

# The Molecular Mechanism of Low-Temperature Decomposition of Hydrogen Sulfide under Conjugated Chemisorption–Catalysis Conditions

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Received September 2, 2005

**Abstract**—The molecular mechanism of interaction of two hydrogen sulfide molecules with the  $(\text{Co}^{\text{III}}-\text{H}_0)_2\text{S}_2(\text{SH}_2)_4$  model active center containing occluded hydrogen was studied by the density functional theory method with the B3P86 hybrid exchange–correlation functional. The reaction was found to occur in the following elementary steps: molecular adsorption of hydrogen sulfide  $\Rightarrow$  dissociative chemisorption  $\Rightarrow$  S–S bond formation in the surface intermediate  $\{2\text{Co}^{\text{III}} - (\mu-\text{S}_2) + 2\text{H}(\text{ads})\}$  with the release of the first hydrogen molecule into the gas phase  $\text{H}_2(\text{g}) \Rightarrow$  the release of the second hydrogen molecule into the gas phase  $\text{H}_2(\text{g}) \Rightarrow$  the formation of cyclooctasulfur in the reaction  $4\text{S}_2(\text{ads}) \rightarrow \text{S}_8(\text{ads})$ . The first three steps occur spontaneously at room temperature, the thermodynamic driving force of the process being the stoichiometric reaction of S–S bond formation at the stage of conjugated chemisorption of two hydrogen sulfide molecules on two adjacent metal ions with the release of the first hydrogen molecule into the gas phase. The catalytic cycle is terminated by the recombination of molecular sulfur  $\text{S}_2$  into cyclooctasulfur  $\text{S}_8$  in the adsorption layer and the release of the second hydrogen molecule into the gas phase.

**DOI:** 10.1134/S0036024406090081

## INTRODUCTION

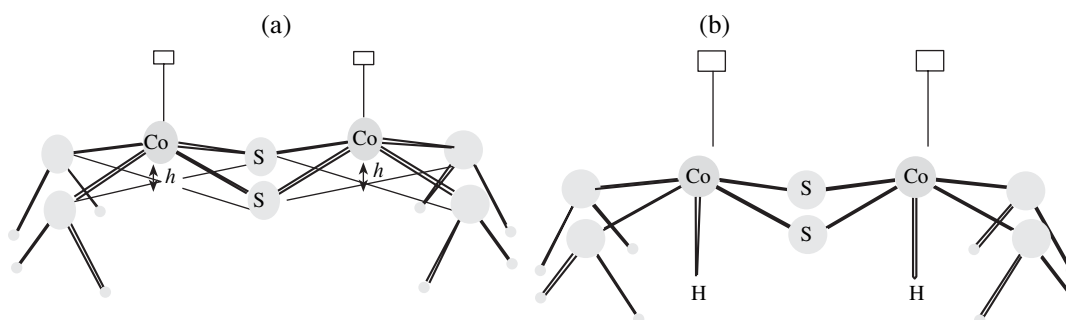
Hydrogen sulfide is one of the major side products of petroleum and natural gas processing, hydrometallurgy, and coal gasification. It is contained in large amounts (up to 50–80%) in gas condensate and natural gas deposits and is a typical product of the decomposition of many mineral and organic substances. At the same time, hydrogen sulfide has a strong poisonous action on living organisms, its maximum permissible concentration for habitable areas is 0.008 mg/m<sup>3</sup> [1]. For this reason, all industrial waste gases require thorough purification from hydrogen sulfide. The amount of hydrogen sulfide processed solely in the hydroprocessing of oil fractions is no less than 50 million tons. The main method for utilizing hydrogen sulfide is its oxidation to elemental sulfur by the Claus method with the use of  $\text{SO}_2$ . The highest degree of sulfur extraction, however, does not exceed 98%, and waste gases contain substantial amounts of sulfur compounds and require additional purification [2]. Much effort is therefore directed toward creating and perfecting methods for additional purification of residual gases (e.g., see [3]). Currently, methods for the direct partial oxidation of hydrogen sulfide with oxygen to elemental sulfur and water have been developed [4]. In all oxidation variants, hydrogen is, however, lost in the form of water. At

the same time, hydrogen sulfide can be a raw material for the production of hydrogen, which is a very valuable chemical product [5].

