

CHEMICAL KINETICS AND CATALYSIS

Purification of Hydrogen Sulfide from Oxygen

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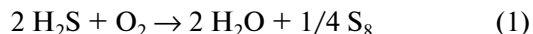
Abstract—A technique for determining the concentration of oxygen in hydrogen sulfide is developed on passing the tested hydrogen sulfide through the stainless steel chips and determining the amount of solid sulfur formed over the catalyst's surface as a result of hydrogen sulfide oxidation by impurities of oxygen. A method for the deep purification of hydrogen sulfide of oxygen is developed. It is shown that under certain conditions, two chemical reactions for the conversion of hydrogen sulfide into two different modifications of sulfur (solid and gaseous) can proceed independently and simultaneously on the catalyst's surface.

Keywords: hydrogen sulfide decomposition, solid sulfur, diatomic gaseous sulfur, oxygen impurity, catalysts deactivation, hydrogen sulfide purification.

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INTRODUCTION

One of the most complex and unpredictable problems encountered in the [1–4] was oxygen in the initial hydrogen sulfide as an uncontrolled impurity. The problem was that the reaction between hydrogen sulfide and oxygen is highly exothermic and proceeds spontaneously at room temperature in the presence of both sulfide and metal catalysts:



($\Delta_r H_{298}^\circ = -105.8$ kcal/mol; $\Delta_r S_{298}^\circ = -55.3$ cal/(mol K); $\Delta_r G_{298}^\circ = -89.3$ kcal/mol; the data for our calculations were taken from [5]).

Apparently for this reason, we cannot identify or control the concentration of oxygen impurities by conventional chromatographic and mass spectrometric means, since hydrogen sulfide is oxidized with the formation of solid sulfur on the surfaces of spectrometer chambers and detectors. No chemical methods for determining oxygen impurities in hydrogen sulfide are found in the literature. Under laboratory conditions, hydrogen sulfide is normally obtained via the acidolysis or hydrolysis of metal sulfide and the reaction of molten sulfur and paraffin [6]. These techniques may not provide the required purity of hydrogen sulfide unless special measures are taken to protect it from oxygen impurities.

EXPERIMENTAL

Hydrogen sulfide was prepared by passing hydrogen through the molten sulfur at 400°C in the presence of sulfide catalysts. The synthesized hydrogen sulfide

was passed through a stainless steel ampule cooled in liquid nitrogen, the stream was cut off, and the cooled ampule was evacuated to remove excess of hydrogen. It would seem that this method eliminates the possible ingress of oxygen, but its actual content can be considerable.

The following method was developed to determine the concentration of oxygen in hydrogen sulfide. The analyzed hydrogen sulfide was passed through stainless steel chips at room temperature for a definite period of time. The catalyst was then washed with benzene, the solvent was evaporated under a hood, and the solid sulfur precipitated out of solution was weighed. The concentration of oxygen in the hydrogen sulfide was determined after simple calculations (Table 1). The resulting solid sulfur blocked the active sites of the investigated catalysts, greatly complicating studies of their catalytic properties.

The UGA-100 quadrupole mass spectrometer (Stanford Research Systems) used in this work to analyze hydrogen sulfide is a versatile residual gas analyzer designed for the rapid analysis of any gas mixture. Fig. 1 shows the background spectrum of the residual gases in the analyzer chamber of a mass spectrometer at the beginning of its operation. The background in the analyzer chamber was due to outgassing from the surface of the chamber and the output of gas ionizer of the residual gas analyzer. These two processes were responsible in all cases for the background spectrum of hydrogen, water, nitrogen, oxygen, and carbon dioxide, since ionization is a fundamental process and cannot be suppressed. Under real conditions, the intensity of the peaks from the background components is greater than in a pure spectrum, due to the impossibility

Table 1. Finding the concentration of oxygen in hydrogen sulfide by passing it through stainless steel shavings at room temperature and determining the amount of solid sulfur formed on the catalyst surface

H ₂ S, mmol			α , %	c , mg	O ₂ , %
c_1	c_2	c_3			
20.9	16.0	4.9	23.6	0.65	0.048
8.7	8.2	0.5	5.75	0.05	0.009
7.5	7.3	0.2	2.67	0.2	0.041
8.5	7.14	1.36	16	5.8	1.07
13.9	13.5	0.4	2.88	0.01	0.001
9.08	8.77	0.31	3.41	0.7	0.011

c , amount of formed sulfur; c_1 , c_2 , and c_3 , amount of fed, accumulated, and decomposed hydrogen sulfide, respectively, mol; α , conversion.

