Effect of Calcination Temperature on the Physicochemical and Catalytic Properties of FeSO₄/SiO₂ in Hydrogen Sulfide Oxidation

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Abstract—The effect of calcination temperature on the state of the active component of iron-containing catalysts prepared by the impregnation of silica gel with a solution of FeSO₄ and on their catalytic properties in selective H₂S oxidation to sulfur was studied. With the use of thermal analysis, XPS, and Mössbauer spectroscopy, it was found that an X-ray amorphous iron-containing compound of complex composition was formed on the catalyst surface after thermal treatment in the temperature range of 400–500°C. This compound contained Fe³⁺ cations in three nonequivalent positions characteristic of various oxy and hydroxy sulfates and oxide and sulfate groups as anions. Calcination at 600°C led to the almost complete removal of sulfate groups; as a result, the formation of an oxide structure came into play, and it was completed by the production of finely dispersed iron oxide in the ε -Fe₂O₃ modification (the average particle size of 3.2 nm) after treatment at 900°C. As the calcination temperature was increased from 500 to 700°C, an increase in the catalyst activity in hydrogen sulfide selective oxidation was observed because of a change in the state of the active component. A comparative study of the samples by temperature-programmed sulfidation made it possible to establish that an increase in the calcination temperature leads to an increase in the stability of the iron-containing catalysts to the action of a reaction atmosphere.

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INTRODUCTION

The amount of hydrogen sulfide obtained at oil refineries in the processes of hydrotreating continuously increases because more and more rigid requirements are imposed on the sulfur content of petroleum refining products (motor fuels) and the fraction of highsulfur oils in the total volume of petroleum refining is increased. At present, the Claus process is widely used for the removal of hydrogen sulfide from acid gases. The main reaction of this process is the oxidation of hydrogen sulfide to sulfur with sulfurous anhydride

$$2H_2S + SO_2 \rightarrow 2H_2O + \frac{3}{n}S_n, \qquad (I)$$

where n = 1 - 8.

However, the waste gas of Claus plants contains a considerable amount of hydrogen sulfide because reaction (I) is reversible; moreover, this waste gas is also characterized by a high water vapor content (to 30 vol %) [1, 2].

The selective oxidation of hydrogen sulfide to sulfur with molecular oxygen is a method for the purification of the waste gas of the Claus process. This approach was implemented in several industrial processes, among which the Superclaus[®] process developed as a result of the joint efforts of specialists from Comprimo, GasTec, and the University of Utrecht (the Netherlands) became the most widely used process in actual practice [3-6]. The selective oxidation of hydrogen sulfide to sulfur (reaction (II)) is irreversible; however, a number of side reactions can occur on the catalyst surface to decrease the yield of sulfur. Thus, the formation of sulfurous anhydride can occur due to reaction (III), which is the reverse of the Claus reaction, the oxidation of the resulting sulfur by oxygen in a gas phase or on the catalyst surface (reaction (IV)), and a parallel reaction of H_2S oxidation to sulfurous anhydride (reaction (V)):

$$H_2S + \frac{1}{2}O_2 \rightarrow \frac{1}{n}S_n + H_2O, \qquad (II)$$

$$\frac{3}{n}S_n + 2H_2O \rightarrow 2H_2S + SO_2, \qquad (III)$$

$$S_{lig} + O_2 \rightarrow SO_2,$$
 (IV)

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$$H_2S + \frac{3}{2}O_2 \to SO_2 + H_2O.$$
 (V)

To reach a maximum yield of sulfur, it is necessary to avoid the occurrence of side reactions leading to the formation of sulfurous anhydride. The contribution of reaction (III) to the formation SO_2 is decreased by the use of supports that are inactive in the Claus reaction, for example, α -Al₂O₃ or SiO₂ [7, 8]. Published data on the effect of supports on the catalytic properties of iron-containing catalysts in the oxidation reaction of hydrogen sulfide with oxygen confirmed that the use of SiO_2 as a support resulted in higher selectivity, as compared with that of TiO₂ and θ -Al₂O₃, which exhibited noticeable activity in the Claus reaction [9]. To decrease the contribution of reaction (IV) to the formation of SO_2 , wide-pore supports are used for the preparation of catalysts for the selective oxidation of hydrogen sulfide to sulfur. It was demonstrated experimentally that a support dominated by mesopores ensures higher activity and selectivity than a support dominated by micropores [10].

