Kinetics and Catalysis, Vol. 42, No. 5, 2001, pp. 657–661. Translated from Kinetika i Kataliz, Vol. 42, No. 5, 2001, pp. 724–729.
Original Russian Text Copyright © 2001 by Kovalenko, Kundo, Novopashina, Kalinkin.

Nonstationary Phenomena in the Low-Temperature Gas-Phase Catalytic Oxidation of H_2S with Oxygen

O. N. Kovalenko, N. N. Kundo, V. M. Novopashina, and P. N. Kalinkin
Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

Received December 22, 1999

Abstract—The conditions of the existence were determined and reasons were revealed for the appearance of periodic oscillations of the SO_2 concentration in the reaction products and warming temperature in the catalyst bed in the oxidation of H_2S with oxygen at temperatures below the dew point of sulfur on the V–Al–Ti oxide catalyst. The formation of polysulfides during the reaction was experimentally found. It was proposed that the adsorption of sulfur and polysulfides on the catalyst surface is responsible for the observed oscillatory processes.

INTRODUCTION

The development of new efficient technologies of sulfur extraction from dilute hydrogen sulfide–containing gases is urgent because environmental requirements imposed on the content of sulfur compounds in natural, fuel, and exhaust gases are becoming more rigid [1, 2].

Hydrogen sulfide oxidation at temperatures below the dew point of sulfur is a promising direction in the development of technologies for the fine purification of gases containing up to 5% H_2S [1, 3]. The oxidation of H_2S at temperatures below the dew point of sulfur provides, as a rule, a higher yield of sulfur; decreases sharply the probability of side reactions of sulfur with hydrocarbons, water, and oxygen to form toxic products; and prevents the removal of the formed sulfur with reaction gases. At the same time, the process of hydrogen sulfide oxidation in the sulfur condensation regime is nonstationary. During the reaction, the sulfur formed is accumulated on the catalyst surface and decrease its activity. This results in the necessity of the periodic regeneration of the catalyst. Therefore, most studies of the catalytic oxidation of hydrogen sulfide in a gas phase were carried out under stationary conditions at temperatures higher than the dew point of sulfur where the stable operation of the catalyst is provided [1, 2, 4–6]. The kinetics of hydrogen sulfide oxidation with oxygen under stationary conditions on the Fe–Cr–Zn oxide catalyst was studied in detail [2, 4–6]. The reaction rate was found to be described by the Langmuir–Hinshelwood equation: the reaction has the first order with respect to hydrogen sulfide, and the order with respect to oxygen varies from 0.5 to 0 depending on the oxygen content.

Previously [7], we studied the oxidation of H_2S with oxygen under the conditions of possible sulfur condensation on the following three oxide catalysts recommended for H_2S oxidation: Fe–Cr–Zn, Cu–Cr–Al, and V–Al–Ti. The V_2O_5–Al_2O_3–TiO_2 catalyst exhibited high activity; however, SO_2 was the main reaction product for this catalyst. It was found that the vanadium-containing catalyst is not sulfidized in the reaction. It was assumed that the active oxygen of the catalyst is retained under reaction conditions and the deep oxidation of hydrogen sulfide can occur to form SO_2. Catalysts based on copper, zinc, and iron oxides are sulfidized in the reaction medium, which results in the removal of active oxygen. Therefore, these catalysts are exceeded in activity by the vanadium-containing catalyst. However, the absence of active oxygen provides their much higher selectivity in the formation of elemental sulfur. The studies of the reaction kinetics on the V–Al–Ti oxide catalyst at the ratio $O_2/H_2S > 2.4$ found previously unknown periodic stepwise changes in the SO_2 concentration in the reaction products accompanied by the corresponding changes in the catalyst temperature. The oscillations of the concentrations of the reacted substances and temperature were assumed to be related to a periodic change in the character of the oxidation and adsorption of reaction components.

This work is aimed at studying the found nonstationary phenomena and revealing the conditions and reasons for their appearance.