Table 2. Experimental conditions for determining oxygen concentration under the conditions of H₂S decomposition over the shavings of stainless steel at room temperature

Ar flow rate	10 mL/min
H ₂ S flow rate	3.17 mL/min
Experiment time	60 min
Amount of fed H ₂ S	120.2 mL or 8.49 mmol
Amount of H ₂ S entrapped in absorber with zinc acetate	7.14 mmol
Total conversion of H ₂ S	$\alpha_{\text{total}} = 15.9\%$
Amount of S _S extracted to benzene from the catalyst after experiment	0.00580 g or 0.18 mmol
H ₂ S conversion to solid sulfur via reaction (1)	$\alpha_{\text{S}} = 2.1\%$
Oxygen content in H ₂ S	1.06 vol %
H ₂ S conversion to gaseous sulfur via reaction (2)	$\alpha_{\text{GAS}} = 13.8\%$

Table 3. Oxygen content in hydrogen sulfide, determined by passing it through stainless steel shavings

No.	H ₂ S flow, mL/min	τ , min	H ₂ S, mmol	S _S , mg	W _{O₂} , vol %
1	3.34	60	8.95	0.34	0.06
2	3.15	72	10.125	1.6	0.25
3	3.17	60	8.49	6.7	1.23
4	3.38	50	7.5	1.2	0.5
5	3.11	60	8.33	6.0	1.13
6	4.07	50	9.03	1.7	0.30
	4.07	40	7.26	0.1	0.012
	4.07	45	8.17	0.1	0.021
7	3.9	120	20.9	0.65	0.048
8	3.9	60	10.45	0.15	0.020
9	3.9	50	8.7	0.05	0.009

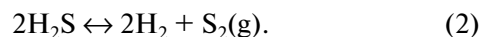
The figures corresponding to hydrogen sulfide purification according to the described technique are in bold.

ity of pumping out the chamber of the analyzer with a turbomolecular pump in the actual period of time required for analysis. However, this is not an obstacle to reliable interpretation of the experimental results, since our software allowed the device to subtract the background spectrum, as in any modern spectrometer.

RESULTS AND DISCUSSION

Figure 2 shows the mass spectrum of the tested hydrogen sulfide. As was noted earlier [1–3], substances with mass $m/z = 64$ a.m.u. and isotopes 65 and 66 a.m.u are always detected in the gas phase along with hydrogen. The content of oxygen impurities cannot be determined because of the background. A difference spectrum was obtained after subtracting the background in the chamber of a mass spectrometer from the mass spectrum (Fig. 3). After subtracting the theoretical spectrum of hydrogen sulfide, the spectrum of the impurities present in the hydrogen sulfide was obtained (Fig. 4). In the difference spectra, we can detect signals from hydrogen, gaseous sulfur with mass $m/z = 64$ a.m.u., and water (weight, 16–18) that apparently formed in the chamber of the spectrometer according to reaction (1).

Chromatographic analysis of hydrogen sulfide does not allow us to determine admixtures of oxygen even at concentrations greater than 2%. We may assume that impurities of oxygen oxidize hydrogen sulfide on the metal surfaces of the pipes in a catalytic unit and in a gas chromatograph with the formation of solid sulfur. When the investigated hydrogen sulfide was passed through the stainless steel shavings, the evolution of hydrogen and gaseous sulfur [1–3] was observed chromatographically:



If the oxygen content exceeded 2%, however, the hydrogen sulfide was almost completely oxidized to solid sulfur (Table 1) and no evolution of gaseous reaction products was observed.