The direct thermal decomposition of hydrogen sulfide to hydrogen and sulfur in the reaction



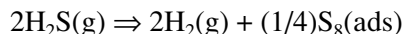
is a strongly endothermic process and can only be performed at high temperatures. The cost of hydrogen is then substantially higher than with known methods for producing it from hydrocarbon materials. Photo-, plasma-, and electrochemical and enzymatic decomposition of hydrogen sulfide according to reaction (1) has not found wide use for the same reason [5]. The number of works concerned with the direct decomposition of hydrogen sulfide to hydrogen and sulfur nevertheless continuously increases [6–21]. At the same time, the use of specially selected catalysts allows the reaction of hydrogen sulfide decomposition to be directed along a new route, which can substantially decrease the temperature necessary for initiating this reaction [22]. This possibility is the subject matter of the present work.



**Fig. 1.** Quantum-chemical models of the active center of sulfide catalysts (a) not containing and (b) containing occluded hydrogen. The electronic configurations of the Co(II) and Co(III) ions are (a)  $d^7$  and (b)  $d^6$ , respectively.

## METHOD OF CALCULATIONS

In order to prove the thermodynamic possibility of hydrogen sulfide decomposition at room temperature, we calculated the energy profile of the reaction



on the surface of a model cobalt catalyst. The calculations were made using the density functional theory method with the B3P86 hybrid exchange-correlation functional [23, 24] and the 6-31G( $d, p$ ) double-zeta basis set including polarization  $d$  and  $p$  functions. The active center was modeled by the  $(\text{Co}^{\text{III}}-\text{H}_0)_2\text{S}_2(\text{SH}_2)_4$  binuclear complex [25] containing occluded hydrogen ( $\text{H}_0$ ). The molecular structure geometric parameters were optimized using the core effective potential (CEP) for the inner shells of cobalt and the 31G double-zeta basis set for the metal valence orbitals (CEP-31G) [26, 27]. Cobalt atoms in the active center model occupy the vertices of square pyramids and are raised by  $h = 0.5 \text{ \AA}$  above the plane of four sulfur atoms, in agreement with the experimental data on the active component of Co/MoS<sub>2</sub> sulfide catalysts [28].

## RESULTS AND DISCUSSION

The discovery of the new catalytic reaction of low-temperature hydrogen sulfide decomposition to hydrogen and elemental sulfur [22] was preceded by our

observation of dihydrogen disulfide ( $\text{H}_2\text{S}_2$ ), which was desorbed from the surface of sulfide catalysts during their programmed-temperature heating [29]. Note that the chemistry of dihydrogen disulfide, as distinct from its analogue (hydrogen peroxide), has been studied very scantily. The properties of the compound have been investigated thoroughly in [30, 31].

The quantum-chemical models of binuclear active centers, in which cobalt ions have the formal oxidation degrees  $\text{Co}^{2+}$  ( $d^7$ ) and  $\text{Co}^{3+}$  ( $d^6$ ), are shown in Fig. 1. Cobalt(III) with the  $d^6$  electronic configuration is formed as a result of the oxidative addition of hydrogen to the active metal atom in the active components of sulfide hydrodesulfurization catalysts [28, 32, 33]. In the quantum-chemical model (Fig. 1), the only parameter rigidly fixed in calculations was the height of the square pyramid constructed of four sulfur ions with the cobalt ion at the vertex in agreement with the structure of the active component of sulfide hydrodesulfurization catalysts [28]. All the other interatomic distances were optimized to minimize the total energy  $E_{\text{total}}$ . The calculated interatomic distances (Table 1) were close to those determined experimentally for the active component structure [28].

