Effect of the Fuel Equivalence Ratio on the Mechanisms of Thiophene Oxidation in Water Vapor at Increased Density of the Reagents

Oxana N. Fedyaeva,* Andrey V. Shishkin, and Anatoly A. Vostrikov

ABSTRACT: The article presents the results of a study of thiophene oxidation in high-density C4H4S/O2 mixtures (ρ_{Thi} = 0.12 and 0.15 mol/dm³, ρ_{O2} = 0.74–1.26 mol/dm³), diluted with water vapor and argon (dilution level x_D = 35–65% mol), at uniform heating (1 K/min) of a stainless-steel tubular reactor up to 823 K. It is established that the temperature of thiophene oxidation onset weakly depends on the nature of the diluent and the oxygen content in the reaction mixture. From the time dependences of the reaction mixtures on temperature and pressure, it follows that the oxidation of thiophene in the water vapor and argon media proceeds according to the mechanisms of homogeneous and heterogeneous reactions. Upon oxidation of thiophene in the stoichiometric mixtures in argon with a small amount of water vapor, as well as in the lean mixtures in water vapor, the contribution of reactions on the surface of the Pt–Rh/Pt thermocouple, inserted into the center of the reaction volume, is increased. Upon oxidation of thiophene in water vapor in the fuel-enriched and stoichiometric mixtures, reactions on the oxidized surface of the reactor wall (primarily iron oxides) prevail. Increasing the density of water vapor both reduces the contribution of heterogeneous reactions on the reactor wall and prevents complete carbon burnout. It is shown that the neutralization of sulfuric acid, resulting from the oxidation of thiophene, with calcium carbonate reduces the corrosion of stainless steel. The X-ray diffraction analysis revealed the presence of ferrochromite, iron and chromium oxides, iron, nickel, and chromium sulfates in the corrosion products.

1. INTRODUCTION

Depletion of light oil reserves and increased consumption of motor fuels lead to the involvement in the processing of heavy oil raw materials (heavy oil, bitumen, tar, and oil shale), characterized by a high content of thiophene derivatives.1–4 The accumulation of waste from the production and processing of such raw materials causes environmental problems, in particular, pollution of nearby water areas.5,6 Incineration of these wastes by conventional methods leads to the release of SO₂ and aerosol particles (primarily soot) into the atmosphere.7,8 Since these wastes are usually waterlogged, the use of high-density water vapor or supercritical water (SCW: T > 647 K, P > 22.1 MPa) can become one of the ways of their environmentally safe processing.9,10 The latter, in particular, is determined by the fact that the final product of oxidation of S-containing organic substances in an aqueous-oxygen mixture is sulfuric acid.11,12 It is obvious that for the development of new technologies based on the combustion of fuels and wastes in dense water vapor or SCW, it is necessary to obtain data on the oxidation features of the individual compounds in these media. Oxidation of several hydrocarbons and heteroatomic compounds was studied earlier.13–15 The present research is aimed at identifying the features of thiophene oxidation, as the simplest aromatic S-containing compound, in an aqueous medium.

From the analysis of the literature, it follows that in the absence of oxidants, thiophene derivatives are thermally stable. Winkler et al.16 used GC–MS to study the composition of thiophene pyrolysis products within the temperature range of 773–1373 K. It was established that at T < 1073 K, significant fragmentation of the thiophene skeleton does not occur; only C–H bonds are cleaved, and the resulting thiophenyl radicals recombine to form di- and terthiophenes as condensation products. At T > 1173 K, skeleton fragmentation becomes more intense and the amount of small S-containing products, such as CS₂ and H₂S increases.16 Katritzky et al.17 showed that at 733 K, thiophene does not transform in SCW for 60 min. Patwardhan et al.,18 when studying the conversion of thiophene in SCW (673 K, 23.5 MPa, reaction time 31 min,
autoclave with stirrer, weight ratio H2O/C16H34 = 1:1, found that the degree of its desulfurization (the proportion of sulfur atoms converted into H2S) did not exceed 3–5%. Qi et al.,19 when studying the conversion of thiophene in SCW (673 K, 23.5 MPa, reaction time 60 min, autoclave with stirrer, weight ratio H2O/C16H34 = 1:1) determined that the degree of desulfurization was equal to 18.8%. According to Timko et al.,20 the SCW conversion of S-containing compounds proceeds via the formation of free radicals, while the transfer of the H atom from the neighboring C–H bond to the sulfur atom is a limiting stage. Kang et al.,21 based on the results of thermal decomposition and SCW conversion of hexyl sulfide and hexanethiol (673 K, 24.7–25.6 MPa, reaction time ≤30 min, autoclave) concluded that water can act as a H-transfer catalyst and reactant; in the absence of water, aromatic sulfur compounds such as thiophenes are produced due to the hydrogen deficiency in thermal decomposition. The results obtained by Khalil et al.,22 show that the degree of hydrothermal conversion of thiophene increases with increasing reaction time (∼72 h), temperature (393–553 K), and hematite concentration (∼0.1 wt %) but decreases with increasing thiophene/water ratio (from 3:7 to 7:3). Yoshida et al.,23 when studying the conversion of thiophene in SCW (673 K, 10–60 min exposure time, Hastelloy C-276 alloy autoclave) in the presence of NaOH (1–5 mol/dm3) and iron powder (≤0.1 mol, 300 mesh), revealed that its complete desulfurization was achieved at the maximum exposure times and the concentration of additives. The authors suggested23 that in the presence of NaOH, thiophene desulfurization proceeds according to the ionic mechanism, while in the absence of iron powder, the process is catalyzed by the reactor wall.

Based on the large activation barrier (>125.5 kJ/mol) of direct oxidation of thiophene by ground-state oxygen, Song et al.,24 concluded that this reaction might be important only in high-temperature processes. In the presence of a catalyst, the activation barrier decreases and a high degree of thiophene conversion can be achieved at moderate temperatures.25 From the above overview, it follows that the amount of data on the thiophene oxidation in a water–oxygen mixture is severely limited, and the mechanisms for the involvement of water and oxygen in this process are not clearly understood.

The present work aims at identifying the effect of the fuel equivalence ratio and dilution level of the C6H6S/O2 mixture on the mechanisms of thiophene oxidation in water vapor and argon at uniform slow heating in a context of the high density of reagents and the diluent. Since argon is an inert diluent, a comparison of the thiophene oxidation in water vapor and argon will allow revealing the role of H2O molecules in this process.

### 2. RESULTS AND DISCUSSION

Taking into account the fact that the final oxidation product of S-containing organic compounds in the water medium is sulfuric acid,11,12 oxidation of thiophene by oxygen is described by the following gross reaction

\[
\text{C}_6\text{H}_6\text{S}(g) + 6.5\text{SO}_2(g) \rightarrow 4\text{CO}_2(g) + \text{H}_2\text{O}(g) + \text{H}_2\text{SO}_4(g)
\]

\[\Delta H_{298}^o = -2776.4 \text{ kJ/mol} \]

Here and below, the reference data26–29 were used in the calculation of thermochemical quantities; the superscripts (g) and (s) correspond to the gaseous and solid state of the substance, respectively.