The formation of an active component, which selectively oxidizes hydrogen sulfide to sulfur in the temperature range of 200-320°C, plays a primary role in the achievement of a high yield of sulfur. The upper temperature limit is restricted by the possibility of a homogeneous reaction of the oxidation of hydrogen sulfide to SO_2 , whereas the lower limit is restricted by a decrease in the rate of oxidation due to the condensation of sulfur on the catalyst surface [11]. It is well known that bulk and supported systems containing Fe(III) compounds are most frequently tested as catalysts for the oxidation of hydrogen sulfide to sulfur in the waste gas of the Claus process [5-9]. The inorganic (Fe(III) nitrate, Fe(III) chloride, Fe(III) sulfate, and Fe(II) sulfate) [12-14] and organic salts of iron (gluconate, citrate, ethylenediaminetetraacetate, and acetylacetonate) [15, 16] were used as the precursors of an active component. In a number of publications, it was shown that the catalysts containing the oxide and sulfate compounds of iron provided the selective oxidation of hydrogen sulfide to sulfur [5, 17-24]; the activity was increased by decreasing the particle sizes of the active phase. However, as a result of the interaction of an active component with hydrogen sulfide, iron disulfide can be formed, in presence of which the oxidation of hydrogen sulfide occurs to sulfurous anhydride, decreasing the reaction selectivity and the yield of sulfur [25, 26]. Consequently, along with high catalytic activity, a requirement imposed on iron-containing catalysts for the selective oxidation of hydrogen sulfide to sulfur is the stability of the active phase to sulfidation.

To increase the resistance of catalysts based on iron oxide to the action of a reaction atmosphere, the use of various modifying additives, for example, Ce [27], Cr [28], and Sn [29] oxides or more complex Fe-containing compounds such as Fe–Ni phosphates [30], was proposed. Although a wide range of publications were devoted to the effects of the nature of an active component and various modifying additives, the effects of heat treatment conditions on the catalytic properties and the stability to sulfidation of iron-containing catalysts for the selective oxidation of hydrogen sulfide have not been adequately studied. Earlier, Bukhtiyarova et al. [31] found that an increase in the calcination temperature (T_c) of catalysts prepared by the impregnation of silica gel with a solution of iron nitrate led to both an increase in their stability to sulfidation and a decrease in the catalytic activity caused by the agglomeration of the resulting particles of α -Fe₂O₃. We failed to find out other publications concerning this subject matter.

The processes of the formation of an active phase in supported Fe-containing catalysts prepared with the use of Fe(II) sulfate are not clearly understood; however, interest in this compound has quickened in the past few years [32–36]. On the one hand, the use of FeSO₄ affords catalysts that are more effective [32, 34]; on the other hand, this compound is a waste product of the manufacture of titanium dioxide and it should be utilized.

The aim of this work was to study the effect of calcination temperature on the state of the active component and the catalytic properties of supported ironcontaining catalysts obtained with the use of Fe(II) sulfate in the reaction of hydrogen sulfide oxidation by oxygen. The study of the comparative stability of samples to the action of hydrogen sulfide was performed by temperature-programmed sulfidation (TPS), which is widely used for investigating the formation of an active sulfide phase of hydrotreating catalysts [37].

EXPERIMENTAL

KSKG silica gel (specific surface area, 287 m^2/g ; average pore diameter, 141 Å; pore volume, 0.81 cm³/g) (OOO KhromAnalit) and FeSO₄ \cdot 7H₂O (Acros Organics) were used for the preparation of catalysts. The silica gel (0.25-0.5 mm) was incipient wetness impregnated with an aqueous solution of Fe(II) sulfate and dried at room temperature for a day and then at 110°C for 4 h. Individual samples of FeSO₄/SiO₂ were calcined at different temperatures (400, 500, 600, 700, and 900°C) in air for 4 h. The resulting samples are referred to as 4FS(400), 4FS(500), 4FS(600), etc. Numbers in parentheses correspond to sample calcination temperatures, and the first number approximately corresponds to the concentration of iron (wt %). According to chemical analysis data, the iron content of the 4FS(700) sample was 3.8 wt %.