Models of molecular adsorption of hydrogen sulfide on cobalt ions with the (a)  $d^7$  and (b)  $d^6$  electronic configurations are shown in Fig. 2. According to Table 2,

**Table 1.** Calculated interatomic distances ( $\text{\AA}$ ) for models (a) and (b) (Fig. 1);  $h = 0.5 \text{ \AA}$

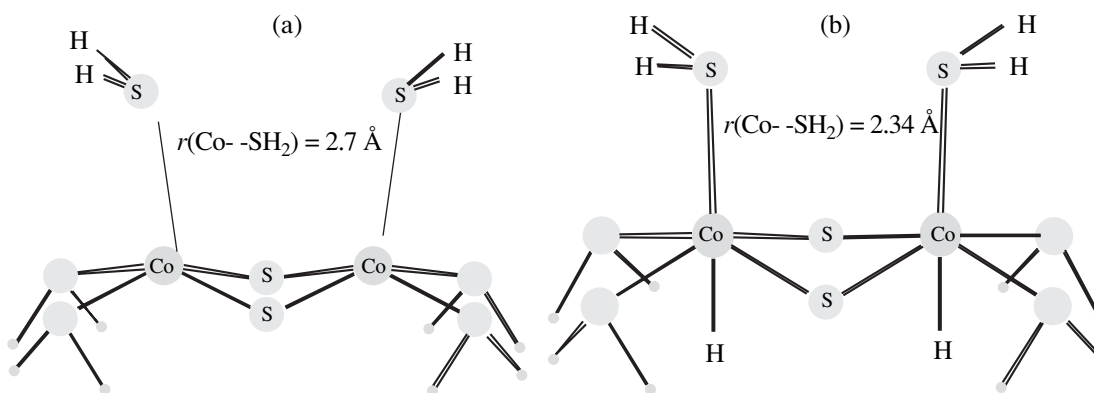
Distance	(a)	(b)
Co–Co	3.18	3.12
Co–S	2.15	2.21
Co–SH <sub>2</sub>	2.23	2.30
S–S	2.7	2.98
Co–H		1.42

Note: The calculated thermodynamic parameters:  $E_{\text{total}} =$  (a)  $-2669.74338$  and (b)  $-2670.96103$  au,  $S_{298} =$  (a) 109.9 and (b) 121.9 cal/(mol K).

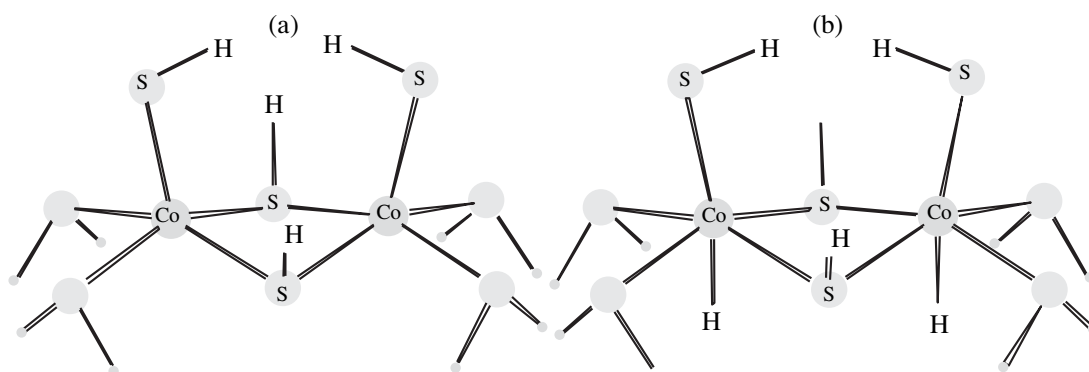
**Table 2.** Calculated  $\Delta H_{298}$  (kcal/mol),  $\Delta S_{298}$  (cal/(mol K)), and  $\Delta G_{298}$  (kcal/mol) values for models (a) and (b) (Fig. 2)

Value	(a)	(b)
$\Delta H_{298}$	–2.2	–12.7
$\Delta S_{298}$	–29.3	–39.6
$\Delta G_{298}$	+6.6	–0.8

