KINETICS AND MECHANISM OF METHANE OXIDATION IN THE PRESENCE OF SEMICONDUCTOR GAS SENSOR MATERIAL COMPONENTS

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ABSTRACT

This work is aimed at solving the problem of improving the selectivity of gas sensors. During the study, the kinetics and mechanism of methane oxidation in the presence of components of a semiconductor gas-sensitive material were investigated. The research was carried out using a gas-sensitive layer based on binary mixtures of cobalt and chromium oxides in a $1CoO + 1Cr_2O_3$ ratio, synthesized by the sol–gel technique.

Keywords: methane, oxidation process, semiconductor sensor, metal oxide, selective sensor.

INTRODUCTION

In recent years, alongside large stationary gas analyzers, there has been growing interest in the development of chemical gas sensors and signal systems based on compact portable thermocatalytic and semiconductor methods for detecting volatile hydrocarbons in gas mixtures and atmospheric air [1–4]. These devices are widely used in the coal, metallurgical, coke, nuclear, and other industries, as well as in the monitoring of exhaust gases from motor vehicles, to detect pre-explosive concentrations of methane and other volatile hydrocarbons in ambient air [5–7]. It is well known that the operation of thermocatalytic and semiconductor gas sensors is based on processes occurring on the surfaces of metal oxides and sulfides, such as CoO, ZnO, NiO, TiO_2, MnO_2, SnO_2, ZrO_2, Cr_2O_3, WO_3, as well as metal sulfides including CdS, SmS, and others, which can be used as sensitive sensor materials for a number of molecular gases and their mixtures, such as carbon monoxide, hydrogen, ammonia, methane, natural gas, and hydrocarbon vapors [8–13]. These sensors make it possible to convert changes in the electrical conductivity of the semiconductor material, arising from gas adsorption on the surface of the gas-sensitive layer, into numerical values corresponding to the concentration of the measured gas components. Therefore, extensive research is being conducted on the operating mechanisms and principles of chemical gas sensors; however, the issue of their selectivity in complex gas mixtures has not yet been fully resolved [14–17]. In practice, this limits their widespread application.

RESEARCH METHODOLOGY

The presented study is aimed at addressing the problem of improving the selectivity of gas sensors. During the research, the kinetics and mechanism of methane oxidation in the presence of semiconductor gas-sensitive material components were investigated. The study was conducted using a layer of binary mixtures of cobalt and chromium oxides ($1CoO + 1Cr_2O_3$) obtained via the sol–gel technique.

The oxidation of methane in the presence of metal oxides, which are components of semiconductor gas-sensitive materials, primarily proceeds toward the thermodynamically most favorable formation of CO_2 and H_2O [18]. This reaction is highly exothermic ($-\Delta H^\circ_{298}$

= 191.8 kcal/mol) and practically irreversible. Under conditions of limited oxygen and temperature, the oxidation (combustion) process occurs in two directions simultaneously, forming both CO_2 and H_2O, as well as CO and H_2O. Additionally, during catalytic oxidation of methane on the surface of the gas-sensitive material, the formation of HCHO, CH_3OH, and HCOOH is also possible.

Based on the available data, the catalytic oxidation of methane in the presence of n- and p-type semiconductor metal oxides with atmospheric oxygen can be distinguished into the following reaction pathways [19–22]:

1.$CH_4 + O_2 \rightarrow CO_2 + H_2O$
2.$CH_4 + O_2 \rightarrow CO + H_2O$
3.$CH_4 + O2 \rightarrow H_2O + CO_2 + CO$
4.$CH_4 + O_2 \rightarrow HCHO + H_2O$
5.$CH_4 + 0{,}5O_2 \rightarrow CH_3OH$
6.$CH_4 + O_2 \rightarrow H_2O + HCOOH$

During the conducted research, the oxidation behavior of methane over the gas-sensitive semiconductor material consisting of cobalt and chrome oxides (1CoO + $1Cr_2O_3$) was investigated. Methane conversion with the selected oxides was carried out in the temperature range of 200–600 °C under a continuous gas flow of 0.5 L/min in a quartz glass reactor with a diameter of 1 cm.

In the experiments, the amounts of CH_4, O_2, CO_2, CO, H_2O, HCHO, CH_3OH, and HCOOH in the reaction products were analyzed using modern optical, electrochemical, and gas chromatographic methods. The formaldehyde concentration in the reaction mixture was determined photometrically using phenylhydrazine [23], methanol content was measured by gas chromatography [24], and formic acid was analyzed using a potentiometric titration method [25]. Gas chromatography was also employed to quantify CH_4, O_2, CO, and CO_2.

RESEARCH RESULTS AND ANALYSIS

Determining the amounts of the aforementioned components in the reaction products under various conditions is crucial for identifying the optimal conditions for oxidation on the surface of the gas-sensitive material and for understanding the direction of the reaction under different circumstances.