The X-ray diffraction patterns of the samples were measured on an XTRA diffractometer (Switzerland) using CuK_{α} radiation (wavelength $\lambda = 1.5418$ Å) at a 20 scanning step of 0.05° and an accumulation time of 3 s per point.

The XPS spectra were recorded on a SPECS electron spectrometer (Germany). The spectrometer was equipped with a PHOIBOS-150 hemispherical analyzer, a nine-channel detector of electrons, and an XR-50 source of characteristic X-ray radiation with an Al/Mg dual anode. Nonmonochromated Al K_{α} radiation (hv = 1486.6 eV) was used for measuring the spectra. The catalyst samples were fixed in a sample holder with the aid of double-sided adhesive tape. The scale of binding energies (BE) was calibrated by the internal standard method using the Si 2p line silicon that is a component of the support (BE = 103.5 eV). The relative concentrations of elements in the analysis zone were determined based on the integrated intensities of XPS lines taking into account the photoionization cross sections of the corresponding terms [38]. The decomposition of spectra into individual components was used for a detailed analysis. Accordingly, an experimental curve was decomposed into a number of lines corresponding to the photoemission of electrons from atoms in different chemical environments after the Shirley background subtraction. Data processing was performed using the CasaXPS program package.

Thermal analysis was performed on a NETZSCH STA 449C-Jupiter thermoanalytical system. The TG, DTG, and DSC curves were recorded over a temperature range from 25 to 600°C in a flow of air at a heating rate of 10°C/min. For the analysis, 20 mg of a test sample was loaded in a corundum crucible, and calcined silicon oxide was used as a reference sample.

The Mössbauer spectroscopic studies were performed at room temperature with a $\text{Co}^{57}(\text{Cr})$ source on powder absorbents 0.5 mm in thickness. Isomeric chemical shifts were measured with reference to iron metal (α -Fe). The procedure used for processing the spectra and obtaining the corresponding parameters was described in detail earlier [39].

The study of the samples by high-resolution transmission electron microscopy (TEM) were performed with the use of a JEM-2010 transmission electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV and a resolution of 0.14 nm. The particles of catalysts were applied to copper gauze by dispersing a suspension of the sample in alcohol with the use of an ultrasonic disperser.

The concentrations of Fe and SO_4^{2-} in the samples were determined by inductively coupled plasma atomic emission spectrometry on an OPTIMA 4300 DV spectrometer from Perkin Elmer.

The catalytic properties were studied in a flow circulation reactor at atmospheric pressure and a temperature of 250°C with the use of a catalyst fraction of 0.25-0.5 mm. An additional test for the circulation ratio of the reaction mixture and the effect of particle sizes on the reaction rate showed that the reaction occurred in the kinetic region under the selected conditions. The volume fractions of reagents in the initial reaction mixture were the following: H₂S, 2.0 vol %; O_2 , 1.0 vol %; water vapor, 30 vol %; and the balance He. The catalytic activity of the samples was characterized by the reaction rate of hydrogen sulfide oxidation and by the selectivity of hydrogen sulfide conversion into sulfur at the following concentrations of reagents in the circulation loop: H₂S, 1.0 vol % and O₂, 0.6 vol % (the degree of hydrogen sulfide conversion was 50%). The concentrations of reagents at the reactor inlet and outlet were determined with the use of a thermal conductivity detector (TCD) after the separation of components on a chromatographic column 3 m in length packed with a modified support of Polysorb-1 + 25% PEG15M [24].

The comparative resistance of the catalysts to sulfidation was studied in a flow quartz reactor with the use of a gas mixture containing 2 vol % H₂S in helium at a flow rate of 1.8 l/h. Before the sulfidation, a flow of helium was passed through the reactor for removing air and then a sulfidizing mixture was passed for 0.5 h. Thereafter, the temperature was increased to 500°C at a heating rate of 8°C/min. The concentration of H₂S in the flow was monitored with the use of a gas chromatograph with a TCD; the samples were taken at regular 1-min intervals. The results of the experiments were represented as the temperature dependence of hydrogen sulfide concentration at the reactor outlet the TPS curves.