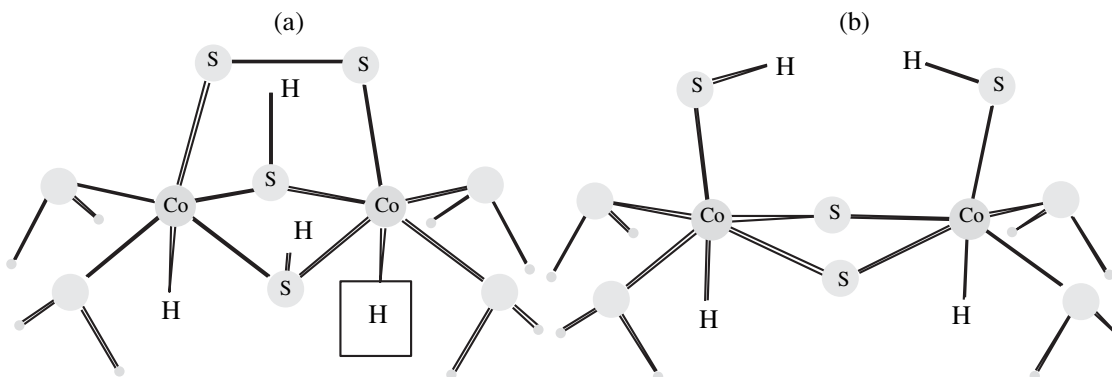
Note: The heats were calculated on the assumption that  $\Delta H_{298} \approx \Delta E_{\text{total}}$ . The calculated thermodynamic parameters:  $E_{\text{total}} =$  (a)  $-3469.20610$  and (b)  $-3470.45701$  au,  $\Delta S_{298} =$  (a) 149.5 and (b) 140.9 cal/(mol K).



**Fig. 2.** Molecular adsorption of hydrogen sulfide at room temperature on cobalt ions (a) not containing and (b) containing occluded hydrogen. The electronic configurations of the Co(II) and Co(III) ions are (a)  $d^7$  and (b)  $d^6$ , respectively.



**Fig. 3.** Quantum-chemical models of the dissociative chemisorption of hydrogen sulfide on cobalt ions with the electronic configurations (a) Co(II),  $d^7$  and (b) Co(III),  $d^6$  (a) not containing and (b) containing occluded hydrogen.



**Fig. 4.** Quantum-chemical models of the surface states of the adsorption complex on Co(III),  $d^6$  ions containing occluded hydrogen after the removal of one hydrogen molecule from chemisorbed hydrogen sulfide according to reactions (a) and (b).

the adsorption of hydrogen sulfide on Co<sup>III</sup> ions ( $d^6$  configuration) occurs spontaneously at room temperature, because this process is exothermic ( $\Delta H < 0$ ) and its Gibbs energy is negative ( $\Delta G < 0$ ). At the same time, adsorption on Co<sup>II</sup> ions ( $d^7$  configuration) is hardly probable ( $\Delta H < 0$ ,  $\Delta G > 0$ ). Accordingly, the equilibrium distance between the cobalt ion and adsorbed

hydrogen sulfide molecule is much shorter for Co<sup>III</sup> ( $d^6$ ) (Fig. 2).

The next stage is the dissociative chemisorption of two hydrogen sulfide molecules on two adjacent cobalt atoms (Fig. 3, Table 3). This reaction can also occur spontaneously only on Co<sup>III</sup> ions with the  $d^6$  configuration (Fig. 3b). The dissociative chemisorption reaction

**Table 3.** Calculated thermodynamic ( $\Delta H_{298}$  and  $\Delta G_{298}$ , kcal/mol, and  $\Delta S_{298}$ , cal/(mol K)) and geometric (interatomic distances, Å, and angles, deg) parameters of the dissociative chemisorption of hydrogen sulfide on cobalt ions with different electronic configurations (Figs. 3a and 3b)

