 20 °C. This reaction is accompanied by the spontaneous heating of the sensing element, which becomes apparent with the increased resistance of its platinum microheater. The microheater temperature change in a hydrogen medium was first measured. It was demonstrated that the sensor microheater temperature increases by 99 and 83 °C in the CGM containing 0.96% vol. hydrogen for the Pt and Pt + 3Pd catalysts, respectively.

These results enable the measurement of hydrogen concentration using a catalytic sensor without heating voltage input. The proposed approach is based on measuring the resistance of the catalytic sensor microheater. This method can be used in hydrogen detectors in the range of pre-explosion concentrations.

Measuring at room temperature solves a number of technical issues:

- selectivity of hydrogen concentration measurement in the mixture with hydrocarbons, since hydrocarbons are inflammable on platinum-group catalysts at room temperature;
- simplification of the measuring circuit, as the application of heating voltage is not required;
- increase in sensor reliability, as platinum microwire burnout is excluded when heated to high temperatures, and natural catalyst degradation at high temperatures is also prevented.
- owing to the absence of heating, the power consumption of gas analyzers with catalytic hydrogen sensors decreases, which facilitates their battery operation;
- increase in the safety of measurement in hydrogen–air mixtures;
- increase in sensor service life, also due to the slowdown of catalyst deterioration with anticatalysts, particularly H₂S.

On the other hand, a thermal catalytic sensor with the Pt and Pt + 3Pd catalysts spontaneously “turns on” when there is hydrogen in the air. If the sensor did not have an explosion-proof housing, such an increase in the temperature of the sensing element of the sensor could lead to disastrous consequences as a result of the transition from the flameless combustion of hydrogen to its flame combustion associated with an explosion. In addition, spontaneous heating can complicate hydrogen sensor calibration in the traditional approach to hydrogen concentration measurements and its subsequent operation in assembly with hydrogen sensors, gas analyzers, and gas monitoring systems.

Thus, the activity of the Pt and Pt + 3Pd catalysts at room temperature is rather a disadvantage in their application in catalytic hydrogen sensors in the traditional approach. Therefore, Pd is the optimal catalyst among all the studied ones.

After scaling, the obtained results can also be used in various fields of technology. In particular, they can be used in flameless combustion systems of hydrogen accumulating in the workplace owing to technological processes, i.e., to prevent the formation of explosive gas mixtures.⁽¹⁸⁾ The study of sensors with platinum-group catalysts (Pt, Pd, and Pt + 3Pd) in the range of hydrogen concentrations up to 100% in the room temperature range is a future research task.

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