RESULTS AND DISCUSSION

Physicochemical Properties

The samples obtained were found X-ray amorphous regardless of calcination temperature. In connection with this, thermal analysis, XPS, and Mössbauer spectroscopy were used for studying the formation of the active component of catalysts in the course of thermal treatment.

Figure 1 shows the TG, DTG, and DSC curves for the 4FS(110) sample. The DTG curve exhibited two weight loss regions: the first of them is caused by the removal of adsorbed water (at 70–120°C), and the second (at 580–700°C) is caused by the decomposition of iron sulfates. The experimental results are consistent with published data. Thus, the decomposition temperature of bulk Fe₂(SO₄)₃ in a flow of air is 490–550°C [40]. The decomposition of bulk FeSO₄ begins at 300°C and passes through the formation and decomposition of complex oxy and hydroxy sulfate compounds—FeOHSO₄ and Fe₂O(SO₄)₂. According to published data, the decomposition of the latter begins at 505°C and becomes complete with the formation of α -Fe₂O₃ after calcination at 830°C [41, 42].

The $[SO_4^{2-}]$: [Fe] ratio was 0.96, as calculated from sample weight losses upon the removal of sulfate ions. This result is consistent with chemical analysis data for the 4FS(110) sample, according to which the $[SO_4^{2-}]$: [Fe] ratio is ~1.01. This ratio decreased to 0.05 after calcination at 700°C; this is indicative of the almost com-



Fig. 1. Thermal analysis curves for the FS(110) sample.



Fig. 2. XPS spectra of 4FS samples calcined at temperatures of (1) 110, (2) 400, (3) 500, (4) 600, (5) 700, and (6) 900°C.

plete decomposition of iron sulfate on the catalyst surface.

In this work, we used XPS to obtain information on the state of the active component in 4FS samples with different calcination temperatures. Figure 2 shows the Fe 2p and S 2s XPS spectra of the 4FS(110), 4FS(400), 4FS(500), 4FS(600), 4FS(700), and 4FS(900) samples. The S 2s line was chosen for analysis in place of the most intense traditionally used S 2*p* line because of the overlapping of the latter (BE ~160–169 eV) with a line due to the support–Si 2*s* (BE ~154.5 eV). Note that the Fe 2*p* spectra of the test catalysts are a doublet of Fe 2*p*_{3/2}–Fe 2*p*_{1/2} with a 2 : 1 ratio between the integrated line intensities (Fig. 2a). As a rule, both the position of the main Fe 2*p*_{3/2} line and the shape of the Fe 2*p* spectrum, namely, the intensities and relative



Fig. 3. Mössbauer spectra of 4FS* catalysts calcined at different temperatures.

positions of shake up satellite lines caused by the manifestation of many-electron processes, are used for the identification of the state of iron. The position and intensity of shake up satellite lines depend on the chemical state of iron. Thus, for instance, in the spectra of FeSO₄, FeO, Fe₂(SO₄)₃, α -Fe₂O₃, and FeOOH, the shake up satellite lines are located 4.3, 5.65, 5.7, 8.05, and 8.5 eV higher on the scale of binding energies with respect to the main Fe $2p_{3/2}$ and Fe $2p_{1/2}$ lines [43]. At the same time, shake up satellite lines were absent from the spectra of iron metal, FeS₂, and Fe₃O₄.

In the Fe $2p_{3/2}$ spectra of the 4FS(110) sample dried at 110°C and 4FS samples calcined at 400 and 500°C, an intense peak characteristic of Fe(III) compounds occurred at 711.0 \pm 0.05 eV. A less intense peak at 714.7 eV corresponds to a shake up satellite. In accordance with published data for FeO, Fe₂O₃, and $Fe_2(SO_4)_3$, the Fe $2p_{3/2}$ binding energies lie in the ranges of 709.5-710.2, 710.95-711.2, and 713.25-713.5 eV, respectively [43-45]. Taking into account the chemical composition of the catalyst, we assume that iron compounds formed on the surface of silica gel after calcination at temperatures of no higher than 500°C contain sulfate groups. Indeed, the [S] : [Fe] atomic ratio for these catalysts lies in the range of 1.1-1.6. In this case, an intense narrow line with BE = 233.3 eV, which belongs to sulfate groups, is observed in the S 2s spectra. For sulfur in the state S^{6+} (SO₄²⁻ groups), the published S 2s binding energies fall within the range of 232.0-237.7 eV [14, 44, 46]. Thus, for instance, the

S 2s binding energy for FeSO₄ \cdot 7H₂O is 232.0 eV [47].