Parameter	(a)	(b)	Parameter	(a)	(b)	Parameter	(a)	(b)
$\Delta H_{298}$	2.2	-28.7	Co-Co	3.30	3.32	Co-S	2.32	2.28
$\Delta S_{298}$	-37.7	-37.8	Co-S	2.27	2.30	S-H	1.34	1.34
$\Delta G_{298}$	12.0	-17.4	S-S	2.96	3.03	$\angle$ CoSH	106.3	103.7
			Co-H		1.48	S-H (ads)	1.35	1.36

Note: The calculated thermodynamic parameters:  $E_{\text{total}} =$  (a) -3469.19206 and (b) -3470.50800 au,  $S_{298} =$  (a) 142.8 and (b) 144.6 cal/(mol K). The parameters of the active center and adsorption complex are given in the second and third table sections, respectively.

**Table 4.** Calculated thermodynamic ( $\Delta H_{298}$  and  $\Delta G_{298}$ , kcal/mol, and  $\Delta S_{298}$ , cal/(mol K)) and geometric (interatomic distances, Å, and angles, deg) parameters of reactions (a) and (b) (Figs. 4a and 4b)

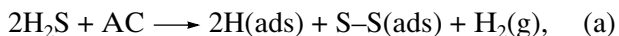
Parameter	(a)	(b)	Parameter	(a)	(b)	Parameter	(a)	(b)
$\Delta H_{298}$	-28.9	-7.1	Co-Co	3.12	3.92	Co-S	2.28	2.28
$\Delta S_{298}$	-59.7	-81.5	Co-S	2.25	2.27	S-S	2.18	
$\Delta G_{298}$	-11.0	17.4	Co-H	1.40	1.48	S-H	1.36	1.34
			S-S	3.18	2.09	$\angle$ CoSH		108.8

Note: The calculated thermodynamic parameters:  $E_{\text{total}} =$  (a) -3469.24854 and (b) -3469.21384 au,  $S_{298} =$  (a) 129.3 and (b) 138.6 cal/(mol K). The parameters for reactions (a) and (b) are given in the second and third table sections, respectively.

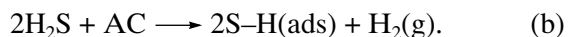
is then substantially exothermic and occurs at room temperature with a substantial gain in the Gibbs energy. Because the dissociation of hydrogen sulfide on  $\text{Co}^{\text{II}}$  ( $d^7$ ) ions at room temperature is thermodynamically unfavorable (Table 3), all subsequent calculations were performed for active centers with occluded hydrogen.

The hydrogen sulfide molecule chemisorbed on the active center (AC) can follow two directions of transformations (Fig. 4). These are

(1) the formation of the S-S bond and the removal of the hydrogen molecule into the gas phase,



and (2) the desorption of the hydrogen molecule from the adsorption complex,



Our calculations show (Table 4) that reaction (a) is characterized by a strong exothermic effect ( $\Delta H_{298} = -28.9$  kcal/mol) and gives a substantial energy gain.

**Table 5.** Calculated thermodynamic parameters of the decomposition of the key intermediate ( $\Delta H_{298}$ , kcal/mol, and  $\Delta S_{298}$ , cal/(mol K))

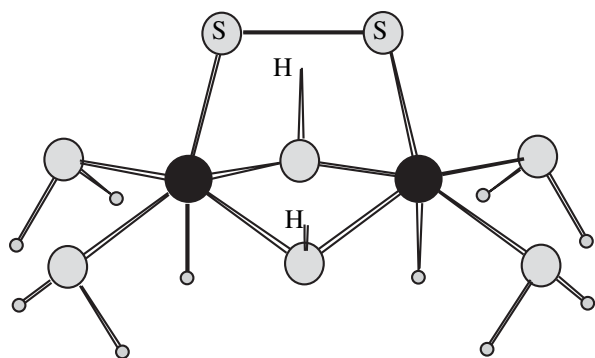
Transformation	$\Delta H_{298}$	$\Delta S_{298}$	$T_p$ , K ( $\Delta G = 0$ )
$\text{AC} + \text{H}_2\text{S}_2(\text{g})$	45.9	52.8	$\geq 870$
$\text{AC} + \text{H}_2(\text{g}) + \text{S}_2(\text{g})$	72.7	78.2	$\geq 930$

The second reaction is unlikely. This leads us to conclude that the formation of the S-S bond in the surface intermediate and the removal of the hydrogen molecule into the gas phase is the stoichiometric reaction of hydrogen sulfide decomposition at room temperature with the formation of a new surface compound, the key intermediate. The S-S bond length, 2.18 Å (Table 4), in the surface intermediate is only slightly larger than in solid sulfur, 2.06 Å.