EXPERIMENTAL

The catalytic oxidation of H_2S with oxygen was studied in a flow-type reactor (outer diameter of 10 mm, height of 15 mm) with a fixed catalyst bed at atmospheric pressure and 100–250°C using model gas mixtures containing 0.5–2 vol % H_2S, oxygen, and nitrogen. The O_2/H_2S ratio was varied from 0.6 to 10. The flow rate of the gas mixture was 60 l/h. A 3-g catalyst sample was taken as a fraction of 0.4–0.6 mm. The heating of the catalyst during the reaction was detected by a thermocouple placed at the end of the catalyst bed.

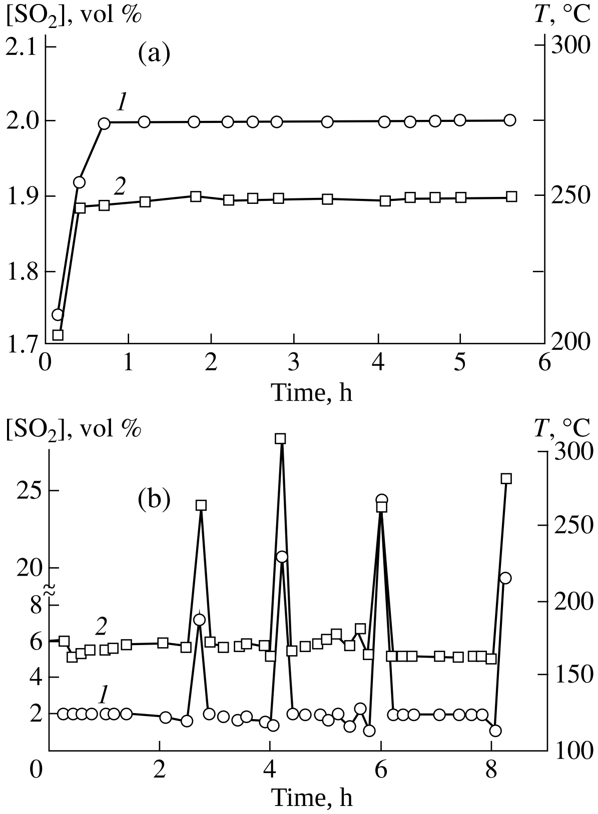

Fig. 1. Plots of the (*1*) SO_2 concentration and (*2*) reaction temperature vs. reaction time at an H_2S concentration in the initial gas mixture of 2 vol %, an O_2/H_2S ratio of 5, and a contact time of 0.2 s. Temperature of the initial gas mixture: (a) 203 and (b) 130°C.

The components of the initial and final gas mixtures were analyzed on two chromatographs connected in series using a single sample. H_2S, SO_2, and H_2O were determined on a Tsvet-500 chromatograph using modified Porapak Q. O_2 and N_2 were determined on an LKhM-8MD chromatograph using molecular sieves NaX. In some experiments, hot exit gases were rapidly dried on a trap packed with $Mg(ClO_4)_2$.

Results were obtained as plots of the conversion of H_2S (X_{H_2S}), concentration of SO_2 in the reaction products, and temperature in the catalyst bed vs. time.

The IK-27-40 industrial catalyst with the composition (wt %) $0.5CaO/5V_2O_5/30Al_2O_3/64.5TiO_2$ prepared by the procedure described in [8] was used as the catalyst. The specific surface area of the catalyst did not exceed 135 m^2/g.

RESULTS AND DISCUSSION

1. Influence of Temperature and O_2/H_2S Ratio on the Course of the Reaction

We studied the influence of the temperature and oxygen concentration on the character of H_2S oxidation. Figures 1–4 demonstrate the conditions of H_2S oxidation. The chosen V–Ti–Al oxide catalyst is highly active at temperatures above the melting point of sulfur (120°C). We found that even at very short contact times (0.003 s) the reaction rate depends on the catalyst grain size. Therefore, virtually all experiments were carried out in the region of internal diffusion. It is difficult to perform H_2S oxidation at temperatures below the melting point of sulfur because the catalyst rapidly loses its activity due to sulfur deposition on its surface.

Figure 1 shows the change in the characteristics of the process with a change in the temperature of the initial gas mixture conveyed to the reactor.

It is seen in Fig. 1a that, at a temperature of the initial gas mixture of 203°C and a temperature at the end of the catalyst bed of 248°C, the reaction occurs in the stationary regime. After ~0.5 h after the beginning of the experiment, the catalyst arrives at a stationary state. During this time, a certain portion of sulfur compounds (on a sulfur basis, 0.1 g sulfur per gram of catalyst) was adsorbed on the catalyst. After the stationary state was achieved, the conversion of H_2S to SO_2 was 100% and the catalyst bed was heated to 45°C.