In the Fe 2p spectra of samples 4 and 5 calcined at 600 and 700°C, respectively, the main Fe $2p_{3/2}$ peak and a shake up satellite are shifted to the regions of 710.1-710.4 and 713-714 eV, respectively; in combination with a decrease in the S 2s line intensity, this is indicative of the decomposition of iron sulfate. This conclusion is consistent with the results of chemical analysis. The temperature of 500°C corresponds to the onset of the decomposition of iron sulfate on the catalyst surface. The sulfur content of the sample calcined at 900°C was lower than the limit of detection by XPS; thus, we can conclude that the complete decomposition of iron sulfate with the formation of iron oxide occurred. In the sample calcined at 700°C, the [Fe]: [Si] ratio was 0.010, whereas it was 0.012 in the 4FS(900) sample. A small change in the value of [Fe]: [Si] with increasing T_c suggests that the agglomeration of the active phase did not occur. In the Fe 2p spectrum of the 4FS(900) sample, the main Fe $2p_{3/2}$ peak and a shake up satellite were observed in regions of 710.4 and 713.3 eV, respectively. Note that this binding energy and the position and intensity of the shake up satellite are not characteristic of iron oxide in the modifications of α -Fe₂O₃ and γ -Fe₂O₃. For these compounds, the observed binding energy was 711 eV; in this case, a clearly pronounced shake up satellite was present in the spectrum at 719 eV [44, 47].

Mössbauer spectroscopy was used for the more detailed characterization of iron-containing compounds formed on the catalyst surface after heat treatment at different temperatures. To increase the sensitivity of this technique, the samples were prepared with the use of Fe(II) sulfate obtained from iron metal with a high concentration of the 57 Fe isotope (99.5%) in accordance with a previously described procedure [48]. The preparation of the FeSO₄ \cdot H₂O compound was confirmed by XRD analysis. The resulting catalyst samples are referred to as 4FS*(400), 4FS*(500), 4FS*(600), etc. Numbers in parentheses correspond to sample calcination temperatures, and the first number approximately corresponds to the concentration of iron (wt %). According to chemical analysis data, the iron content of the $4FS^{*}(700)$ sample was 3.4 wt %.

Figure 3 shows the Mössbauer spectra of 4FS* samples measured at room temperature. The spectra of the samples calcined at 500°C or lower are quadrupole doublets characteristic of the paramagnetic state of a substance. After calcination at 600°C, a magnetically ordered phase was formed on the surface of silica gel and its concentration increased with T_c .

Table 1 summarizes the interpretation of the spectra. In the samples calcined at temperatures of no higher than 500°C, three nonequivalent positions of iron, Fe1, Fe2, and Fe3, were detected; they differed in the value of quadrupole splitting or the degree of distortion of a local environment. Comparing the Mössbauer parameters of these states with the parameters of iron sulfate derivatives [49–53], we can con-

