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Development of A Polymer Material for A Chemical Sensor Gas-Sensitive Element that Determines Hydrogen Sulfide Based on Pan

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ABSTRACT: Recently, in chemical sensors of gases operating at low temperatures, polymeric materials with semiconducting properties are used as a gas sensitive element. One of these materials is polyacrylonitrile (PAN). The use of PAN based film as a gas sensitive material has great potential for creating sensors that operate at room temperature without heating.

Development of a technology for the production of metal-containing films based on polyacrylonitrile to create unheated sensors for detecting hydrogen sulfide and studying their properties [1].

A semiconductor sensor for detecting hydrogen sulfide, made using fuels and lubricants based on polyacrylonitrile (PAN), received the symbol "P.SS-H_2S".

It was investigated that the analytical signal of a hydrogen sulfide sensor ($\sigma_{gas}/\sigma_{weather}$) based on tungsten and copper oxides depends on the amount of the detected component (S_{H2S}) in the mixture.

The developed sensors: S.S-H_2S WO_3-5% CuO, S.S-H_2S WO_3-10% CuO and P. S.S-H_2S can be used for analytical control of hydrogen sulfide content in objects of various nature.

KEYWORDS: polyacrylonitrile, semiconductor sensor, catalyst, selectivity, sensitivity elements, copper oxide, tungsten oxide, hydrogen sulfide.

INTRODUCTION

In the world, as a result of scientific and technological progress, in the context of the rapid development of industry, the creation of chemical sensors and signaling devices that ensure the safety of industrial and residential buildings is of great theoretical and practical importance. One of the accidents observed in residential and industrial buildings is hydrogen sulfide poisoning and its explosion. Typically, the lowest explosive concentration (PPK) of hydrogen sulfide is 5% and the maximum explosive concentration (UPC) is 16%. In connection with the increase in the production and consumption of oil and gas in the country, it is important to develop express methods, reliable sensors and alarms that control the composition of atmospheric air at industrial and residential buildings [2].

The world pays special attention to the creation of inexpensive chemical sensors that provide reliable and fast control of the leakage and accumulation of explosive and toxic gases, including hydrogen sulfide. Analysis of research in the field of gas sensor production in industrialized countries has shown that the use of semiconductor sensors is the most reliable means of preventing the risk of poisoning. With the development of various sectors of the economy, mainly in the transport, energy, oil and gas industries, the need to ensure the safety of atmospheric air at industrial and residential facilities on a global scale is growing. Therefore, research aimed at the development of fast, sensitive and selective sensors that reliably control the composition of atmospheric air in closed ecosystems, including research within the framework of this master's thesis, are today one of the urgent problems of analytical chemistry [3].

This scientific research to a certain extent contributes to the implementation of the tasks set by the Decrees of the President of the Republic of Uzbekistan and the Resolutions on measures to accelerate the development of the industry of the republic, as well as other regulatory legal acts related to this. activity [4].

An analysis of the available research literature confirms that many studies of both foreign and domestic scientists have been focused on the synthesis of nanocomposite materials using the sol-gel technology and the development of sensors based on them. In particular, foreign researchers A. Sheikh, K. Prabir, K. Perso, G. Dodd, D. Rutkevich, P. Mardilovich, A. Govyadinov, S. Kh. and others were engaged in the development of methods for the synthesis of gas-sensitive sol-gel materials and control of the composition of the gas mixture.

Uzbek scientists, including B.D. Kabulov, A.M. Nasimov, T.K. Khamrakulov, N.S. Zokirov, A.M. Gevorgyan, Z.A., made a significant contribution with their research to the development of methods and sensors for monitoring environmental objects.

MAIN PART

The principle of operation of a semiconductor sensor is based on a change in the electrical conductivity of a semiconductor film as a result of the adsorption of hydrogen sulfide. To ensure high sensitivity to certain types of gases, a thin layer of catalytically active elements (Pt, Cu, Ni, Pd) with the addition of tin oxide (SnO_2) is applied to the surface of an aluminum oxide plate.