The further decrease in the temperature of the initial gas mixture to 130°C and in the temperature at the end of the catalyst bed to 163°C resulted in the periodic oscillations of the SO_2 concentration in the exit gases and of the temperature in the reactor. The temperature at the end of the catalyst bed reached 300°C at the instant of inflammation, and the SO_2 concentration increased by a factor of 12 with respect to the concentration of converted H_2S and became equal to 25.3 vol % SO_2 in the exit gases (Fig. 1b). At the initial gas mixture composition 2 vol % H_2S + 13 vol % O_2, the amount of oxygen in the gas phase is sufficient for the complete oxidation of sulfur by the reaction

$$S + O_2 = SO_2.$$

Probably, the active oxygen of the catalyst participates in the reaction, and V^{5+} is reduced to lower oxidation states at the instant of inflammation. In the next cycle before the new inflammation, the catalyst is reoxidized.

A decrease in the temperature of the initial gas mixture to the sulfur solidification temperature ceases the oscillatory processes and simultaneously decreases the catalyst activity due to sulfur deposition (Fig. 2).

We also found that the appearance and character of oscillations can be controlled by changing the O_2/H_2S molar ratio or temperature of the initial gas mixture. In particular, a change in the temperature of the initial gas mixture during the reaction can induce the transition from a stationary regime of the process to a nonstationary regime and vice versa. Figure 3 shows that a decrease in the temperature of the initial gas mixture during the reaction from 200 to 120°C resulted in the inflammation regime, and the subsequent temperature increase to 200°C resulted again in the regime of stable operation. The data obtained at a constant temperature of the gas mixture but with a change in the O_2/H_2S

molar ratio showed the behavior described below (Fig. 4). At the oxygen to hydrogen sulfide ratio $O_2/H_2S = 2$ and the temperature much lower than the dew point of sulfur, sulfur was adsorbed on the catalyst, resulting in a decrease in the hydrogen sulfide conversion in a certain time interval. An increase in the oxygen concentration sharply increased the temperature in the catalyst bed by 150°C; adsorbed sulfur compounds were oxidized to SO_2; and the SO_2 concentration in the gas phase increased by a factor of 5, as compared with the H_2S concentration in the reaction mixture. After the adsorbed sulfur compounds were removed, the catalyst temperature decreased to the initial level. The cycle of oscillations of the concentration of formed SO_2 and temperature can be repeated by a repeated change in the O_2/H_2S ratio.

2. Region of Existence of Oscillations

The region of the existence of oscillations depends first on the temperature. At a temperature of the gas mixture of 200°C or higher, the oxidation rate of H_2S is high and oxidation occurs predominantly to SO_2 [2]. Therefore, reduced sulfur species are not accumulated in considerable amounts on the catalyst surface. By contrast, at temperatures below the melting point of sulfur, the sulfur formed is condensed to cover the catalyst surface. The temperature below 120°C is insufficient for sulfur ignition and catalyst regeneration. At intermediate temperatures of the gas mixture of 130–150°C, sulfur adsorption resulted periodically in ignition. Polysulfides formed by incomplete H_2S oxidation or the reaction of H_2S with adsorbed sulfur can initiate a self-accelerating oxidation reaction resulting in ignition. The O_2/H_2S ratio similarly affects the adsorption and ignition of sulfur compounds. An increase in this ratio leads to the fast oxidation of adsorbed sulfur species to SO_2. Low O_2/H_2S ratios result in catalyst deactivation due to sulfur deposition. Intermediate O_2/H_2S ratios result in the appearance of the oscillatory mode.

3. Reasons for the Appearance of Oscillatory Processes

The reason for the ignition of the catalyst bed should be revealed to explain the mechanism of oscillatory processes. At a concentration of H_2S in the initial gas mixture of 2 vol % and temperatures up to 200°C, the formed sulfur is almost completely condensed in catalyst pores [9]. It was assumed that the ignition of elemental sulfur condensed in catalyst pores can be a step responsible for the heating of the catalyst bed. To confirm this assumption, we experimentally determined the ignition temperature of sulfur adsorbed on the catalyst during the reaction. The experiment was carried out in a flow-type reactor. The experimental conditions for the determination of the ignition temperature were similar to those of preceding experiments but the initial gas mixture did not contain hydrogen sulfide.