In this paper, we investigate the oxidation features of high-density C6H6S/O2 mixtures diluted with argon and water vapor. Table 1 shows the partial pressure of reagents and diluents fed into the reactor, their amount [n0(C6H6S), n0(O2), n0(D), and n0(CaCO3)], the fuel equivalence ratio ϕ, and the dilution level x0 of the mixture. As can be seen, tests were carried out with rich, stoichiometric, and lean C6H6S/O2 mixtures (ϕ = 0.80–1.33) at their dilution level x0, ranging from 35 to 64% mol.

### 2.1. Oxidation of Thiophene in the Argon Medium in the Presence of a Small Amount of Water Vapor

The oxidation of thiophene in the argon/water vapor medium was studied in C6H6S/O2 stoichiometric mixtures at their dilution levels x0 = 64 and 57% mol (tests 1 and 2, respectively). Figures 1a and 2a show the change in the temperature difference \(\Delta T = T_{in} - T_{out}\) as a function of time t and temperature \(T_{out}\) during thiophene oxidation in tests 1 and 2, respectively. Here and below, \(T_{out}\) corresponds to a given increase in the reactor wall temperature at a rate of 1 K/min, and \(T_{in}\) is the temperature of the reaction mixture measured by an internal thermocouple. Note that the initial and final sections of the curves \(\Delta T(t, \phi_{in})\) lie in the negative region of \(\Delta T^*\) due to the lag in the temperature of the reaction mixture from the reactor wall temperature during heating.

Table 2 shows the following parameters of the curves \(\Delta T(t, \phi_{in})\) and the reaction mixture: \(T_{out}^*\) and \(T_{in}^*\) are the temperatures of the reactor wall and the reaction mixture, respectively, at which oxidation begins; \(T_{out}^*\) and \(T_{in}^*\) are the temperatures corresponding to the end of oxidation and

| test (diluent) | partial pressure (MPa) | amount of components (mmol) | ϕ | x0 (%) mol | \(P_R\) (MPa) |
|---------------|----------------------|-----------------------------|---|-------------|--------------|
| 1 (Ar + H2O)  | 1.87 3.82            | 7.6 48.6                    | 100.6 (1.7) | 1.01 64     | 4.72         |
| 2 (Ar + H2O)  | 2.52 3.85            | 10.1 65.4                   | 100.4 (1.7) | 1.01 57     |              |
| 3 (H2O)       | 10.1                 | 50                           |              |              |              |
| 4 (H2O)       | 1.92                 | 10.1 49.5                   | 50           | 1.33 46     | 1.26         |
| 5 (H2O)       | 2.52                 | 10.1 65.4                   | 50           | 1.01 40     | 1.38         |
| 6 (H2O)       | 3.18                 | 10.1 82.5                   | 50           | 0.80 35     | 1.76         |
| 7 (H2O)       | 3.22                 | 10.1 80.2                   | 50           | 0.80 35     | 1.94         |
| 8 (H2O)       | 3.17                 | 10.1 80.9                   | 100          | 0.81 52     | 1.62         |

"Here \(\phi = 6.5n_0(C_6H_6S)/n_0(O_2)\) is the fuel equivalence ratio according to the stoichiometric coefficients of reaction 1 and \(x_0 (%) = 100n_0(D)/[n_0(D) + n_0(C_6H_6S) + n_0(O_2)]\) is the dilution level of the C6H6S/O2 mixture. "Residual amount of water in the heated part of the reactor calculated using the reference data" is given in brackets. \(P_R\) is the pressure in the reactor after the end of the test at a temperature of 298 K.
increase in the temperature of the reaction mixture; oxidation.

The numbers of the curves correspond to the numbers of tests in Table 1. (tests in Table 1. The numbers of the curves correspond to the numbers of tests in Table 1.

Figure 1. Dependence of the temperature increment $\Delta T$ (curve 1) (a), the pressure $P$ (curve 1’) of the reaction mixture, and the rate of pressure change $dP/dt$ (curve 1”) (b) on the time $t$ and the set reactor temperature $T_{\text{set}}$ during the oxidation of thiophene in argon with a small amount of water vapor in test 1 ($x_0 = 64\%$ mol). Time $t = 0$ corresponds to the start of reactor heating. The numbers of the curves correspond to the numbers of tests in Table 1.

reaching the curve of the baseline; $t_{\text{onset}}$ is the duration of oxidation; $T_{\text{set}}$ and $T_{\text{out}}$ are the temperatures corresponding to the maximum on the curve $\Delta T(t_{\text{onset}}); \Delta T_{\text{max}}$ is the maximum increase in the temperature of the reaction mixture; $\Sigma C_p$ is the heat capacity of the reaction mixture at a temperature of 700 K, calculated using the reference data. $\Delta T_{\text{ad}}$ is calculated temperature increment of the reaction mixture due to heat release during reaction 1 under adiabatic conditions. The calculation method of the above values is described in detail in some works.

It is obvious that in the context of the present work, the temperature $T_{\text{out}}$ recorded by the internal thermocouple, will be determined by the endothermic evaporation processes of thiophene and water (the enthalpy of their evaporation at 400 K is $\Delta H_{\text{ev}} = 29.0$ and $39.3$ kJ/mol, respectively). Endothermic decomposition reactions of thiophene and intermediates, and exothermic oxidation reactions in the gas phase and on the surface of the Pt–Rh/Pt thermocouple. The exothermic reactions on the reactor wall almost do not affect the indications of the thermocouple $T_{\text{in}}$ due to the high heat capacity $C_p = 548$ J/kg·K and the thermal conductivity $\lambda = 21$ W/m·K of stainless steel, as well as the stabilizing effect of the thermoprogrammer, which regulates the reactor heating by reducing the heater power. Note that under adiabatic conditions, heat release at complete thiophene oxidation ($n_0(C_4H_4S) = 7.6$ and $10.1$ mmol, $Q = 21.1$ and $28.0$ kJ) in reaction 1 could have led to an increase in the reactor temperature, whose mass was $m = 3.6$ kg, by $\approx 10.7$ and 14.2 K, or the temperature of the gas contained in the reactor at homogeneous combustion—by several thousand degrees (Table 2).

The thiophene oxidation onset temperature in tests 1 and 2 is $T_{\text{onset}} = 419$ K and does not depend on the dilution level $x_0$ (Table 2). However, with a further increase in temperature, the thiophene oxidation dynamics in tests 1 and 2 differ. As can be seen in Figure 1a, the dependence $\Delta T(t_{\text{onset}})$ obtained in test 1 has two maxima at $T_{\text{out}} = 546$ and 705 K ($\Delta T_{\text{max}} = 14$ and 23 K, respectively). The first maximum on the curve $\Delta T(t_{\text{onset}})$ corresponds to the minimum of the pressure change rate $dP/dt(t_{\text{onset}})$, while the second more intense maximum is not reflected in the pressure change (Figure 1b). The pressure drop of the reaction mixture against the background of an increase in temperature at $T_{\text{out}} = 540$–552 K is apparently caused by a decrease in the number of reacting species due to condensation reactions, which is consistent with the data.