When the sensor is heated to operating temperature (up to about 400 ° C) using a single block heating element, hydrogen sulfide is adsorbed on the surface of the sensing layer. The absorption rate depends on the concentration of the gas. Under the influence of processes on the surface, the electrical conductivity of the sensor changes, i.e. the sensor signal is characterized by a change in the resistance of the gas-sensitive layer, which corresponds to the amount of hydrogen sulfide adsorbed on the sensor surface. sensitive layer. The signal value depends on the sensor model and the nature of the gas being detected. The advantages of semiconductor sensors include their low cost and simple wiring diagram. The disadvantages include the lack of a working resource (about 1 year) due to a change in the working layer interacting with controlled substances. The use of semiconductors for determining the concentration of hydrogen sulfide is based on the change in conductivity during the reverse chemisorption of these substances.

The use of semiconductor metal oxides, which are active and selective catalysts for chemical oxidation reactions in the development of semiconductor sensors, makes it possible to improve the metrological parameters of the sensor due to their high chemical stability, thermal stability, and high resistance.

The processes occurring on the surface of a semiconducting metal oxide can be regarded as a reaction of heterogeneous catalytic oxidation-reduction of a gas in the presence of oxygen converted into an electronegative ion. Atmospheric oxygen removes electrons from the conduction band as a result of adsorption on the surface of the gas-sensitive metal oxide layer (for n-type semiconductors), thereby increasing the resistance of the layer.

Reducing gases in the atmosphere (hydrogen sulfide, hydrogen, etc.) Interact with adsorbed oxygen ions, reducing their surface concentration. In this case, the released electrons return to the conduction band [5].

Along with the activity and stability of the catalyst, its most important feature is its selectivity (selectivity). Therefore, the problem of selectivity remains very important both in catalysis and in analytical chemistry. It should be noted that when studying the processes of oxidation of combustible components in a mixture of gases, the main attention of researchers is paid to the choice of active catalysts, and the problems of catalyst selectivity have not been properly solved. In this regard, the primary task of research devoted to the creation of an H_2S sensor is the selection of selective catalytic systems with high performance characteristics. In order to develop a catalyst for a selective semiconductor hydrogen sulfide sensor, the laws of oxidation of combustible substances in the presence of metal oxides have been studied.

The experiments were carried out on a special setup with a fixed catalyst bed.

Experiments on the choice of a catalyst and optimal conditions for the oxidation of combustible substances were carried out at a temperature of 350 ° C and a flow rate of the supplied gas-air mixture of 10 l / h. The activity and selectivity of metal oxides were studied in the presence of gases such as H_2, CO, CH_4, and NH_3 present in the exhaust gases from various sources along with hydrogen sulfide. The number of components in the mixture in the experiments, (%): C_{H2S}-2.20, C_{NH3}-2.20, C_{CO2}-2.20, C_{H2}-2.20, C_{CO}-2.45, C_{CH4}-2.50. CoO, NiO, Fe_2O_3, MnO_2, WO_3, CuO, and Bi_2O_3, which are the most active catalysts for the oxidation of reducing gases, were used as catalysts, and the results of studying the activity and selectivity of individual metal oxides during oxidation of these gases are shown in Table 1.

Table 1 : Results of a study of the catalytic activity of metal oxides in the oxidation of reducing gases (n = 5, P = 0.95, experiment temperature 350 ° C).