			2	*		
	IS ± 0.005, mm/s	$H \pm 5$, kOe	QS ± 0.03, mm/s	W± 0.05, mm/s	$A \pm 0.03$	Position
FS-110°C	0.419	_	0.49	0.33	0.38	$Fe1 - Fe_2O(SO_4)_2 \cdot xH_2O$
	0.426	_	0.80	0.31	0.34	$Fe2 - FeOHSO_4 \cdot 2H_2O$
	0.420	_	1.13	0.30	0.17	Fe3 – FeOHSO ₄
	1.157	_	1.61	0.36	0.04	Fe ²⁺ in Fe1
	1.187	_	2.14	0.37	0.06	Fe ²⁺ in Fe2
	1.245	_	2.59	0.23	0.02	Fe ²⁺ in Fe3
FS-400°C	0.411	_	0.48	0.34	0.44	Fe1
	0.424	_	0.80	0.32	0.37	Fe2
	0.425	_	1.13	0.33	0.19	Fe3
FS-500°C	0.401	_	0.52	0.33	0.37	Fe1
	0.410	_	0.90	0.38	0.45	Fe2
	0.398	_	1.34	0.42	0.17	Fe3
FS-600°C	0.412	442	0	0.31-1.07	0.05	B1 in ε -Fe ₂ O ₃
	0.507	398	0	0.81-0.99	0.04	B2 in ε -Fe ₂ O ₃
	0.300	362	0	2.18	0.08	B2 in ε -Fe ₂ O ₃
	0.376	231	0	2.27-2.76	0.15	A in ε -Fe ₂ O ₃
	0.336	_	0.55	0.43	0.16	Fe1* – oxide
	0.325	_	0.91	0.58	0.44	Fe2* – oxide
	0.349	_	1.55	0.56	0.07	Fe3* – oxide
FS-700°C	0.404	461	0	0.41	0.03	B1
	0.374	432	0	0.77	0.06	B2
	0.423	389	0	1.83	0.24	B2
	0.344	248	0.26	0.58-1.96	0.13	Α
	0.334	_	0.62	0.48	0.14	Fe1*
	0.314	_	0.93	0.67	0.37	Fe2*
	0.385	_	1.92	0.49	0.03	Fe3*
FS-900°C	0.374	441	-0.45	0.19-0.48	0.09	B1
	0.352	415	-0.71	0.18-0.69	0.05	B2
	0.389	382	-0.21	0.50-1.23	0.22	B2
	0.233	249	0	0.72-1.53	0.29	Α
	0.383	_	0.74	0.37	0.07	Fe1*
	0.311	-	0.80	0.84	0.17	Fe2*
	0.362	_	1.76	0.89	0.11	Fe3*

 Table 1. Mössbauer parameters of FS* catalysts calcined at different temperatures

Note: IS is the isomeric chemical shift relative to α -Fe, H is the hyperfine field on the iron nucleus, QS is quadrupole splitting, W is the absorption line width (the widths of internal and external lines, which demonstrate the magnetic nonuniformity of given positions in a crystal are specified for the sextets), and A is the fractional position population.



Fig. 4. Dependence of the relative concentration of iron-containing phases in 4FS* catalysts on calcination temperature.

clude that the local environments of the Fe1, Fe2, and Fe3 positions are close to the environments in the $Fe_2O(SO_4)_2 \cdot H_2O$, FeOHSO₄ $\cdot H_2O$, and FeOHSO₄ compounds, respectively. These designations are used in Table 1. The Mössbauer procedure provides information on the local characteristics of the positions rather than the phase composition. In principle, the Fe1–Fe3 positions can be related to positions in a compound of a complex composition with a weakly ordered distribution of hydroxyl, oxygen, and sulfate groups.

Judging by the values of isomeric chemical shifts, iron in a trivalent state was present in all of the samples other than FS*(110). In accordance with the values of quadrupole splitting, three positions of Fe²⁺ detected in FS*(110) can be attributed to the states Fe1–Fe3. After calcination at 400°C, Fe²⁺ was oxidized to Fe³⁺. In the range of 110–500°C, the chemical shifts of all of the three states Fe1–Fe3 smoothly decreased to indicate that iron compounds gradually lost crystal water.

Two effects were observed in the Mössbauer spectra after the calcination of catalysts at 600°C. First, a magnetically ordered phase appeared, in which four nonequivalent iron positions were revealed (A, B1–B3). Second, the chemical shifts of the states Fe1–Fe3 sharply decreased to the values characteristic of Fe³⁺ in an octahedral coordination to oxygen. The observing changes in the spectra suggest that the catalyst loses sulfate groups in the course of calcination at 600°C and hydroxo sulfates decompose with the simultaneous formation of new oxide lattices. The question of the type of these lattices is still an open question because the Mössbauer procedure makes it possible to determine only the local characteristics of positions. Three nonequivalent positions of iron, Fe1*–Fe3* with the characteristic values of quadrupole splitting, remain in the oxide phase; that is, octahedrons, which were present in hydroxo sulfates, serve as the building blocks of oxide phases. The quadrupole splitting of ~0.6 mm/s (Fe1 positions) is usually inherent in the octahedrons of oxide compounds with the cubic packing of oxygen atoms, in which the adjacent octahedrons have a shared edge, and this structure has tetrahedral along with octahedral interstitial sites. The quadrupole splitting of ~0.9 mm/s (Fe2 positions) is characteristic of oxides with the hexagonal packing of oxygen atoms, in which the octahedrons are faceshared. We attribute Fe3 positions with large quadrupole splitting (QS ~1.3–1.7 mm/s) to interblock iron, possibly, with a distorted octahedral coordination.