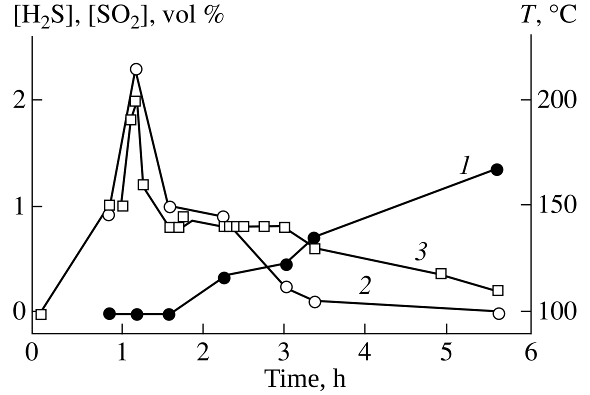

Fig. 2. Plots of the (*1*) H_2S concentration, (*2*) SO_2 concentration, and (*3*) reaction temperature vs. reaction time at an H_2S concentration in the initial gas mixture of 2 vol %, an O_2/H_2S ratio of 5, and a contact time of 0.2 s. Temperature of the initial gas mixture 100°C.

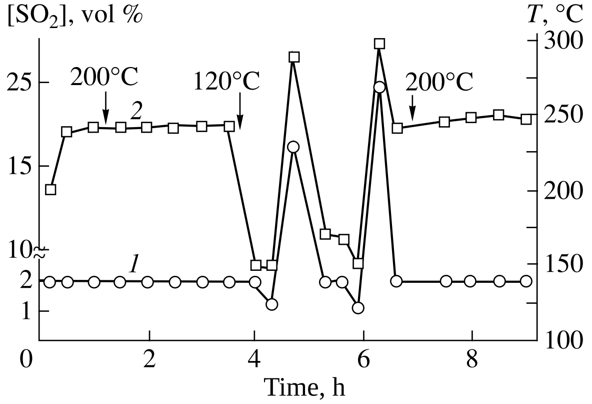

Fig. 3. Plots of the (*1*) SO_2 concentration and (*2*) reaction temperature vs. reaction time at an H_2S concentration in the initial gas mixture of 2 vol %, an O_2/H_2S ratio of 5, and a contact time of 0.2 s. The temperature of the initial gas mixture changed during the reaction.

The results of the experiment compared to the thermogravimetric analysis data and published data on the ignition of bulk sulfur are collected in the table.

The tabulated data show that the dispersion of sulfur in the catalyst pores decreases the ignition temperature of sulfur, depending on the oxygen content of the gas mixture, by 105°C (11 vol % O_2) and 200°C (21 vol % O_2), as compared to the ignition of bulk sulfur. However, the temperature observed at the beginning of sulfur ignition in the reaction is lower by 140°C than that in a mixture without hydrogen sulfide.

Based on these data, we cannot explain the appearance of oscillatory processes observed in the reaction by only the ignition of sulfur localized on the catalyst surface. The results obtained show that sulfur adsorbed on the catalyst in the reaction medium exhibited a higher reactivity. At least partially bound sulfur species