The formation of condensation reaction products was indicated, in particular, by the fact that the surface of the thermocouple (Figure 3a) and the inner surface of the reactor were covered with a uniform layer of soot. According to Zhao et al., the formation and growth of soot particles are promoted by sulfates formed during the combustion of fuel. It is obvious that the second maximum on the curve $\Delta T(t_{\text{onset}})$ is due to the oxidation of thiophene and/or the products resulting from condensation reactions directly on the surface of the Pt–Rh/Pt thermocouple, which does not cause an additional increase in the temperature and pressure of the reaction mixture. Note that the thermal consumption for heating the open section of the thermocouple (the junction diameter was 1.0 mm, the diameter and length of the conductors were 0.35 and 12 mm, respectively) per 100 K was 0.8 J, and corresponded to the heat released during oxidation of $\approx 0.4$ μmol of thiophene in reaction 1. The heat capacity and density of platinum were assumed to be equal to $C_p = 132$ J/kg·K and $\rho_{\text{Pt}} = 21.45$ g/cm$^3$.

Obviously, the oxidation of thiophene directly on the surface of the Pt–Rh/Pt thermocouple results from dissociative adsorption of thiophene and oxygen on the platinum surface.
The initial sticking coefficient decreases exponentially with increasing coverage. According to Zyubin et al., when studying the transformation of thiophene on the Pt(111) surface, revealed that the cleavage of the C=S bond and the formation of a metallocycle intermediate occur during chemisorption, in which the S atom is replaced by a Pt surface atom. Using NEXAFS spectroscopy, it was found that the cleavage of the C=S bond begins at 290 K and ends at 470 K; the Pt=S bond remains stable up to 1000 K. Bonzen and Ku, when studying the kinetics of O2 adsorption on the pure platinum surface, revealed that the cleavage of the C=O bond is broken, and the bound oxygen is stored on the platinum surface.

Stöhr et al., studying the transformation of thiophene on the Pt(111) surface, revealed that the dissociation energy of the O2 molecule is 498 kJ/mol and the dissociation energy of the Pt=O bond decreases from 405 to 270 kJ/mol with an increase in the coverage of platinum with oxygen, the oxidation of thiophene on the platinum surface occurs at lower activation barrier than in the gas phase. An increase in the amount of thiophene and oxygen (a decrease in the dilution level xD) in test 2 (Table 1) led to more intense oxidation compared to test 1. As can be seen in Figure 2a, the oxidation of thiophene in test 2 was accompanied by an explosion. It is obvious that the process was initiated on the surface of the Pt-Rh/Pt thermocouple and then propagated into the gas phase. This contributed not only to an increase in the temperature increment but also to an increase in the reactor wall temperature above the set value. Figure 2b shows the dependence of the temperature of thermocouples T1−T8 and the change in the power of the resistive heater W on time t and set temperature Tset in test 2. It is seen that at the moment of maximum heat release at Tmax in test 2, the temperature of thermocouples T1, T2, and T3 increased by 8, 15, and 5 K, respectively, relative to the set value. The difference in the temperature increment of thermocouples T1−T3 results from the different heat removal and a specific quantity of metal of the reactor parts. When the temperature of thermocouple T3 increased above the set value, the resistive heater was turned off (W = 0 W), which, due to the lag effect, has led the reactor temperature to decrease below the set value of Tset (see the insert in Figure 2b). The subsequent sharp increase in the heater power ensured that the reactor reached the set temperature mode. Based on the fact that the explosion was short-lived and ended with almost complete burning-out of

---

**Table 2. Characteristic Points of Curves in Figures 1, 2, 5, and 7 and Thermodynamic Parameters of the Reaction Mixtures**

| test (φ; xD) | T∞ (K) | T(2/3α) (K) | T(2/3β) (K) | t1 (min) | T(2/3α) (K) | T(2/3β) (K) | ΔTmax (K) | ΣC (J/K) | ΔTset (K) |
|-------------|--------|-------------|-------------|---------|-------------|-------------|-----------|---------|----------|
| 1 (1.01; 64) | 424    | 419         | 799         | 797     | 375         | 705         | 727       | 23      | 3.47     | 6073   |
| 2 (1.01; 57) | 424    | 419         | 607         | 604     | 187         | 534         | 953       | 419     | 4.21     | 6675   |
| 4 (1.33; 46) | 427    | 421         | 568         | 565     | 142         | 548         | 548       | 0       | 4.11     | 5133   |
| 5 (1.01; 40) | 425    | 419         | 614         | 612     | 189         | 532         | 533       | 1       | 4.51     | 6226   |
| 6 (0.80; 35) | 424    | 419         | 738         | 736     | 313         | 648         | 844       | 196     | 4.92     | 7137   |
| 7 (0.80; 35) | 715    | 713         | 629         | 753     | 124         | 4.92        | 7137      |         |          |        |
| 8 (0.81; 52) | 423    | 417         | 717         | 715     | 294         | 632         | 854       | 222     | 6.71     | 5238   |

**Table 3. Composition and Amounts of the Products of Thiophene Oxidation in Argon and Water Vapor (mmol)**

| products       | argon + water vapor | water vapor |
|----------------|---------------------|-------------|
|                | 1       | 2     | 4      | 5      | 6      | 7      | 8     |
| Ar             | 100.6   | 100.4 |         |         |         |        |       |       |
| O2             | 0.40    | 0.40  | 0.40   | 0.39   | 7.57   | 9.76   | 3.39  |       |
| CO             | 0.30    | 0.40  | 0.36   | 0.27   | 0.32   | 0.63   | 0.23  |       |
| CO2            | 26.61   | 37.46 | 32.91  | 36.00  | 39.17  | 39.12  | 37.53 |       |
| CH2−CH==CH2    | 0.16    | 0.21  | 0      | 0.01   | 0.01   | 0      | 0.01  |       |
| CH2−CH−CHO     | 0       | 0.03  | 0.02   | 0.02   | 0.02   | 0.02   | 0.03  |       |
| CH2==CH−COOH   | 0       | 0     | 0.01   | 0.01   | 0.02   | 0      | 0.01  |       |
| C4H4S          | 0.27    | 0.06  | 0.06   | 0.24   | 0.14   | 0.05   | 0.40  |       |
| Xe (mol %)     | 87.5    | 92.7  | 81.5   | 89.1   | 97.0   | 92.9   |       |       |
| (CO)8          | 0.18    | 0.06  | 0.12   | 0.32   | 0.59   | 0.13   |       |       |
| (CO2)8         | 0.72    | 0.81  | 6.56   | 1.91   | 5.25   | 0.52   |       |       |
| Yc (mol %)     | 96.6    | 98.2  | 99.7   | 98.0   | 99.5   | 113.5  | 99.4  |       |

*Subscript R refers to substances produced via annealing the reactor at 873 K for 90 min.*
thiophene [reducing $\Delta T$ to the base level (Figure 2a)], we assumed that in test 2, there was a detonation of the reaction mixture, which was initiated by the occurrence of a shock wave in the near-surface region of the Pt–Rh/Pt thermocouple. The detonation led to the destruction of the ceramic shell of the thermocouple (Figure 3b) and damage to the strain gage transducers, which was manifested in a sharp decrease in its readings after the passage of the shock wave (Figure 2a).