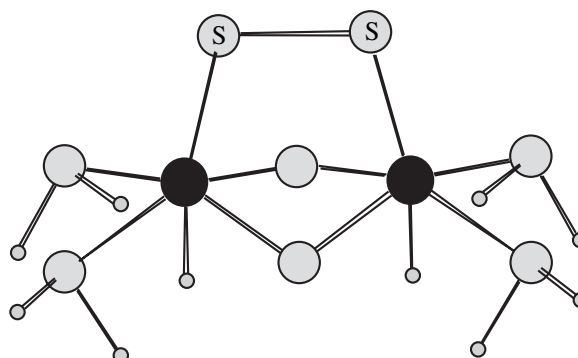
Subsequent transformations of the key intermediate (Fig. 5) can follow several directions. On the one hand, thermal decomposition can occur (Table 5) with the release of either dihydrogen disulfide  $\text{H}_2\text{S}_2$  or hydrogen and molecular sulfur  $\text{S}_2$  into the gas phase. Both these reactions are strongly endothermic and require large energy expenditures. We calculated the equilibrium temperature  $T_{\text{eq}}$  at which the Gibbs energy of the process satisfies the inequality  $\Delta G \leq 0$ , that is, at which the reaction can occur spontaneously (Table 5);  $T_{\text{eq}}$  was found to be about 900 K. This is why dihydrogen disulfide was observed in the gas phase when catalysts with adsorbed hydrogen sulfide were heated [29]. Calculations for the gas phase reaction



gave  $\Delta H_{298} = 26.9$  kcal/mol,  $\Delta S_{298} = 23.4$  cal/(mol K), and  $\Delta G \leq 0$  at  $T_{\text{eq}} \geq 1150$  K (the thermodynamic parameters were taken from [34]). The passage to catalytic conditions does not change the thermodynamic characteristics of reactions (the parameters of the initial and final state must be the same as in the absence



**Fig. 5.** Quantum-chemical model of the key surface intermediate after the removal of the first hydrogen molecule from chemisorbed hydrogen sulfide according to reaction (a).



**Fig. 6.** Quantum-chemical model of the surface state after the removal of the chemisorbed hydrogen molecule into the gas phase from the key intermediate (Fig. 5).

of a catalyst). Closeness of the calculated  $T_{eq}$  values is therefore evidence of a good quantum-chemical description of the surface reaction (Table 5) and gas-phase reaction (2).

On the other hand, the following sequence of elementary events is possible. First, the chemisorbed hydrogen molecule is removed from the key intermediate into the gas phase (Fig. 6). This reaction requires substantial energy expenditures from the outside and can only occur at fairly high temperatures (Table 6). Next, molecular sulfur  $S_2$  is removed from the adsorbed state on the active center (Fig. 6). The thermal removal of molecular sulfur into the gas phase is a strongly endothermic process ( $\Delta H_{298} = 47.3$  kcal/mol,  $\Delta S_{298} = 43.1$  cal/(mol K)) and can occur spontaneously at  $T_{eq} \geq 1097$  K. It follows that thermal routes terminating the catalytic cycle require substantial energy expenditures from the outside and can occur only at high temperatures. There is, however, one more possibility of terminating the catalytic cycle, which is the recombination (oligomerization) of molecular sulfur  $S_2$  into cyclooctasulfur  $S_8$  on the surface of the catalyst without its desorption into the gas phase (Fig. 7, Table 7).