Catalyst	Complete oxidation of the gas,% $\bar{x} \pm \Delta x$				
	H_2S	NH_3	CH_4	H_2	CO
Fe_2O_3	80,0±0,3	100,0±0,9	11,8±0,1	82,5±0,7	51,5±0,4
CoO	61,0±1,0	82,5±1,5	68,7±0,4	98,0±0,8	85,0±0,9
NiO	34,0±0,3	60,0±1,0	33,4±0,4	66,0±0,5	67,0±0,8
MnO_2	69,0±0,5	88,0±1,0	49,8±0,6	100,0±1,3	100,0±1,0
Cr_2O_3	62,0±0,5	62,1±1,0	29,5±0,3	64,0±0,5	80,0±0,9
CuO	92,0±1,2	28,4±0,5	16,6±0,4	18,0±0,9	19,5±0,3
WO_3	100,0±1,4	56,0±0,4	42,0±0,4	98,0±1,1	41,1±0,5
MoO_3	48,3±0,3	33,5±0,3	19,7±0,1	30,4±0,2	25,0±0,2
V_2O_5	36,0±0,4	56,0±0,5	7,8±0,1	35,5±0,4	36,0±0,5
Bi_2O_3	32,0±0,3	23,0±0,1	31,4±0,3	57,0±0,6	31,0±0,4

The experiments were repeated five times. According to the data in Table 1, the oxidation of hydrogen sulfide was observed at 350 ° C on all investigated catalysts. At the same time, the highest levels of hydrogen sulfide oxidation were observed in oxides of tungsten, iron, copper and manganese.

Experiments at 350 ° C made it possible to determine the following sequence of the activity of metal oxides during the oxidation of hydrogen sulfide in the course of the experiments: WO_3> CuO> Fe_2O_3> Mn_2O_3> Cr_2O_3> CoO> MoO_3> NiO> Bi_2O_3. , oxides were placed in a row, reducing their catalytic activity). Of the oxides studied, the oxides of tungsten, copper, and iron are the most active in the oxidation of hydrogen sulfide. In the presence of these oxides, more than 80% of hydrogen sulfide is converted at 350 ° C. However, the presence of catalysts based on tungsten and iron oxides does not provide selectivity for the oxidation of hydrogen sulfide. Of the catalysts studied, copper oxide was found to be the most selective. As a result of experiments, in parallel with hydrogen sulfide, strong oxidation of hydrogen, carbon monoxide and ammonia was observed in the presence of tungsten and iron oxides at 350 ° C. Low oxidation of H_2, CO, NH_3 and CH_4 was observed in the presence of copper oxide. Therefore, the selectivity of CuO in detecting H_2S in the presence of H_2, CO, NH_3 and CH_4 is high.

As a result of experiments for a sensitive semiconductor hydrogen sulfide sensor, the most active catalysts consisting of tungsten and iron oxides were selected. These catalysts are characterized by high activity in the interaction of oxygen with H_2S. However, catalysts based on the investigated metal oxides do not provide selectivity for the determination of individual components of a mixture of hydrogen sulfide, hydrogen, carbon monoxide and hydrocarbons, which are common in various natural and technological objects. In most catalytic processes, the catalytic activity and selectivity of individual oxides can be altered by adding other oxides to them to form new chemical compounds or solid solutions. Therefore, further studies were carried out in the presence of a binary mixture of the most active (WO_3,) and selective (CuO) metal oxides. In this case, special attention is paid to the selectivity of the studied catalytic systems. The experiments were carried out at a temperature of 325 ° C with different ratios of tungsten and copper oxides and at the rate of 5 l / hour of an air-gas mixture. The results of these experiments are presented in Table 2.

Table 2 : Influence of the ratio of the components and the reaction temperature on the activity and selectivity of the catalyst based on WO_3 (the amount of mass in the mixture, ,%:
C_{H2S}-2,20, C_{NH3}-2,20, C_{SO2}-2,20, C_{H2}-2,20, C_{CO}-2,45, C_{CH4}-2,50).