The results of the mass spectrometric analysis of thiophene oxidation products, as well as the values of the degree of carbon burnout $X_C$ and the carbon balance $Y_C$, calculated from these data, are given in Table 3. Carbon oxides, propene, propanal, and a residual amount of thiophene were found in the composition of the products. Obviously, the presence of $C_3H_6$ in the products resulted from the decomposition of thiophene on the platinum surface and the presence of $C_2H_5CHO$ as a result of partial oxidation of propene. As can be seen in Figure 4, a $t$-independent increase in the composition of the products. Obviously, the presence of a small amount of $O_2$ and thiophene in the products is due to their residue in capillary connecting the reactor to the adjusting valve. A smaller amount of unreacted thiophene and a larger $X_C$ value was obtained in test 2, where the largest temperature increment $\Delta T_{\text{max}}$ was detected (Table 2). The maximum loss of carbon ($X_C = 96.6\%$) was detected in test 1, which is explained by the significantly larger amount of soot on the thermocouple surface (Figure 3a) and the fact that its annealing was carried out without analysis of gas products (see Section 4).

2.2. Oxidation of Thiophene in the Water Vapor. The transformation of thiophene in water vapor was studied in the absence of $O_2$, rich, stoichiometric, and lean $C_4H_4S/O_2$ mixtures at a dilution level $x_d$ ranging from 35 to 52 mol % (Table 1). Figure 4 shows the temperature dependences of the saturated vapor pressure of water and thiophene.

Figure 4. Temperature dependences of the saturated vapor pressure of water (1) and thiophene (4), the water vapor pressure corresponding to the density $\rho(H_2O) = 0.761$ (2) and 1.481 mol/ dm$^3$ (3), plotted based on the reference $P=\rho-T$ data. Insert shows scaling temperature range of 350–475 K. The arrows indicate the conditions corresponding to the complete evaporation of water and thiophene.

saturated vapor pressure of water and thiophene, as well as the pressure of water vapor after its complete evaporation in the isochoric process. Based on the values of $n_0(C_4H_4S)$ and $n_0(H_2O)$ (Table 1), the reactor volume occupied by gas, and the reference $P=\rho-T$ data, it is easy to estimate that thiophene will completely transfer into the gas phase at $T_{ev} = 424$ K, while water—at $T_{ev} = 502$ (tests 3–7) and 542 K (test 8). As can be seen in Figure 4, at $T < 444$ K, the partial pressure and hence the density of saturated thiophene vapor is greater than that of water vapor. From these data, it also follows that part of the heat released during the oxidation of thiophene will be spent on its evaporation and evaporation of water up to $T_{ev}$.

Dependences of the increments of temperature, the pressure of the reaction mixture, and the rate of pressure change on time and set reactor temperature in tests 3–5 are shown in Figure 5. Here also shown are the dependences $T$ that characterize the behavior of the reaction system in the absence of thiophene and oxygen (in test 3°, the reactor was filled with water and nitrogen; see Section 4). From a comparison of the dependencies $\Delta T(t, T_{out})$, it can be seen (Figure 5a) that curve 3 is located above curve 3° up to 770 K. Obviously, this is due to the greater thermal conductivity of the $C_4H_4S/H_2O/N_2$ mixture than the $H_2O/N_2$ mixture. The dip in curve 3, as well as in curves 4 and 5, within the temperature range of 380–420 K can be associated with the evaporation of thiophene. The smaller dip in curves 4 and 5 than in curve 3 is the result of the superposition of endothermic evaporation and exothermic oxidation. The type of dependencies $P(t, T_{out})$ and $dP/dt(t, T_{out})$, obtained in test 3 corresponds to a larger number of species in the gas phase and a higher rate of pressure increase due to thiophene evaporation at $T < 424$ K than in test 3° (Figures 5b,c). The maximum of the $dP/dt$ derivative (curves 3 and 3°) corresponds to the complete evaporation of water.

The gas products formed in test 3 include the following components (mmol): $H_2=0.02$, $CH_4=0.01$, CO=0.03, and $CO_2=0.12$. The absence of $H_2S$ in the composition of volatile products may be due to both its solubility in water (0.378 wt % at 298 K) and sulfitation of the reactor wall.39
thiophene conversion (≈0.4% mol), calculated based on the amount of CO₂, CO, and CH₄, turned out to be an order of magnitude less than in the works.¹⁸,¹⁹ One of the reasons for this could be the polymerization of thiophene on the surface of the reactor wall at the initial stage of its heating. As established by Cheng et al.,⁴⁰ upon adsorption on the iron surface, thiophene loses both H atoms at position 2 relative to the sulfur atom, which leads to its polymerization and desorption of H₂. Harraz et al.⁴¹ observed the formation of a polythiophene layer on the surface of α-Fe₂O₃ nanoparticles. Our assumption is also based on the fact that after opening the reactor, a dark bloom was detected on its wall (not observed in other tests), which could be removed only after repeated annealing and mechanical cleaning.

At oxidation of thiophene in water vapor (tests 4 and 5), the temperature increment ΔTₘₐₓ was significantly less than that at oxidation in argon with a small amount of water vapor (test 2). At the same time, the temperature of the thiophene oxidation onset in tests 5 and 2 coincided (Tₘₐₓ = 419 K), while in test 4, it was slightly higher (Tₘₐₓ = 421 K) due to the lower amount of nₒ(O₂) (Tables 1 and 2). An increase in the amount of nₒ(O₂) in test 5 increased the contribution of homogeneous reactions, as indicated by an increase in the oxidation time tₙₒ and the area under the curve ΔT(t, Tₘₐₓ) (Figure 5a). As in tests 3 and 3', the presence of the first maxima on the dP/dtₜₒ curves (Figure 5c), obtained in tests 4 and 5, is associated with complete evaporation of water. The second maxima on curves 4 and 5 at Tₘₐₓ = 703–723 K, respectively, characterize the oxidation of the products of condensation reactions. The composition of the oxidation products obtained in tests 4 and 5 was almost the same, except for a larger amount of unburned thiophene in test 4 (X_C and (CO₂)R values in Table 3). In contrast to the results of Khalil et al.,²² maleic acid and SO₂ were not detected in the products obtained in tests 4 and 5, which is explained by their further oxidation by a water–oxygen mixture to acrylic acid (eventually to CO₂) and H₂SO₄, respectively. As can be seen in Figure 3, the soot particle size in test 5 was larger than in tests 1 and 2, apparently due to the larger amount of sulfates formed.³²

Comparison of the thiophene oxidation in tests 2 and 5, corresponding to the same amount of nₒ(C₄H₄S) and nₒ(O₂) (Table 1), indicates that the contribution of homogeneous oxidation reactions in water vapor is significantly less than that in argon (Figures 2a and 5a). This can be assumed to be caused not only by the higher heat capacity of water vapor,³⁷ which prevents the development of intense combustion, but also by the involvement of H₂O molecules in the heterogeneous oxidation of thiophene on the surface of the reactor wall (the surface of iron oxides). As noted by Khalil et al.,²² upon the oxidation of thiophene by lattice oxygen from hematite, the latter is transformed into magnetite; however, due to interaction with water, magnetite again is transformed into hematite. A similar conclusion was made by Hosseinipour et al.,⁴² based on the research results of the SCW conversion of heavy oil in the presence of iron oxide nanoparticles. Even though in the present work, the inner surface of the reactor was annealed in an atmosphere of O₂ (see Section 4) to obtain the oxide layer before each test, the formation of Fe₃O₄ could also be caused by the oxidation of iron with water⁴³ or a water–oxygen mixture. Besides, in this work, the Fe₃O₄ → Fe₂O₃ transition could have also occurred in the reaction of magnetite with molecular or atomic oxygen. Note that both magnetite and hematite were detected in corrosion products isolated from the reactor after the end of the tests (see below). This means that in the present study, heterogeneous catalytic oxidation of thiophene occurred on the surface of both the Pt–Rh/Pt thermocouple and the reactor wall (iron oxides) in a Fenton-like process.⁴⁴ We also do not exclude the effect of other metals (e.g., chromium) contained in stainless steel on the oxidation reactions. However, based on the results of a study of SCW oxidation of aromatic compounds in the presence of a Cr₂O₃/Al₂O₃ catalyst and data on the stability of Cr₂O₃ in this process,⁴⁶ it follows that the contribution of chromium oxides to the oxidation of thiophene is secondary.