The magnetically ordered phase, which resulted from calcination at 600°C, manifested itself as sextets in the Mössbauer spectra. In this phase, four nonequivalent positions of iron were identified, whose Mössbauer parameters are close to the parameters of the ε -Fe₂O₃ oxide [54, 55]. Positions A relate to the tetrahedral positions, whereas positions B1–B3 relate to three nonequivalent octahedral positions of this oxide. The fraction of the ε -Fe₂O₃ phase in the material increased with T_c , and a cation redistribution over the positions occurs.

Figure 4 shows changes in the relative concentrations of iron-containing phases in the catalyst with increasing T_c . According to experimental data, the ε -Fe₂O₃ phase, whose structure has the cubic packing of oxygen atoms, is formed at a temperature of 600°C based on Fe1* positions, which have predominantly the cubic packing of oxygens. Because of this, the Fe2* phase population with the predominantly hexagonal packing of oxygen atoms increases. Recall that the phase of $\text{FeOHSO}_4 \cdot \text{H}_2\text{O}$ is the precursor of the Fe2* phase. As T_c is further increased, the concentration of the ϵ -Fe₂O₃ phase increases.

To support the conclusion on the formation of the ε -Fe₂O₃ phase, we prepared a series of samples with a higher iron content of 5.65 wt % for the sample calcined at a temperature of 900°C (6FS). The X-ray diffraction patterns of 6FS samples calcined at 400–700°C do not contain reflections, whereas the X-ray diffraction pattern of the 6FS(900) sample exhibits a number of the clearly pronounced peaks, which correspond to a well-crystallized phase (Fig. 5). In accordance with published data, the observed reflections at $2\theta = 27.636$, 29.949, 32.901, 35.215, 36.691, 40.111, 45.646, 52.941, 60.973, and 63.372° belong to the ε -Fe₂O₃ phase, which was described recently [54, 55]. Note that no traces of the α -Fe₂O₃ phase were observed in this case.

The TEM study of the 4FS(900) sample made it possible to establish that, after calcination at 900°C, iron oxide particles in a highly dispersed state with the average particle size of 3.2 nm were present on the surface of silica gel (Fig. 6).

Thus, the set of the experimental results allows us to conclude that a compound with a complex composition is formed upon the impregnation of silica gel with a solution of Fe(II) sulfate and thermal treatment at 400–500°C. The components of this compound are oxide, sulfate, and hydroxide groups as the anions, and the cations of iron (Fe³⁺) are located in three non-equivalent positions characteristic of various oxy and hydroxy sulfates: Fe₂O(SO₄)₂ · H₂O, FeOHSO₄ · 2H₂O, and FeOHSO₄. Calcination at 600°C leads to the almost complete removal of sulfate groups. As a result, the formation of an oxide structure comes into play; after calcination at 900°C, it completes by the formation of finely dispersed iron oxide (the average particle size of 3.2 nm) with the structure of ϵ -Fe₂O₃.

The Fe 2*p* XPS spectrum of iron oxide with the structure of ε -Fe₂O₃ has characteristic properties that can be used for the identification of this phase: the positions of the main Fe 2*p*_{3/2} peak and a shake up satellite are observed at 710.4 and 713.3 eV, respectively. This binding energy and the position and intensity of the shake up satellite are uncharacteristic of iron oxide in the α -Fe₂O₃ and γ -Fe₂O₃ modifications.

