Development of a selective sensor for the determination of hydrogen

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Abstract. The composition of the catalyst (70% ZrO₂ and 30% Cu₂O) and the optimal conditions for the selectivity of hydrogen oxidation in the presence of combustible ingredients have been developed. Using a selected catalyst and optimal conditions, selective thermocatalytic hydrogen sensors are manufactured. In the range of hydrogen concentrations of 0.11 – 4.10% vol. the dependence of the sensor signal on the concentration is rectilinear. With continuous operation of the sensor for 1000 hours, the signal value remains stable. The presence of carbon monoxide (up to 1.4%), ammonia (up to 1.7%), and methane (up to 1.2%) in the analyzed mixture does not affect the value of the output signal of the hydrogen sensor. The developed sensors can be used as part of automatic gas analyzers and signaling devices.

1. Introduction
To ensure the safety of operations in many facilities, particularly in the production of hydrogen, methanol, and ammonia in mines and mines, constant monitoring of the hydrogen content in the air is required [1]. In recent years, there has been a tendency to increase the number of studies related to the creation of chemical sensors of combustible gases based on the thermocatalytic method [2]. Thermocatalytic sensors (TCR) and analyzers are among the most promising devices and installations for monitoring the combustible components of a mixture of gases, in particular hydrogen [3, 4].

2. Methods
The analytical signal of the TCR is the output voltage proportional to the concentration of the determining component in the analyzed mixture [5,6]. Structurally, a thermocatalytic hydrogen sensor (TKS-H₂) is a pair of sensing elements and a pair of resistors included in the bridge circuit [7]. Sensitive elements, depending on the purpose, are divided into measuring and compensating sensitive elements. Both sensitive elements are located in the reaction chamber [8]. The catalyst for the measuring sensor element of known sensors is a mixture of platinum and palladium obtained in certain ratios. The main disadvantage of these sensors is the lack of selectivity in determining the individual components of a gas mixture [9]. One of the possible ways to ensure the selectivity of the thermocatalytic determination is to use a measuring sensor element with a selective catalyst for the oxidation process of the component being determined.
This work aims to ensure the selectivity of the thermocatalytic determination of the volume concentration of gas (H₂) using optimal conditions and a selective catalyst for the hydrogen oxidation process.

3. Results and discussion

To develop a selective thermocatalytic sensor for the continuous selective determination of hydrogen in the presence of such combustible air ingredients as carbon monoxide, ammonia, and methane, the laws of oxidation of combustible substances on various catalysts were studied. The development of a catalyst for selective TKS-H₂ was carried out on a flow-type installation with a stationary catalyst layer. During the experiments, the catalytic characteristics of several individual oxides and their mixtures were studied... The selection of the catalyst and the optimal conditions for the oxidation of combustible substances was carried out at a temperature of 100-300 °C, the feed rate of the gas-air mixture was 10 l/h, the content of the combustible component in the mixture (% vol.): H₂-2.20; CO-2.45; NH₃-2.00 and CH₄-2.50. Experiments on the selection of selective catalysts for TCR-H₂ were carried out in the presence of metal oxides (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Sn, Bi, etc.), which according to [10] are the most active catalysts of the oxidation process. Experiments carried out in the range of 100-300 °C allowed us to establish the following series of activity of metal oxides during the oxidation of hydrogen (the oxides are arranged in order of decreasing their catalytic activity during the oxidation of hydrogen by air oxygen): Co₃O₄>MnO₂>Cu₂O>ZrO₂>SnO₂>CuO>ZnO>CdO>Cr₂O₃>Fe₂O₃>V₂O₅>Bi₂O₃.

It should be noted that the highest selectivity in the oxidation of hydrogen in the presence of carbon monoxide of ammonia and methane is observed on catalysts based on Si₃O and ZrO₂. The results of studying the activity and selectivity of Si₃O and ZrO₂ in the process of oxidation of combustible gases are shown in table 1.