The dependences of the temperature increment, the pressure of reaction mixture, and the rate of pressure change on the time and set reactor temperature in tests 6–8 conducted with the lean C₄H₄S/O₂ mixtures are shown in Figure 6. Test 7 differs from test 6 by the presence of CaCO₃ in the reaction system, while test 8 differs from test 6 by a twofold increase in the amount of water. As it follows from the data shown in Figures 5 and 6, the thiophene oxidation dynamics in tests 6–8 differs from that in tests 4 and 5, primarily by a longer duration of oxidation tₙₒ and a larger temperature increment ΔTₘₐₓ (Table 2). It is obvious that the latter proceeds from an increase in the O₂ content in the reaction mixture and, as a consequence, an increase in the degree of platinum coverage with oxygen, resulting, according to O’Brein et al.,³⁷ to increase the oxidation rate. As a result, the maximum temperature increment in tests 6, 7, and 8 was ΔTₘₐₓ = 196, 124, and 222 K, respectively. Moreover, in tests 6 and 8, this increment in temperature was reflected in the time dependences of pressure (Figures 6b,c). At the same time,
Unlike test 2 (Figure 2b), the reactor wall temperature did not exceed the set value of \( T_{\text{out}} \).

The lower value of \( \Delta T_{\text{max}} \) in test 7, than in tests 6 and 8, is explained by the greater contribution of heterogeneous oxidation of thiophene on the surface of the cell with \( \text{CaCO}_3 \). We were not able to reliably determine the oxidation onset temperature \( T_{\text{onset}} \) and, accordingly, the duration of oxidation \( t_{\text{ox}} \) in test 7 due to the high heat consumption for heating the cell and the predominance of heterogeneous oxidation, which was not recorded by the \( T_{\text{in}} \) thermocouple. Despite the larger amount of water filled into the reactor, the maximum temperature increment \( \Delta T_{\text{max}} \) in test 8 was greater, and the flash occurred at a lower temperature, \( T_{\text{max}} \), than in test 6 (Tables 1 and 2). This may be because an increase in the density of water vapor suppresses heterogeneous reactions on the reactor wall (the metal oxide’s surface) due to the adsorption of water molecules.\(^48\) In general, a comparison of the reactor wall (the metal oxide’s density of water vapor suppresses heterogeneous reactions on \( \text{O}_2 \), reactions on the surface of the Pt surface of the reactor wall predominate, while with an excess of \( \text{unreacted O}_2 \) and substances formed during the oxidation of \( \text{thiophene in water vapor} \) allows concluding that with oxygen maximum temperature increment \( \Delta T_{\text{max}} \) in test 8 was greater, and the flash occurred at a lower temperature, \( T_{\text{max}} \), than in test 6 (Tables 1 and 2).

The results of the mass spectrometric analysis of gas products (Table 3) show that an increase in the \( \text{O}_2 \) content in the reaction mixture from test 4 to test 6 \((\varphi = 1.33–0.80)\) leads to an increase in the degree of carbon burnup from 81.5 to 97% mol. However, an increase in the water density in test 8 contributes to a decrease in the \( \phi_{\text{C}} \) value to 92.9%. The largest amount of unreacted \( \text{O}_2 \) and substances formed during annealing of the reactor was obtained in test 7, which is due to the presence of a cell with \( \text{CaCO}_3 \) in the reactor. It is obvious that the excess of the \( \phi_{\text{C}} \) value to 92.9%.

\( \begin{align*}
\phi_{\text{C}} = 100\% - 1.33 - 0.80 = 81.5% \\
\phi_{\text{C}} = 100\% - 1.33 - 0.80 = 97% \\
\phi_{\text{C}} = 100\% - 1.33 - 0.80 = 92.9%
\end{align*}\)

\( \Delta T_{\text{min}} \) in test 7 was caused by the release of \( \text{CO}_2 \) resulting from the neutralization of sulfuric acid with calcium carbonate. Based on the values of \( \phi_{\text{C}} \) and \( n_0(\text{C}_4\text{H}_4\text{S}) \), it is easy to calculate that only 54% of the amount of sulfuric acid formed by reaction 1 has transformed into \( \text{CaSO}_4 \) (Figure 7). However, the corrosion of stainless steel has noticeably decreased.

Figure 8 shows the phase composition of corrosion products formed during the oxidation of thiophene in water vapor and subsequent annealing of the reactor in tests 4 and 7. In addition to chromium ferrite, magnetite, hematite, nickel sulfate, iron sulfate, and hydroxy sulfate, shown in the form of bar charts in Figure 8b–g, the following products were detected: chromite, \( \text{CrFeO}_3 \) (PDF card 00-034-0248); chromium oxide, \( \text{Cr}_2\text{O}_3 \) (PDF Card 00-012-8793); chromium sulfate, \( \text{CrSO}_4 \) (PDF card 00-021-0244).

A comparison of the XRD patterns obtained in tests 4 and 7 shows that in the latter case, the relative intensity of the bands corresponding to nickel and iron sulfates is significantly less. The presence of iron, nickel, and chromium sulfates in corrosion products can be a consequence of the interaction of sulfuric acid with both the oxide layer on the surface of the reactor wall and directly with stainless steel. Studies of corrosion of the nickel alloy in an aqueous solution of sulfuric acid \((T \leq 773 K, P \leq 38 MPa)\) have shown\(^9\) that the most intense corrosion occurred in liquid water at 423–503 K due to the dissolution of the oxide layer; at \( T > 503 K \), the alloy surface was passivated, and the corrosion rate significantly decreased. As applied to the results of the present work, this means that the bulk of iron, nickel, and chromium sulfates was formed after the end of the test during the cooling of the reactor. Therefore, the discharge of the hot reaction mixture from the reactor and/or the addition of neutralizing agents (hydroxides and carbonates of alkaline or alkaline earth metals) into the reactor will reduce the corrosion of structural materials.

It should be noted that some features of the thiophene oxidation in water vapor, detected in this work, were observed by us during the oxidation of dibenzothiophene under similar conditions.\(^5\) However, due to the greater resistance of dibenzothiophene to oxidation and the low pressure of its saturated vapor, these features were manifested poorly, which required further research on the oxidation of thiophene as the simplest aromatic S-containing compound. This resulted in obtaining reliable data that broaden the understanding of the oxidation mechanisms of thiophene derivatives in dense water vapor.