Catalytic Properties

Table 2 summarizes the steady-state reaction rates of H_2S oxidation obtained as a result of studying the activity of catalyst samples. The selectivity of hydrogen sulfide conversion into sulfur was 100% on all of the synthesized samples under the reaction conditions. As follows from the above data, the reaction rate of hydrogen sulfide oxidation increased by a factor of



Fig. 5. X-ray diffraction pattern of the 6FS(900) sample.



Fig. 6. Electron micrograph of the 4FS(900) sample.

1.3 as T_c was increased from 500 to 700°C, whereas the activity insignificantly decreased after treatment at higher temperatures. As a rule, an increase in T_c leads to the agglomeration of the active component of supported catalysts and, as a result, to a decrease in the activity [56]. The increase in the catalyst activity observed in this work as T_c was increased from 500 to 700°C can be explained by the fact that sulfate groups are removed in this temperature range. The experimental result suggests that the activity of the formed oxide was higher than that of the initial compound,

Table 2. Catalytic activity of 4FS samples calcined at different temperatures in the reaction of H_2S oxidation with oxygen

Calcination temperature, °C	Oxidation reaction rate w , mol H ₂ S g ⁻¹ s ⁻¹
500	9.51×10^{-6}
600	1.22×10^{-5}
700	1.26×10^{-5}
900	1.15×10^{-5}



Fig. 7. TPS curves for 4FS samples calcined at 500, 700, and 900°C.

which contained sulfate groups in its composition. A further increase in T_c to 900°C did not lead to a considerable decrease in the activity; this was likely a consequence of the high thermal stability of the formed phase. The stability of the samples to agglomeration was confirmed by XPS and TEM data.

Figure 7 shows the results of the study of the stability of 4FS samples calcined at different temperatures to sulfidation. The comparative analysis of the TPS curves shows that a maximum decrease in the concentration of H₂S, which reflects the absorption of hydrogen sulfide by the catalyst due to the conversion of the iron oxide phase into iron disulfide, shifted toward higher temperatures with increasing the $T_{\rm c}$ of the samples. The TPS curves also exhibited two peaks of hydrogen sulfide absorption upon the interaction of hydrogen sulfide with the 4FS(500) and 4FS(700) samples. This shape of the TPS curves, which was repeatedly reproduced for the samples with different iron contents, suggests the presence of particles with different stability to sulfidation. The hypothesis on the heterogeneous phase composition of the compounds formed upon the thermal treatment of the catalysts in the temperature range of 500-700°C is the most probable explanation. An increase in T_c to 900°C leads to an increase in the stability of the sample to sulfidation: the maximum of hydrogen sulfide absorption shifts toward higher temperatures. The TPS curve exhibits one peak, which suggests the uniform composition of the resulting iron-containing compounds.

CONCLUSIONS

The study of catalyst samples prepared by the impregnation of silica gel with a solution of Fe(II) sulfate and calcined at different temperatures was performed by thermal analysis, XPS, and Mössbauer

spectroscopy. This study allowed us to reveal the regularities of the conversion of surface compounds formed on the silica gel surface. After thermal treatment in the temperature range of 400–500°C, a compound containing oxygen and sulfate groups as the anions was present on the surface of silica gel. According to Mössbauer spectroscopic data, the cations of iron (Fe³⁺) in these compounds are located in three nonequivalent positions characteristic of oxy and hydroxy sulfates of different composition: $Fe_2O(SO_4)_2$. H₂O, FeOHSO₄ · 2H₂O, and FeOHSO₄. Calcination at 600°C leads to the almost complete removal of sulfate groups; as a result, the formation of iron oxide with the structure of ϵ -Fe₂O₃ comes into play to be complete after calcination at 900°C. The average particle size of the resulting ε -Fe₂O₃ particles is 3.2 nm. An increase in $T_{\rm c}$ from 500 to 700°C leads to an increase in the catalyst activity in the reaction of the selective oxidation of hydrogen sulfide, which can be explained by a higher activity of iron oxide, as compared with sulfate compounds. A further increase in the calcination temperature to 900°C leads to only an insignificant decrease in activity, which is explained by the high stability of the formed ε -Fe₂O₃ particles to agglomeration. With increasing the temperature of calcination, an increase in the stability of the iron-containing catalysts to the action of a reaction atmosphere is observed in the entire test range of calcination temperatures.

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