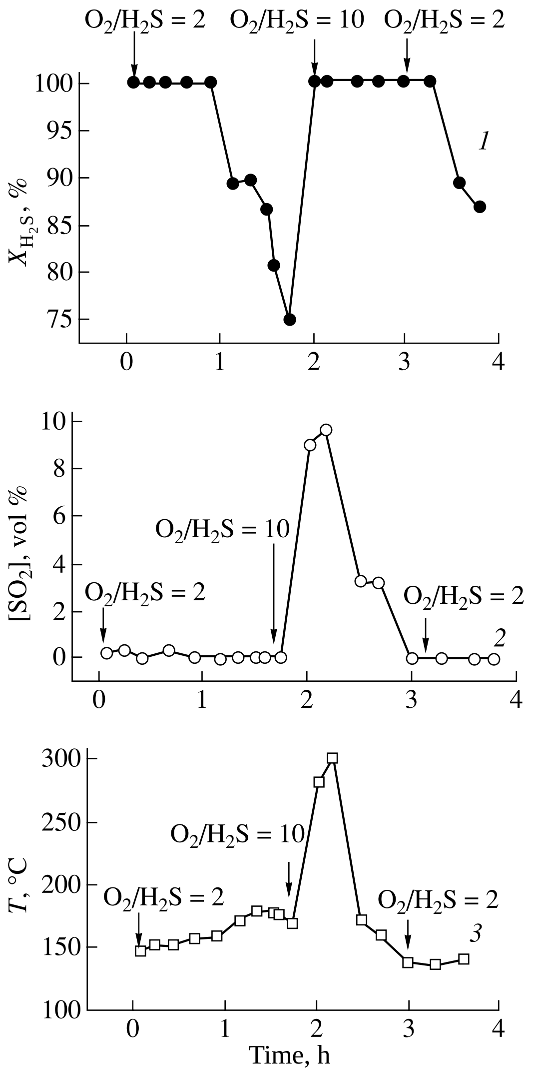

Fig. 4. Plots of the (*1*) H_2S conversion (X_{H_2S}), (*2*) SO_2 concentration, and (*3*) reaction temperature vs. reaction time at an H_2S concentration in the initial gas mixture of 2 vol %, a temperature of the initial gas mixture of 145°C, and a contact time of 0.2 s. The O_2/H_2S molar ratio changed during the reaction.

with a higher reactivity are formed, most likely on the catalyst surface along with elemental sulfur.

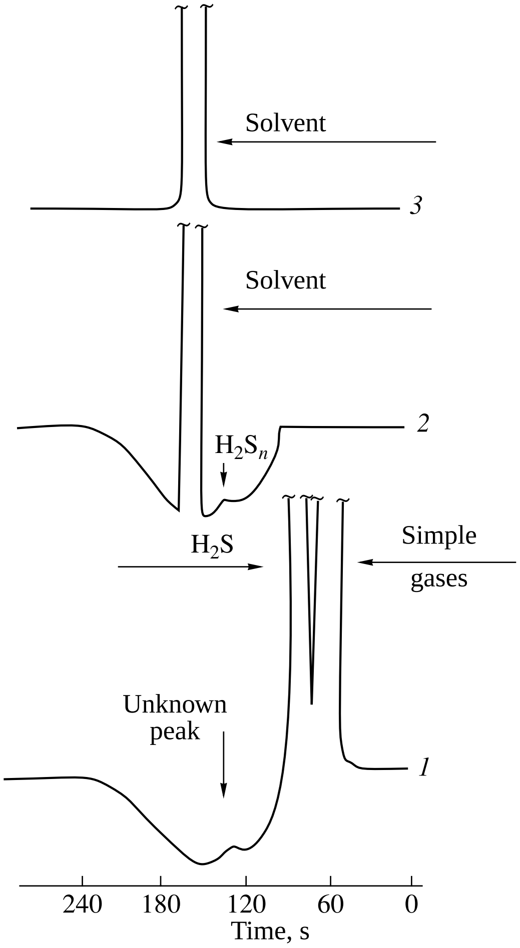

Fig. 5. Chromatograms of (*1*) the reaction gas mixture, (*2*) hydrogen polysulfide extracted with diethyl ether, and (*3*) solvent.

Sulfur atoms linked to form polysulfide chains are known to exhibit a high reactivity toward oxidation reactions. For example, in aqueous neutral and alkaline solutions, polysulfide ions are readily oxidized with oxygen to sulfur at room temperature [10]. The oxidation of H_2S in solutions can have a self-accelerating, autocatalytic character due to the accumulation of more reactive intermediate polysulfides. Similar processes can occur during gas-phase oxidation on the catalyst surface. The amount of polysulfides and the length of a polysulfide chain increase during oxidation, which is accompanied by an increase in the reactivity. When polysulfides are accumulated in a concentration higher than a certain limit, the oxidation process can be inten-

Ignition temperatures of bulk sulfur and sulfur adsorbed on the catalyst in different gas atmospheres

Sample	Composition of gas mixture, vol %	Ignition temperature, °C
Sulfur adsorbed on catalyst	$2H_2S + 11O_2 + 87N_2$	145
The same	$11O_2 + 89N_2$	285
The same (thermogravimetric analysis data)	air	190
Bulk sulfur [1]	air	390

sified to result in the ignition and desorption of the accumulated sulfur compounds in the form of SO_2.