Table 1. Activity and selectivity of Cu₂O and ZrO₂ in the process of oxidation of combustible gases (content in the mixture: C_H₂-2.05; C_CO-1.96; C_NH₃-1.08; C_CH₄-1.85).

| Composition of the catalyst | Temperature experience, °C | Degree of oxidation (x±Δx), % | CH₄ | H₂ | CO | NH₃ |
|----------------------------|---------------------------|-------------------------------|-----|----|----|-----|
| Cu₂O                       | 100                       | -                             | 46.5±0.3 | 8.0±0.2 | -   |
|                            | 200                       | -                             | 100.0±0.8 | 17.5±0.3 | 5.0±0.2 |
|                            | 300                       | 11.6                          | 100.0±1.0 | 31.0±0.5 | 18.0±0.3 |
|                            | 100                       | -                             | 21.0±0.4 | - | - |
| ZrO₂                       | 200                       | -                             | 64.0±0.2 | 18.0±0.2 | -   |
|                            | 300                       | -                             | 100.0±0.6 | 27.6±0.1 | 6.5±0.1 |

As follows from the data given (table 1), CH₄ NH₃ in the presence of Cu₂O and ZrO₂ at 200°C practically do not oxidize. At 100 °C in the presence of Cu₂O, the degree of oxidation of hydrogen and carbon monoxide by air oxygen is equal to 46.5; 8.0 %, respectively; thus, the conducted studies show that catalysts based on individual metal oxides do not provide high selectivity in the thermocatalytic determination of individual components in a mixture of gases, which are often found together in various natural and technological objects. The obtained data indicate the possibility of using Cu₂O and ZrO₂ as a catalyst for a selective thermocatalytic hydrogen sensor.

The results of studying the effect of copper(I) ratios and zirconium oxides on the degree of oxidation of combustible gases on the surface of the catalyst of the TKS-H₂ sensitive measuring element are presented in table 2. As follows from the above data (table 2), the developed catalyst in a wide range of component ratios is characterized by high activity and selectivity of hydrogen oxidation in the presence of combustible substances.
The selection of optimal nutrition are experiments, a gas mixture with a composition sensor were laid on a compensation sensor element is made using aluminum oxide, etc.

In the experiments, it was found that noted on the diagram tape and was taken as the beginning of the time reference. In the results of the segment of a diagram tape, 15 cm long. The change in the concentration at the input of TCR "Industrial automatic gas analyzers". The calibration characteristic of the thermocatalytic sensor was determined at a temperature of 20°C and a pressure of 760 mmHg, and are relative humidity of 60%. The experiments were carried out in the conditions hydrogen concentration of 0.1-4.5% vol.

As follows from the figure, the optimal power supply for a thermocatalytic hydrogen sensor is 1.6 V. An increase or decrease in the power supply value from the optimal value is accompanied by a decrease in the value of the useful analytical signal and deterioration in the selectivity of the hydrogen determination.

| Composition of the catalyst, mass. % | Degree of oxidation(x±Ax), % |
|-----------------------------------|-----------------------------|
| Cu2O–ZrO2(20-80)                  | H2  96.0±0.8                |
|                                  | CO  -                        |
|                                  | CH4 -                        |
|                                  | NH3 -                        |
| Cu2O–ZrO2(30-70)                  | 100.0±0.8                   |
|                                  | 1.0±0.1                     |
|                                  | -                           |
|                                  | -                           |
| Cu2O–ZrO2(40-60)                  | 100.0±1.0                   |
|                                  | 2.5±0.4                     |
|                                  | -                           |
|                                  | --                          |
| Cu2O–ZrO2(50-50)                  | 100.0±1.1                   |
|                                  | 4.5±0.4                     |
|                                  | -                           |
|                                  | -                           |

Thus, as a result of the conducted studies on the activity and selectivity of metal oxides, the composition and ratio of the catalyst components (30% Cu2O–70% ZrO2) for the sensitive measuring element of the selective thermocatalytic hydrogen sensor was selected. This catalyst provides selective oxidation of hydrogen in the presence of carbon monoxide, methane, and ammonia, which are often found with hydrogen, in the atmospheric air of mines, process gases, exhaust gases of motor vehicles, etc.

Taking into account the urgency of the problem, a selective thermocatalytic hydrogen sensor was manufactured, which includes two sensitive elements (measuring and compensating), and two resistors connected to the bridge circuit. The measuring sensor element of the sensor contains a catalytic coating (70% ZrO2 30% Cu2O) that provides selective oxidation of hydrogen in the presence of carbon monoxide, ammonia, and methane. The compensation sensor element is made using aluminum oxide, which ensures the identity of its design with the measuring sensor element. A batch (5 pcs) of selective TCR-H2 operating as part of an automatic hydrogen analyzer was tested. The developed sensors were examined to determine their metrological characteristics and compare the results with well-known domestic and foreign samples.