Table 2 shows the experimental conditions for determining the oxygen concentration in hydrogen sulfide in a typical experiment. A flow of hydrogen sulfide in argon was passed through the stainless steel chips, in the most of cases (unless the impurity concentration of oxygen is not higher than 2 vol %) hydrogen and gaseous sulfur evolution was observed by chromatography according to the reaction (2) [1–3]. After a definite period of time (Table 2), hydrogen sulfide feeding was stopped, and the catalyst was purged with argon and washed with benzene. Following evaporation of the solvent, the mass of the formed solid sulfur was determined and used to calculate the oxygen concentration in the tested hydrogen sulfide (Table 2). Subtracting the conversion of hydrogen sulfide to solid sulfur according to reaction (1) from the overall conversion of hydrogen sulfide, we obtained the conversion of hydrogen sulfide decomposition according to

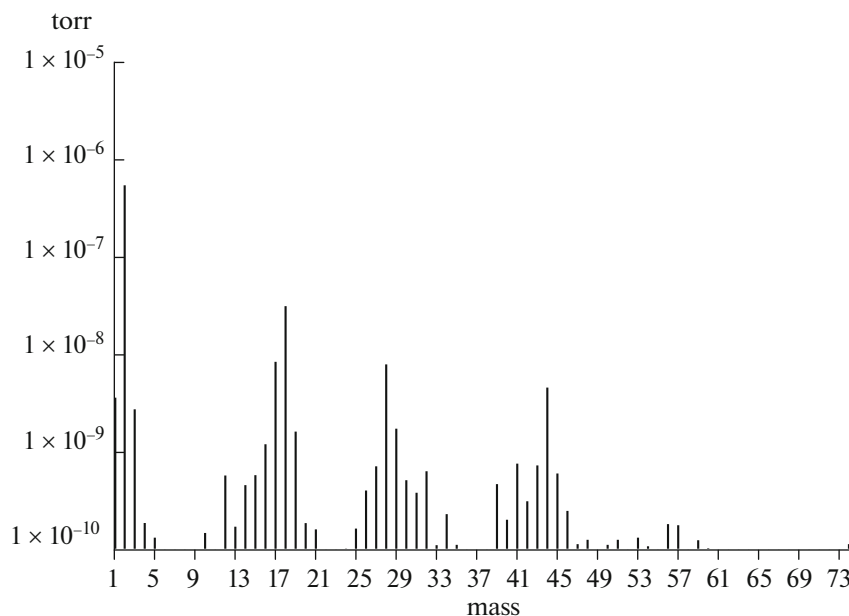


Fig. 1. Background mass spectrum in the RGA-100 spectrometer's chamber at the beginning of its operation.

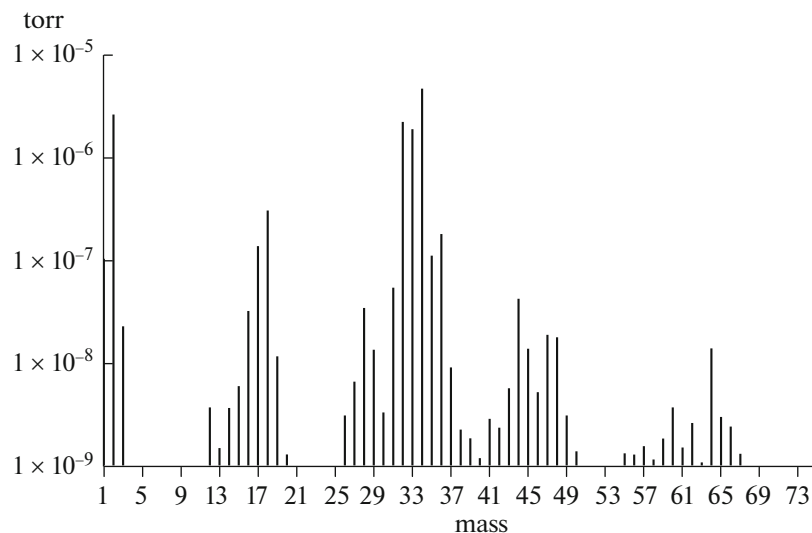


Fig. 2. Mass spectrum of the tested hydrogen sulfide with an oxygen content of 0.5%.

reaction (2). Two chemical reactions of hydrogen sulfide decomposition with the formation of two different modifications of sulfur, solid and gaseous, thus occurred simultaneously and independently over the metal catalyst.