An additional factor indicative of the existence of intermediate compounds during H_2S oxidation in the gas phase was the detection of an unidentified peak directed opposite to that of H_2S, which could belong to polysulfides, in the chromatographic analysis of the reaction products. The rapid drying of hot exit reaction gases followed by direct chromatographic analysis (without separation of components) is the necessary condition for the detection of the peak.

To identify the peak, we synthesized hydrogen polysulfide by the acid decomposition of ammonium polysulfide and the extraction of the resulting H_2S_n with diethyl ether according to the procedure published in [11]. The chromatograms of hydrogen polysulfides, the solvent, and an unknown peak are presented in Fig. 5. The shape and the emergence time of the peak of hydrogen polysulfide are consistent with those of the peak to be identified. The data obtained confirm the participation of hydrogen polysulfide as an intermediate in the low-temperature gas-phase oxidation of H_2S.

Polysulfides, which exhibit acidic properties, are retained on the catalyst surface due to the interaction with basic sites of the catalyst and can partially be desorbed to the gas phase under the action of acidic components contained in the gas mixture (H_2S and SO_2).

Polysulfide oxidation can be an autocatalytic reaction. During oxidation, the polysulfide chain grows to form polysulfides that are more reactive in oxidation and contain more sulfur atoms. This can result in the autocatalytic character of the oxidation and in the ignition of adsorbed sulfur compounds.

CONCLUSIONS

Based on the studies, the following conclusions can be drawn:

(1) The conditions were determined for the existence of periodic oscillations of the concentration of SO_2 as a reaction product and of the temperature of H_2S oxidation with oxygen at temperatures below the dew point of sulfur on the V–Al–Ti oxide catalyst: molar ratio $O_2/H_2S \geq 2$; temperature of the initial gas mixture 100–150°C. The appearance and character of oscillations can be controlled by changing the O_2/H_2S ratio or the temperature of the initial gas mixture during the reaction.

(2) The formation of hydrogen polysulfides as intermediate products of H_2S oxidation was experimentally established.

(3) A reason for the ignition of adsorbed sulfur-containing products can be the self-accelerating reaction of polysulfides with active oxygen in the vanadium-containing catalyst.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 98-03-32312a.

REFERENCES

1. Grunval'd, V.R., *Tekhnologiya gazovoi sery* (Technology of Gaseous Sulfur), Moscow: Khimiya, 1992.
2. Alkhazov, T.G. and Amirgulyan, N.S., *Sernistye soedineniya prirodnykh gazov i neftei* (Sulfur-Containing Compounds of Gas and Oil), Moscow: Khimiya, 1989.
3. Tsybulevskii, A.M. and Morgun, L.V., *Khim. Interes. Ust. Razv.*, 1997, vol. 5, p. 129.
4. Alkhazov, T.G., Kozharov, A.I., and Mirzoev, I.M., *Zh. Prikl. Khim.*, 1991, vol. 64, no. 1, p. 261.
5. Alkhazov, T.G., Aronova, L.L., and Filatova, O.E., *Zh. Prikl. Khim.*, 1991, vol. 64, no. 11, p. 2250.
6. Terorde, R.J.A.M., van den Brink, P.J., Visser, L.M., *et al.*, *Catal. Today*, 1993, no. 17, p. 217.
7. Kovalenko, O.N., Kundo, N.N., Novopashina, V.M., and Khanaev, V.M., *React. Kinet. Catal. Lett.*, 1998, vol. 64, no. 1, p. 129.
8. RF Patent 2053838.
9. *Gmelins Handbuch Der Anorganischen Chemie, Schwefel*, Weinheim: Verlag Chemie, 1953, vol. 9.
10. Kundo, N.N. and Keier, N.P., *Kinet. Katal.*, 1970, vol. 11, no. 1, p. 91.
11. Nekrasov, B.V., *Kurs obshchei khimii* (General Chemistry), Moscow: Goskhimizdat, 1952, p. 295.