The TKS-H2 test procedure includes the full scope of control and special tests related to the selection of the optimal sensor power supply, the study of dynamic, calibration, and other characteristics, as well as the identification of the selectivity and stability of the sensor. The experiments were carried out at a temperature of 202°C and a pressure of 730 10 mm Hg. In the experiments, a gas mixture with a hydrogen concentration of 0.1-4.5% vol was used, the feed rate of which was kept constant at 20 l/h.

The dependence of the signal value on the power supply was studied in the range of 1.0-3.0 V. The experiments were carried out under normal conditions on the example of a gas-air mixture with a hydrogen concentration of 1.20% vol. The results obtained on the selection of optimal nutrition are shown in figure 1.

As follows from the figure, the optimal power supply for a thermocatalytic hydrogen sensor is 1.6 V. An increase or decrease in the power supply value from the optimal value is accompanied by a decrease in the value of the useful analytical signal and deterioration in the selectivity of the hydrogen determination. The dynamic characteristics of the TKS-H2 were tested with a sudden change in the hydrogen concentration at the sensor input. The experiments used HS with a hydrogen concentration of 1.60, 2.23, and 2.80% vol. Checking the dynamic characteristics of the sensor was accompanied by a continuous recording of the transition process of the diagram tape of the recording device, the speed of which was chosen such that the transition process schedule was adequate to GOST 133220-81 "Industrial automatic gas analyzers". The general technical parameters of the sensor were laid on a segment of a diagram tape, 15 cm long. The change in the concentration at the input of TCR-H2 was noted on the diagram tape and was taken as the beginning of the time reference. In the results of the experiments, it was found that the time of the TCR-H2 transition process is 8-10 s.

The calibration characteristic of the thermocatalytic sensor was determined at a temperature of 20°C, a pressure of 760 mmHg, and are relative humidity of 60%. The experiments were carried out in the range of the hydrogen concentration of 0.44-4.10% vol. Each test point was characterized by six values: three for the forward and three for the reverse cycles of concentration change. The sensor signal was
recorded by a digital voltmeter after a constant value was set (at least 3 minutes after the PGS was applied).

Some results of determining the calibration characteristic of the hydrogen sensor are presented in table 3, from which it follows that in the studied interval, the dependence of the analytical signal of the sensor on the concentration of hydrogen in the HS is rectilinear. The sensor stability tests were performed under normal conditions. In the experiments, a mixture with an H₂ content of 0.44% by volume was used.

Table 3. Calibration characteristic of the TCR of hydrogen.

| H₂ content in the mixture, % volume | Sensor signal (x±Δx), mV       | S    | Sr*10² |
|------------------------------------|--------------------------------|------|--------|
| 0.11                               | 3.0±0.04                       | 0.31 | 0.5    |
| 0.44                               | 12.4±0.14                      | 0.16 | 1.2    |
| 1.60                               | 46.0±0.36                      | 0.25 | 0.5    |
| 2.23                               | 62.4±0.36                      | 0.30 | 0.5    |
| 2.80                               | 79.0±0.37                      | 0.30 | 0.4    |
| 4.10                               | 117.0±0.31                     | 0.26 | 0.2    |

Checking the values of the input signals in time was monitored during continuous operation of the TCR for 1000 hours. The input signal measurement during a regulated time interval was recorded on the chart tape of the recording device while simultaneously recording the temperature and pressure of the environment. When processing the test results, random single outliers of the output signal were not taken into account, with the duration of each outlier not exceeding 10 seconds and the number of outliers not exceeding three during each day of operation of the thermocatalytic sensor. The results of the 1000-hour experiment are presented in table 4, from which it follows that the output signal of TKS-H₂ is stable during a regulated time interval. The change in the value of the output signal for a regulated time interval was estimated by the maximum divergence of the sensor signal:

\[ Δtg = (U_{p_{max}} - U_{p_{min}}) \times 100/U_{sc} \]  

where \( tg \) is the limit of the permissible change in the output signal for a regulated time interval; \( U_{p_{max}} \) and \( U_{p_{min}} \) are the maximum and minimum signal discrepancies; \( U_{sc} \) is the scale of the device (KSP 0-50 mV). Calculations show that the \( tg \) value for a regulated time interval is 2.2%. The selectivity of the thermocatalytic sensor for hydrogen was determined in the presence of carbon monoxide, methane, and ammonia.
The dependence of the sensor signal on the concentration is rectilinear. With continuous operation of the sensor, the value remains stable. The presence of carbon monoxide (up to 1.4%), methane (up to 4.5%), and ammonia do not affect the sensor signal.