№ T/p	Catalyst composition,%	H_2S	NH_3	SO_2	H_2	CO	CH_4
The temperature of the oxidation process –300°C							
1	1CuO+99 WO_3	69,2	6,3	12,1	5,5	3,7	1,6
2	5CuO+95 WO_3	83,1	4,7	5,1	6,5	4,6	0,6
3	10CuO+90 WO_3	90,5	4,4	3,2	7,4	6,5	0,6
The temperature of the oxidation process –325°C							
4	1CuO+99 WO_3	75,0	6,8	13,1	6,0	4,0	1,7
5	5CuO+95 WO_3	90,0	5,1	5,5	7,0	5,0	0,7
6	10CuO+90 WO_3	98,0	4,8	3,5	8,0	7,0	0,7
The temperature of the oxidation process –350°C							
7	1CuO+99 WO_3	81	7,3	14,0	6,5	4,3	1,8
8	5CuO+95 WO_3	97,2	5,5	5,9	7,6	5,4	0,8
9	10CuO+90 WO_3	100	5,2	3,8	8,6	7,6	0,8
The temperature of the oxidation process –400°C							
10	1CuO+99 WO_3	92,6	8,4	16,2	7,4	4,9	2,1
11	5CuO+95 WO_3	100,0	6,3	6,8	8,6	6,2	0,9
12	10CuO+90 WO_3	100,0	5,9	4,3	9,9	8,6	0,8

From the data in Table 2 it can be seen that in most cases the activity of a mixture of oxides in the oxidation of combustible gases is relatively high compared to the catalytic activity of individual catalysts based on oxides (see Table 1). The most active and selective of the studied catalytic systems in the oxidation of hydrogen sulfide corresponds to the content of 10CuO + $90WO_3$. At 325 ° C in the presence of this catalyst, the degree of hydrogen sulfide conversion varies from 71% to 95%. The oxidation state of the remaining components of the combustible gas in the presence of 10CuO + $90WO_3$ varies from 0.7 to 8.0%. The data obtained show that a mixture of copper and tungsten oxide can be used as a gas-sensitive layer for a selective semiconductor hydrogen sulfide sensor.

Thus, as a result of studying the activity and selectivity of individual and binary metal oxides in the oxidation of combustible gases, the composition of the catalyst (CuO + WO_3) was chosen for the gas-sensitive material of semiconductor hydrogen sulfide sensors. The activity and selectivity of a catalyst is significantly influenced by the ratio of its components in addition to its composition.

In the studied range, the oxidation of hydrogen sulfide in the presence of CuO + WO_3 increases with an increase in temperature from 300 to 400 ° C. The increase in the oxidation of H_2S is directly proportional to the content of copper oxide in the catalyst. Oxidation of hydrogen sulfide in the presence of 5CuO + $95WO_3$ and 10CuO + $90WO_3$ at temperatures of 325-400 ○ C is almost complete (98-100%). It should be noted that as the temperature rises, along with hydrogen sulfide, the oxidation of other components (NH_3, H_2, etc.) in gas mixtures increases.

The experiments carried out have shown an increase in the selectivity of the sensor element material, corresponding to an increase in the amount of CuO in the studied catalysts. The most active and selective in the oxidation of hydrogen sulfide in the presence of NH_3, H_2, CH_4 and CO is a catalyst based on 10CuO + $90WO_3$. At 350 ° C in the presence of this catalyst, 100% oxidation of H_2S is ensured. Under such conditions, the rate of conversion of other components is much lower than that of hydrogen sulfide.

OUTPUT

Studies show that catalysts based on binary mixtures of metal oxides (copper and tungsten) provide selective determination of hydrogen sulfide by the composition of semiconductors from various natural and technological objects containing ammonia, hydrogen, carbon monoxide and hydrocarbons. In this regard, in subsequent experiments, a mixture of copper and tungsten oxides in a ratio of 1: 9 was used as a gas-sensitive material for a semiconductor hydrogen sulfide sensor. Thus, as a result of studying the activity and selectivity of catalysts based on individual and mixed metal oxides, highly efficient catalysts for the semiconductor H_2S sensor were selected. The selected catalysts provide high selectivity of the semiconductor gas-sensitive material over a wide range of temperatures and concentrations.

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