\( \Delta T_{\text{max}} \) in test 7 due to the high heat consumption for heating the cell and the predominance of heterogeneous oxidation, which was not recorded by the \( T_{\text{in}} \) thermocouple.
3. CONCLUSIONS
In this research, the oxidation of thiophene in argon and water vapor at high reagent density is studied for the first time. The experimental method is based on measuring the time dependencies of the reaction mixture temperature using a Pt−Rh/Pt thermocouple inserted into the center of the reaction volume at uniform slow heating of the reactor. It is established that the oxidation of thiophene in the argon and water vapor media proceeds according to homogeneous (in the volume of the reaction mixture) and heterogeneous (on the surface of the reactor wall and Pt−Rh/Pt thermocouple) reactions. In the water vapor medium, under oxygen deficiency and at a stoichiometric amount of O₂, heterogeneous oxidation of thiophene on the surface of the reactor wall (primarily iron oxides) prevails. The increase in water vapor density suppresses heterogeneous reactions on the reactor wall, apparently, due to the adsorption of water molecules. With an excess of O₂ in the water vapor medium and a stoichiometric amount of O₂ in the argon medium, thiophene oxidation dominates on the surface of the Pt−Rh/Pt thermocouple. In the case of the high density of the reagents, the latter can lead to detonation combustion regimes. It is shown that sulfuric acid formed during the oxidation of thiophene in water vapor causes corrosion of stainless steel that can be reduced by adding CaCO₃. The results obtained show the need to take into account heterogeneous processes occurring on the reactor wall when developing technologies for processing heavy oil raw materials in SCW or dense water vapor, especially in the case of using concentrated solutions and/or reactors with a large ratio of the reactor wall surface to its volume.

4. MATERIALS AND METHODS
The experiments were carried out using the test facility described in detail in works.15,14 A schematic sketch of the reactor is shown in Figure 9. The reactor (with an internal diameter of 30 mm, a length of 90 mm, and wall thickness of 15 mm) and structural elements were made of stainless steel (analogous to AISI 321H). The reactor was located in a cylindrical furnace heated by a resistive heater. The heating rate was controlled by a thermostimulator equipped with a PID controller and a chromel−alumel thermocouple T₂ mounted on the outer wall of the reactor. Additionally, the reactor temperature was measured by two chromel−alumel thermocouples T₁ and T₃ located at its butt ends. The temperature of the reaction mixture Tᵢ was measured by a Pt−Rh/Pt thermocouple (type S) inserted into the center of the reaction volume through the butt end of the reactor. The choice of Pt−Rh/Pt thermocouple to measure temperature was due to its corrosion resistance in an oxidizing S-containing atmosphere. The Pt−Rh/Pt thermocouple was placed in a corundum two-channel tube 2 (with an outer diameter of 3 mm). The open end of the thermocouple protruded from the corundum tube by 13 mm and was located in the center of the reaction volume. The pressure of the reagents was measured by a strain gauge transducer 9 (with a measurement limit of 100 MPa). The temperature and pressure measurement errors were ±0.5 K and ±0.03 MPa, respectively. Time dependences of temperature and pressure were recorded in the digital form with a frequency of 10 Hz. Reagents were fed into the reactor through a capillary 5 welded into the central part of the reactor wall through an adjusting valve 6. The reactor volume inside the furnace (reaction volume) was 65.7 cm³, while the reactor volume outside the furnace (the channel for entering the thermocouple into the reactor and the capillaries connecting the reactor to the adjusting and shut-off valves) was 1.4 cm³. Before feeding with reagents, the reactor was evacuated using a prevacuum pump.

The following reagents were used in tests: thiophene (99%, Alfa Aesar), oxygen (99.95% vol), argon (99.99% vol), nitrogen (99.95% vol), calcium carbonate (>99.9%), and distilled water. In tests 1 and 2, where argon was used as a diluent of the C₅H₅S/O₂ mixture, the nonheated reactor volumes were filled with water to prevent condensation of thiophene (the boiling point Tᵢ = 357.3 K).30 To do this, water (3.0 cm³) was filled into the reactor using a syringe through a rubber membrane 7 installed on the nipple of the reagent supply valve 6 (Figure 9). The reactor was then heated to a temperature T₂ = 403 K and thermostated for 45 min. During this time, a certain portion of the water (≈1.4 cm³) was recondensed into nonheated volumes of the reactor. Then, at Tᵢ = 403 K, the excess water was discharged from the reactor to a pressure of 0.1 MPa (saturated water vapor pressure at 298 K), which allowed the water to be kept in nonheated volumes. After cooling the reactor to Tᵢ = 303 K, it was filled with 0.6 or 0.8 cm³ of thiophene (with a density of 1.059 g/cm³ at 298 K)30 and then, argon and oxygen to a given pressure.

Tests 3° and 3 were calibration tests performed without adding O₂ to the reaction system. In these tests, N₂ was used as a buffer gas since its thermophysical properties are close to those of O₂. The amount of N₂ (≈66 mmol) charged into the reactor corresponded to the amount of O₂ required for complete oxidation of thiophene. In tests 3° and 3, after filling the reactor with water (1.8 cm³), it was heated to T₂ = 403 K and kept at this temperature for 45 min (at that, a certain portion of the water (≈1.4 cm³) was recondensed into nonheated volumes). In test 3°, after cooling the reactor to Tᵢ = 302 K, it was filled with 0.5 cm³ of water and nitrogen to a pressure of 2.52 MPa. In test 3, after cooling the reactor to Tᵢ = 303 K, 0.8 cm³ of thiophene, 0.5 cm³ of water, and nitrogen were successively filled to a pressure of 2.58 MPa. In tests 4−8, the reactor filling procedure was similar to that in test 3. To fill nonheated volumes, 1.8 cm³ (tests 4−7) and 2.7 cm³ (test 8) of water were filled into the reactor. After heating the reactor to T₂ = 403 K, holding at this temperature for 45 min, and cooling down to Tᵢ = 303 K, 0.8 cm³ of thiophene, 0.5 cm³ of water, and oxygen were successively fed into the reactor to a
given pressure, that is, in tests 4–7 and 8, the heated part of the reactor contained \( \approx 50 \) and 100 mmol of water, respectively. In test 7, thiophene oxidation was conducted in the presence of CaCO\(_3\). Calcium carbonate was fed into the reactor in a square cell 4 (with a length of 25 mm, and wall height of 5 mm) made of 0.2 mm thick stainless-steel sheet. After filling with reagents, the reactor was heated to 823 K at a rate of 1 K/min.

The amounts of reagents and diluent were determined based on their temperature and partial pressure, as well as the reactor volume using the reference \( \rho-P-T \) data.\(^{27}\) The value of \( n_0(CaCO_3) \) corresponds to two times the amount of CaCO\(_3\) required to neutralize sulfuric acid resulting from thiophene oxidation during the reaction

\[
CaCO_3(s) + H_2SO_4(g) \rightarrow CaSO_4(s) + H_2O(g) + CO_2(g),
\]

\[\Delta H_{298}^0 = -118 \text{ kJ/mol} \tag{2}\]

The choice of CaCO\(_3\) as a neutralizing agent is due to its low solubility in water (1.4-10\(^{-2}\) g/dm\(^3\) at 298 K).\(^{38}\)