| Table 4. Signal stability of the thermocatalytic hydrogen sensor (n = 5, P = 0.95). |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Time, hour | The value of the environment parameters, °C | x±Δx | S | Sr*10^2 |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| temperature, °C | pressure, mmHg. | Temperature | Pressure | Temperature | Pressure | Temperature | Pressure | Temperature | Pressure |
| 1 | 20.5 | 733 | 12.8±0.3 | 0.30 | 2.5 |
| 24 | 20.5 | 733 | 12.8±0.4 | 0.37 | 2.9 |
| 48 | 20.5 | 733 | 12.7±0.2 | 0.20 | 1.6 |
| 120 | 20.6 | 730 | 12.4±0.1 | 0.10 | 0.8 |
| 240 | 20.4 | 746 | 12.2±0.3 | 0.30 | 2.5 |
| 360 | 20.5 | 742 | 12.0±0.2 | 0.16 | 1.3 |
| 480 | 20.0 | 740 | 13.2±0.3 | 0.18 | 1.3 |
| 600 | 20.4 | 732 | 13.1±0.3 | 0.20 | 1.5 |
| 720 | 20.7 | 736 | 12.1±0.4 | 0.35 | 2.9 |
| 840 | 20.6 | 736 | 12.9±0.4 | 0.30 | 2.3 |
| 960 | 20.1 | 741 | 12.8±0.2 | 0.20 | 1.6 |
| 980 | 20.2 | 730 | 12.5±0.3 | 0.30 | 2.4 |
| 1000 | 20.5 | 740 | 12.4±0.3 | 0.25 | 2.0 |

The experiments were carried out when sensor 2 was powered. The input of the TCR was fed to the GS for 5 minutes with the recording of the device reading. The device was tested using 5 parallel definitions for each HS. The results obtained in determining the selectivity of the developed sensors are presented in table 5.

| Table 5. Results of determination of selectivity of TCR of hydrogen. |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Introduced hydrogen, % vol | Hydrogen found, % vol | x±Δx | S | Sr * 10^2 |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| H₂(1.40) + air(rem) | 1.41±0.04 | 0.032 | 2.3 |
| H₂(1.40) + CO (1.40) + air(rem) | 1.49±0.03 | 0.023 | 1.6 |
| H₂(1.40) + CH₄(1.20) + air(rem) | 1.42±0.03 | 0.024 | 1.7 |
| H₂(1.40) + NH₃(1.70) + air(rem) | 1.43±0.04 | 0.032 | 2.2 |

As follows from the data, the developed sensor allows you to selectively detect hydrogen in the presence of carbon monoxide, methane, and ammonia. The error of the TCR due to non-measured components does not exceed 4.5%; thus, as a result of the conducted research, a technology for manufacturing a selective thermocatalytic sensor has been developed, which provides selective control of the hydrogen content in a wide range of concentrations and parameters (temperature, pressure, humidity, etc.) of the environment.

4. Conclusion
The activity of metal oxides in the process of oxidation of combustible substances is studied. The composition of the catalyst (70% ZrO₂ and 30% Cu₂O) and the optimal conditions for the selectivity of hydrogen oxidation in the presence of combustible ingredients have been developed. Selective thermocatalytic hydrogen sensors are manufactured using the selected catalyst and optimal conditions.

It is established that the highest signal of the sensor for hydrogen is provided at the value of its power supply of 1.6 V. The increase and decrease in the power supply are accompanied by a decrease in the value of the useful signal of the sensor. In the range of hydrogen concentrations of 0.11 – 4.10% vol, the dependence of the sensor signal on the concentration is rectilinear. With continuous operation of the sensor for 1000 hours, the signal value remains stable. The presence of carbon monoxide (up to 1.4%),
ammonia (up to 1.7%), and methane (up to 1.2%) in the analyzed mixture does not affect the value of the output signal of the hydrogen sensor.

The developed sensors are not inferior in accuracy and reproducibility to known analogs, while maintaining the following characteristics: expressiveness, portability, ease of operation, and manufacture. The developed sensors can be used as part of automatic gas analyzers and signaling devices are relative.

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