Analysis of the conducted experiments showed that, under the studied conditions (atmospheric pressure, temperature range of 200–600 °C, O_2/CH_4 ratio of 7, and a gas flow rate of 0.5 L/min), no HCHO, CH_3OH, or HCOOH were detected in the methane oxidation products over the selected gas-sensitive material components. This indicates that with a 90% ZnO + 10% CoO oxide mixture, methane oxidation at atmospheric pressure and within the studied temperature range does not proceed along pathways producing HCHO, CH_3OH, or HCOOH.

Therefore, in (1CoO + $1Cr_2O_3$) subsequent experiments, the degree of methane oxidation and the reaction pathway under various conditions were monitored by observing the dynamic changes in CO, CO_2, and unreacted CH_4 in the reaction mixture. In parallel experiments, the amount of carbon dioxide in the reaction products was additionally determined by titration of the absorbed CO_2 in a solution of 0.1 N sodium hydroxide before and after the reaction with 0.1 N hydrochloric acid.

The formation of CO and CO_2 corresponds to reactions that release significant amounts of heat:

$CH_4 + 0.5\ O_2 \leftrightarrow CO + 2\ H_2 + 35.6$ kJ/mol
$CH_4 + 2\ O_2 \leftrightarrow CO_2 + 2\ H_2O + 890$ kJ/mol

This explains why natural gas, which mainly consists of methane, is used as a heat source, which in turn necessitates that the developed semiconductor sensor is capable of detecting natural gas.

Simultaneous separation of methane oxidation products in a single gas chromatographic column presented certain difficulties. Therefore, the composition of the combustion exhaust gases was analyzed using a “Chromatic-Crystal” gas chromatograph and a “Gasochrom-3101” chromatograph equipped with three special columns.

These chromatographs allow detection of O_2, CO, N_2, H_2, CO_2, and hydrocarbons up to C_4. Separation is performed in three stages across different columns: the first column is filled with activated coal, the second with zeolite (molecular sieve), and the third with silica gel. Air and argon were used as carrier gases, with a carrier gas flow rate of 80 cm^3/min.

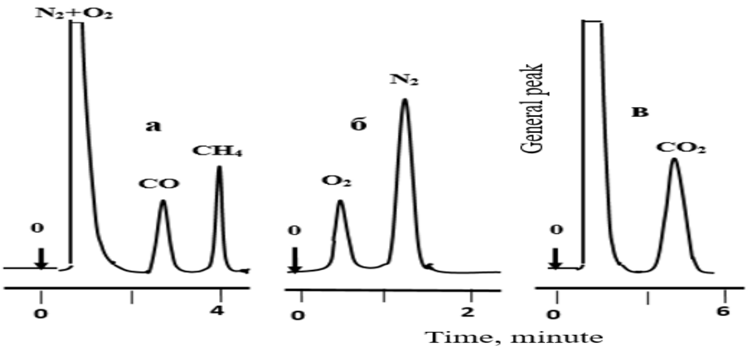

Figure 1. Appearance of the chromatogram of the gas mixture obtained using the “Gasochrom-3101” chromatograph.

As shown in the figure, in the first column filled with activated charcoal, N_2 and O_2 appear as a single peak, while CO and CH_4 are fully separated. Since the gases separated in this column are registered using a thermocatalytic detector, CO_2 in the mixture is not detected. In the second column filled with NaX zeolite, O_2 and N_2 that were not separated in the first column are resolved. In the third column filled with silica gel, all gases except CO_2 elute as a single peak, while CO_2 is detected as a separate peak.

Table 1.

Retention times of methane oxidation products in columns 1–3 of the “Gasochrom-3101” chromatograph.

Component	Retention Time, secund	Component	Retention Time, secund
O_2	37	CH_4	238
N_2	88	CO_2	251
CO	164		

The gas chromatographic analysis results presented in Figure 1 and Table 1 confirm that it is possible to determine unreacted methane as well as the reaction products CO and CO_2 in the oxidation process. Therefore, in subsequent experiments, the “Gasochrom-3101” instrument was used to analyze the products of methane oxidation under various conditions.

After 400 °C, only CO_2 and H_2O were detected in the reaction products. This indicates that at 400 °C, the initial methane in the mixture undergoes complete oxidation according to the first reaction equation, producing CO_2 and H_2O as products.

The results of methane conversion at different temperatures are shown in Figure 2. From the figure, it is seen that in the temperature range of 200–400 °C, methane oxidation increases sharply – from 4% to 85%. At 450 °C, the conversion reaches 94%, and the maximum of 100% is achieved in the 490–500 °C range.