After turning off the heating, the reactor in the furnace was cooled to room temperature for more than 12 h. Then, the nonreacted substances was determined as follows. The reactor was removed by annealing the thermocouple and ceramic shell wall occurred, before running each test, the inner surface of the reactor was cleaned of the corrosion layer. Then, to obtain a dense oxide layer, the inner surface of the reactor was annealed in an O\(_2\) environment (approx 0.7 MPa at 298 K) at a temperature of 873 K for 60 min. Due to the interaction with the reaction mixture, a bloom appeared on the Pt–Rh/Pt thermocouple. This bloom was removed by annealing the thermocouple and ceramic shell in a muffle furnace in the air at 1103 K for 100 min. Note that the temperature \( T_{in} \) in all the tests was measured using just a single Pt–Rh/Pt thermocouple. The composition of solid products was analyzed using a powder X-ray diffractometer XTRA Thermo (phase identification was carried out according to the reference data).\(^{19}\)

\section*{AUTHOR INFORMATION}

\begin{table}[h]
\caption{Table 1}
\begin{tabular}{|c|c|c|}
\hline
Author & Institution & Email Address \\
\hline
Oxana N. Fedyaeva & Kutateladze Institute of Thermophysics SB RAS, Novosibirsk 630090, Russia; orcid.org/0000-0003-3088-5404; Email: fedyaeva@itp.nsc.ru &  \\
\hline
Andrey V. Shishkin & Kutateladze Institute of Thermophysics SB RAS, Novosibirsk 630090, Russia; orcid.org/0000-0001-6177-4876 &  \\
\hline
Anatoly A. Vostrikov & Kutateladze Institute of Thermophysics SB RAS, Novosibirsk 630090, Russia; orcid.org/0000-0001-6177-4876 &  \\
\hline
\end{tabular}
\end{table}

\section*{ACKNOWLEDGMENTS}

The work was supported by the Russian Foundation for Basic Research (grant number 18-29-06005). The authors thank M. Y. Sokol for mass spectrometric analysis of gas products and D. A. Yatsenko for XRD analysis of samples.

\section*{REFERENCES}

1. Javadi, R.; de Klerk, A. Desulfurization of Heavy Oil. Appl. Petrochem. Res. 2012, 1, 3–19.
2. Fedyaeva, O. N.; Antipenko, V. R.; Vostrikov, A. A. Conversion of Sulfur-Rich Asphaltite in Supercritical Water and Effect of Metal Additives. J. Supercrit. Fluids 2014, 88, 105–116.
3. Fedyaeva, O. N.; Antipenko, V. R.; Dubov, D. Y.; Kruglyakova, T. V.; Vostrikov, A. A. Non-isothermal Conversion of the Kashpir Sulfur-Rich Oil Shale in a Supercritical Water Flow. J. Supercrit. Fluids 2016, 109, 157–165.
4. Kovalenko, E. Y.; Gerasimova, N. N.; Sagachenko, T. A.; Min, R. S.; Patrakov, Y. F. Characteristics of Products of Thermal Decomposition of Heavy Oil Asphaltene under Supercritical Conditions. Energy Fuels 2020, 34, 9563–9572.
5. Wake, H. Oil Refineries: a Review of Their Ecological Impacts on the Aquatic Environment. Estuar. Coast Shelf Sci. 2005, 62, 131–140.
6. Tang, J.; Wang, M.; Wang, F.; Sun, Q.; Zhou, Q. Eco-toxicity of Petroleum Hydrocarbon Contaminated Soil. J. Environ. Sci. 2011, 23, 845–851.
7. Lighty, J. S.; Veranth, J. M.; Sarofim, A. F. Combustion Aerosols: Factors Governing Their Size and Composition and Impactions to Human Health. J. Air Waste Manag. Assoc. 2000, 50, 1565–1618.
8. Ferek, R. J.; Hobbs, P. V.; Herring, J. A.; Laursen, K. K.; Weiss, R. E.; Rasmussen, R. A. Chemical Composition of Emissions from the Kuwait Oil Fires. J. Geophys. Res. 1991, 97, 14483–14489.
9. Rocha, D. H. D.; Silva, R. J. Exergoenvironmental Analysis of an Ultra-Supercritical Coal-Fired Power Plants. J. Clean. Prod. 2019, 231, 671–682.
10. Cui, C.; Li, Y.; Wang, S.; Ren, M.; Yang, C.; Jiang, Z.; Zhang, J. Review on an Advanced Combustion Technology: Supercritical Hydrothermal Combustion. Appl. Sci. 2020, 10, 1645.
11. Wang, T.; Xiang, B.; Liu, J.; Shen, Z. Supercritical Water Oxidation of Sulfide. Environ. Sci. Technol. 2003, 37, 1955–1961.
12. Ma, H. H.; Wang, S. Z.; Zhou, L. Sulfur transformations during supercritical water oxidation of methanthiol and thirane. Adv. Mater. Res. 2012, 610–613, 1377–1380.
13. Fedyaeva, O. N.; Artamonov, D. O.; Vostrikov, A. A. Effect of H\(_2\)O and CO\(_2\) on Propane, Propene, and Isopropenanol Oxidation at Elevated Pressure. Combust. Flame 2019, 199, 230–240.
14. Fedyaeva, O. N.; Artamonov, D. O.; Vostrikov, A. A. Heterogeneous–Homogeneous Oxidation of Pyrrole in Water Vapor at Elevated Pressure. Combust. Flame 2019, 210, 183–192.
15. Fedyaeva, O. N.; Shishkin, A. V.; Vostrikov, A. A. Oxidation of Dibenzothiophene in Water Vapor and Argon at Increased Pressure. J. Eng. Thermophys. 2020, 29, 549–560.
16. Winkler, J. K.; Karow, W.; Rademacher, P. Gas-Phase Pyrolysis of Heterocyclic Compounds, Part 1 and 2: Flow Pyrolysis and Annihilation Reactions of Some Sulfur Heterocycles: Thiophene,
Benzothiophene, and Dibenzothiophene. A Product-Oriented Study. J. Anal. Appl. Pyrolysis 2002, 62, 123−141.

(17) Katritzky, A. R.; Barcock, R. A.; Balasubramanian, M.; Greenhill, J. V.; Siskin, M.; Olmstead, W. N. Aqueous High-Temperature Chemistry of Carbon- and Heterocycles. 21. Reactions of Sulfur-Containing Compounds in Supercritical Water at 460°C. Energy Fuels 1994, 8, 498−506.

(18) Patwardhan, P. R.; Timko, M. T.; Class, C. A.; Bonomi, R. E.; Kida, Y.; Hernandez, H. H.; Tester, J. W.; Green, W. H. Supercritical Water Desulfurization of Organic Sulfides is Consistent with Free-Radical Kinetics. Energy Fuels 2013, 27, 6108−6117.

(19) Qi, W.; Li, Y.; Liu, Z.; Li, X.; Jiang, Y.; Sun, H. Decomposition Mechanism of Thiophene Compounds in Heavy Oil under Supercritical Water. Chem. Eng. Sci. 2020, 228, 115979.

(20) Timko, M. T.; Ghoniem, A. F.; Green, W. H. Upgrading and Desulfurization of Heavy Oils by Supercritical Water. J. Supercrit. Fluids 2015, 96, 114−123.

(21) Kang, J.; Sim, S.; Jung, H.; Han, B.; Lee, Y.-W. Desulfurization of Hexyl Sulfide and Hexanethiol Using Supercritical Water. J. Supercrit. Fluids 2020, 158, 104734.

(22) Khalil, M.; Lee, R. L.; Liu, N. Hematite Nanoparticles in Aquathermolysis: a Desulfurization Study of Thiophene. Fuel 2015, 145, 214−220.