A simple and effective method was thus developed to purify hydrogen sulfide of oxygen impurities. A stainless steel ampule containing hydrogen sulfide was cooled at a temperature of -115°C in a bath of frozen ethanol for several hours to bring hydrogen sulfide

into the solid state. The gas phase was then pumped out from the ampule to a residual pressure of 10^{-1} – 10^{-2} torr, resulted in removing the gaseous oxygen. As the result of this purification procedure, we obtained hydrogen sulfide with an oxygen content of less than 0.05% (Table 3). As it is known from studying a variety of catalysts, such concentrations of oxygen impurities do not lead to catalyst deactivation in reaction (2) of hydrogen sulfide decomposition.

CONCLUSIONS

Simple and effective techniques for determining the concentration of oxygen impurities in hydrogen sulfide and purifying hydrogen sulfide of oxygen impurities were developed. It was shown that by passing hydrogen sulfide through the metal catalyst two reactions of hydrogen sulfide decomposition with the formation of two different modifications of sulfur, solid and gaseous, proceed over the catalyst's surface simultaneously and independently.

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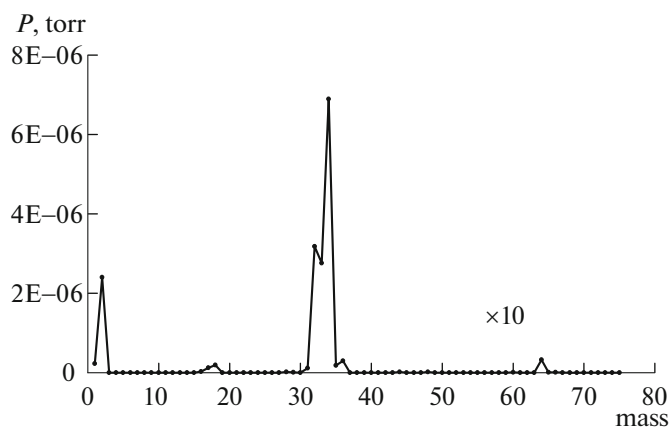


Fig. 3. Difference mass spectrum after subtracting the background mass spectrum in Fig. 2. The intensity of the peak with $m/e = 64$ is magnified 10 times.

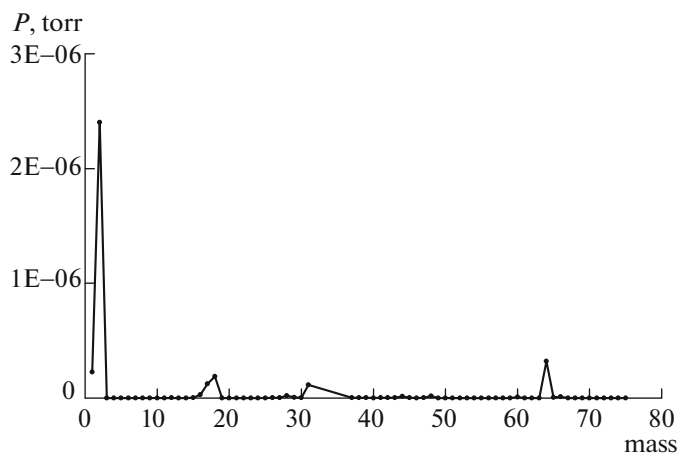


Fig. 4. Difference mass spectrum of gaseous sulfur impurities $m/z = 64$ a.m.u. and water $m/z = 16-18$ a.m.u. in the tested hydrogen sulfide containing 0.5% oxygen.