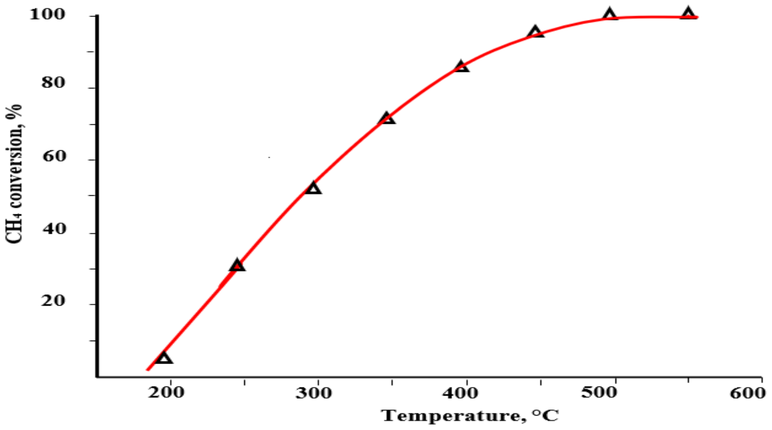

Figure 2. Dependence of methane oxidation (conversion) on temperature.

Comparison of the results presented in Figure 2 with literature data on catalysts [26, 27] commonly used for methane oxidation demonstrates that the selected semiconductor metal oxides consisting of cobalt and chromium oxides exhibit higher activity than other commonly used oxide catalysts. For example, catalysts based on CeO_2 and ZrO_2, which are known for relatively high activity in methane oxidation, achieve 50% and 100% methane conversion at t_{50} = 440 °C and t_{100} = 600 °C, respectively. In contrast, according to the results in Figure 2, the 1CoO + $1Cr_2O_3$ mixture reaches t_{50} = 375 °C and t_{100} = 490 °C.

Analysis of the results shows that changes in temperature on the surface of the gas-sensitive material not only affect the rate of methane oxidation but also significantly influence the reaction pathway and the composition of the products.

The temperature dependence of the composition of methane oxidation products is presented in Figure 3.

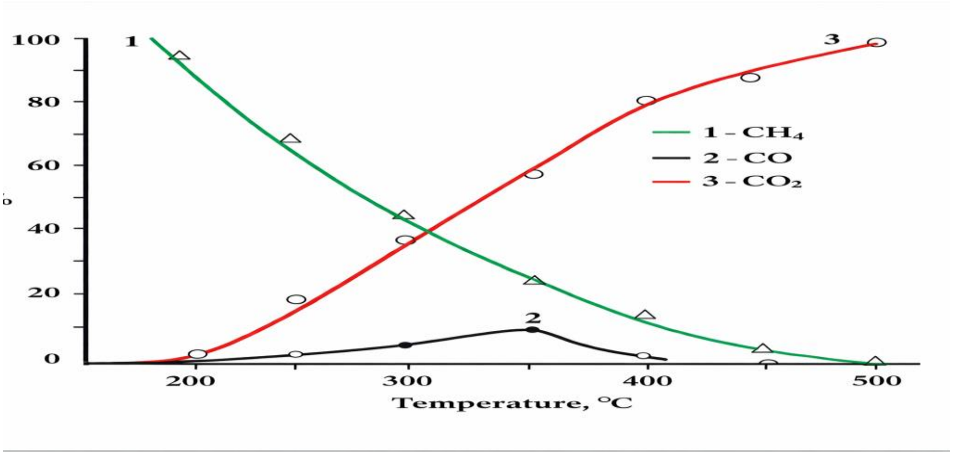

Figure 3. Dependence of methane oxidation product composition on reaction temperature.

From Figure 3, it can be seen that in the temperature range of 200–450 °C, the methane content in the reaction products decreases from 95% to 6%. Using the selected catalyst, 100% methane conversion (i.e., methane completely consumed in the products) is achieved at a temperature of 490 °C.

The composition of CO and CO_2 in the reaction products also changes with temperature. At 200 °C, the reaction product consists of 95% CH_4, 4% CO_2, and 1% CO. At 350 °C, these values are 28% CH_4, 61% CO_2, and 11% CO. The CO content reaches its maximum of 11% at 350 °C. At higher temperatures, CO_2 content continues to increase while CO content decreases. As a result, at 400 °C, the product composition is 16% CH_4, 81% CO_2, and 3% CO. The CO_2 content reaches its maximum (100%) at a temperature of 490–500 °C.

CONCLUSIONS

The results presented in Figures 2 and 3 indicate that the oxidation mechanism of CH_4 on the surface of the gas-sensitive material components in the selective semiconductor methane sensor (1CoO + $1Cr_2O_3$) proceeds along several temperature-dependent pathways.

In the temperature range of 200–400 °C, the simultaneous presence of CO and CO_2 in the reaction products suggests that reactions 1 and 2 occur in parallel on the surface of the gas-sensitive material. The rate of reaction 2, which produces CO, reaches its maximum at 400 °C.

At temperatures above 400 °C, all combustible gas formed on the catalyst surface is completely oxidized to CO_2, and the methane oxidation mechanism follows primarily reaction 1. The conducted study demonstrates that, using a sensor based on the 1CoO + $1Cr_2O_3$ gas-sensitive material, the detectable component (methane) in gas mixtures is fully oxidized to CO_2 at temperatures above 450 °C, confirming the sensor's ability to detect methane effectively under these conditions.

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