(23) Yoshida, S.; Takekaki, K.; Miwa, K.; Wakahara, M. Desulfurization of Thiophene in Alkaline Supercritical Water Studied by 1H and 13C NMR. Chem. Lett. 2004, 33, 330−331.

(24) Song, X.; Fanelli, M. G.; Cook, J. M.; Bai, F.; Parish, C. A. Mechanisms for the Reaction of Thiophene and Methylthiophene with Singlet and Triplet Molecular Oxygen. J. Phys. Chem. A 2012, 116, 4934−4946.

(25) Zhang, Y.; Wang, R. Recent Advances on Catalyst and Systems for the Oxidation of Thiophene Derivatives in Fuel Oil with Molecular Oxygen. Mini-Rev. Org. Chem. 2018, 15, 488−497.

(26) Antón, V.; Artigas, H.; Lomba, L.; Giner, B.; Lafuente, C. Thermochemical Properties of the Thiophene Family. J. Therm. Anal. Calorim. 2016, 125, 509−518.

(27) Thermophysical Properties of Fluid Systems. NIST Chemistry WebBook, NIST Standard Reference Database No 69; Lemmon, E. W., McLinden, M. O., Friend, D. G., Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg MD, 20899, 2018; http://webbook.nist.gov/chemistry/fluid/.

(28) Hubbard, W. N.; Scott, D. W.; Frow, F. R.; Waddington, G. Thiophene: Heat of Combustion and Chemical Thermodynamics Properties. J. Am. Chem. Soc. 1955, 77, 5855−5857.

(29) Lindin, P. A.; Andreeva, L. L.; Molchok, V. A. The Constants of Inorganic Compounds: Handbook; Drofa: Moscow, 2006; [In Russian].

(30) NIST Chemistry WebBook. NIST Standard Reference Database Number 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg MD, 20899, 2018; https://webbook.nist.gov/chemistry/.

(31) Guva, A. Y. Brief Thermophysical Handbook; Sibvuzizdat: Novosibirsk, 2002; [In Russian].

(32) Zhao, Y.; Ma, Q.; Liu, Y.; He, H. Influence of Sulfur in Fuel on the Properties of Diffusion Flame Soot. Atmos. Environ. 2016, 142, 383−392.

(33) Stöhr, J.; Gland, J. L.; Kollin, E. B.; Koestner, R. J.; Johnson, A. L.; Muetterties, E. L.; Sette, F. Desulfurization and Structural Transformation of Thiophene on the Pt(111) Surface. Phys. Chem. Lett. 1984, 53, 2161−2164.

(34) Khan, N. A.; Hwu, H. H.; Chen, J. G. Low-Temperature Hydrodesulfurization of Thiophene on Ni/Pt(111) Bimetallic Surfaces with Monolayer Ni Coverage. J. Catal. 2002, 205, 259−265.

(35) Bonzel, H. P.; Ku, R. On the Kinetics of Oxygen Adsorption on a Pt(111) Surface. Surf. Sci. 1973, 40, 85−101.

(36) Zybina, A. S.; Zybina, T. S.; Dobrovoll'skii, Y. A.; Volokhov, V. M. Oxygen Behavior on the Platinum Surface: a Quantum-Chemical Modeling. Russ. J. Inorg. Chem. 2013, 58, 803−807.

(37) Daubert, T. E.; Hutchison, G. Vapor Pressure of 18 Pure Industrial Chemicals; AICHE Symposium Series; ACS, 1990; Vol. 86, pp 93−114.

(38) Perry's Chemical Engineers' Handbook, 7th ed.; Perry, R. H., Green, D. W., Maloney, J. O.; McGraw-Hill: New York, 1997.

(39) Fedyaeva, O. N.; Vostrikov, A. A. Disposal of Hazardous Organic Substances in Supercritical Water. Russ. J. Phys. Chem. B 2012, 6, 844−860.

(40) Cheng, L.; Bocarsly, A. B.; Bernasek, S. L.; Ramanarayanan, T. A. Adsorption and Reaction of Thiophene on the Fe(100) Surface: Selective Dehydrogenation and Polymerization. Surf. Sci. 1997, 374, 357−372.

(41) Harraz, F. A.; Faisal, M.; Jalalah, M.; Almadily, A. A.; Al-Sayari, S. A.; Al-Assir, M. S. Conducting Polythiophene/a-Fe2O3 Nanocomposite for Efficient Methanol Electrochemical Sensor. Appl. Surf. Sci. 2020, 508, 145226.

(42) Hosseinpour, M.; Fatemi, S.; Ahmadi, J. J.; Morimoto, M.; Akizuki, M.; Oshima, Y.; Fumoto, E. The Synergistic Effect between Supercritical Water and Redox Properties of Iron Oxide Nanoparticles during in-situ Catalytic Upgrading of Heavy Oil with Formic Acid. Isotopic Study. Appl. Catal., B 2018, 230, 91−101.

(43) Vostrikov, A. A.; Fedyaeva, O. N.; Shishkin, A. V.; Sokol, M. Y.; Zaikovskii, A. V. Synthesis of Fe2O3 Nanoparticles during Iron Oxidation by Supercritical Water. Tech. Phys. Lett. 2012, 38, 955−958.

(44) Pereira, M. C.; Oliveira, L. C. A.; Murad, E. Iron Oxide Catalysts: Fenton and Fenton-like Reactions − a Review. Clay Miner. 2012, 47, 285−302.

(45) Ding, Z.-Y.; Aki, S. N. V. K.; Abraham, M. A. Catalytic Supercritical Water Oxidation: An Approach for Complete Destruction of Aromatic Compounds. Innovations in Supercritical Fluids; ACS Symp. Series; ACS: Washington, 1995; pp 232−245.

(46) Aki, S. N. V. K.; Ding, Z.-Y.; Abraham, M. A. Catalytic Supercritical Water Oxidation: Stability of Cr2O3 Catalyst. AIChE J. 1996, 42, 1995−2004.

(47) O’Brein, C. B.; Jenness, G. B.; Dong, H.; Vlachos, D. G.; Lee, I. C. Deactivation of Pt/Al2O3 during Propane Oxidation at Low Temperatures: Kinetic Regimes and Platinum Oxide Formation. J. Catal. 2016, 337, 122−132.

(48) Vostrikov, A. A.; Fedyaeva, O. N.; Shishkin, A. V.; Tretyakov, D. S.; Sokol, M. Y. Features of Low-Temperature Oxidation of Hydrogen in the Medium of Nitrogen, Carbon Dioxide, and Water Vapor at Elevated Pressure. Int. J. Hydrogen Energy 2018, 43, 10469−10480.

(49) Kritzer, P.; Boukis, N.; Dinjus, E. Corrosion of Alloy 625 in High-Temperature, High-Pressure Sulfate Solutions. Corrosion 1998, 54, 689−699.

(50) Fedyaeva, O. N.; Vostrikov, A. A.; Shishkin, A. V.; Sokol, M. Y.; Borisova, L. S.; Koshirteev, V. A. Conversion of Brown Coal in Sub- and Supercritical Water at Cyclic Pressurization and Depressurization. Russ. J. Phys. Chem. B 2012, 6, 793−803.

(51) Powder Diffraction File, PDF-4+; Release 2012.