The solid sulfur polymorph stable under usual conditions is rhombic sulfur  $S_\alpha$  [35]. Other solid sulfur allotropes (a total of 22 polymorphs) are also known; these allotropes tend to transform into  $\alpha$ -sulfur. Rhombic sulfur contains nonplanar cyclooctasulfur molecules. At 113°C, rhombic sulfur melts to produce a mobile straw-colored liquid. Liquid mobility is explained by the ability of its constituents, crown-shaped cyclooctasulfur molecules, to easily move with respect to each other. At 120–159°C, molten sulfur predominantly consists of stable cyclooctasulfur molecules. Above 159°C, eight-membered sulfur rings begin to rapidly open with the formation of  $\cdot S_n \cdot$  biradicals. Above the sulfur boiling point (444.6°C), gas-phase sulfur largely consists of molecular sulfur  $S_2$ ,  $S_4$ , and  $S_6$ . Cooling gas-phase sulfur to the solid state is accompanied by its recombination (oligomerization) to

cyclooctasulfur. The reaction occurs at room temperature spontaneously and is accompanied by a very strong exothermic effect ( $\sim 100$  kcal/mol according to the experimental data [36]). It follows that the energy of recombination of molecular sulfur into cyclooctasulfur in the state of adsorption on the surface of the catalyst can balance energy expenditures in the preceding stage, that of the desorption of the hydrogen molecule

**Table 6.** Calculated thermodynamic ( $\Delta H_{298}$  and  $\Delta G_{298}$ , kcal/mol, and  $\Delta S_{298}$ , cal/(mol K)) and geometric (interatomic distances, Å, and angles, deg) parameters for the removal of the chemisorbed hydrogen molecule from the key intermediate (Fig. 6)

Parameter	Value	Distance	$r$ (Å)
$\Delta H_{298}$	25.5	Co–Co	3.04
$\Delta S_{298}$	35.9	Co–S	2.20 (2.29)
$T_{eq}$	710	Co–H	1.48
		S–S	3.01 (2.04)

Note: The calculated parameters for the triplet and singlet states:  $E_{total} = -3467.99375$  and  $-3467.9711$  au,  $S_{298} = 133.3$  and  $124.7$  cal/(mol K), respectively. The  $r$  values for the chemisorbed S–S molecule are given in parentheses.

**Table 7.** Calculated thermodynamic ( $\Delta H_{298}$  and  $\Delta G_{298}$ , kcal/mol, and  $\Delta S_{298}$ ,  $S_{298}$  cal/(mol K)) and geometric (Å) parameters for the recombination (oligomerization) of surface sulfur

Parameter	Calculated	Experimental	Parameter	Calculated	Experimental
$\Delta H_{298}$	-78.4	-98.9	$S_{298}$ ( $S_2$ )	54.5	54.5
$\Delta S_{298}$	-116.0	-115.3	$S_{298}$ ( $S_8$ )	102.0	102.7
$\Delta G_{298}$	-43.6	-64.2	S–S ( $S_2$ )	1.91	1.89
			S–S ( $S_8$ )	2.08	2.06

Note: The calculated parameters for the  $S_2$  and  $S_8$  molecules are  $E_{total} = -796.95745$  and  $-3187.95476$  au, respectively.

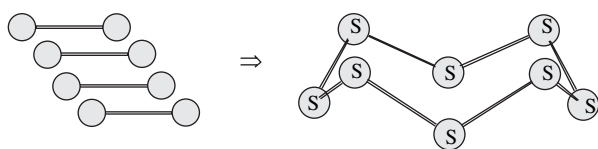


Fig. 7. Recombination (oligomerization) of surface sulfur.

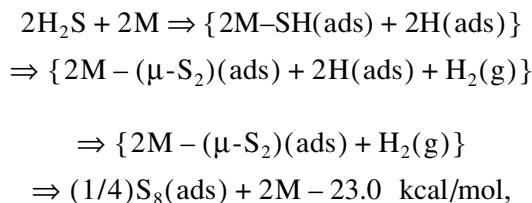
from the key intermediate (Table 6). This is why the closure of the catalytic cycle of low-temperature hydrogen sulfide decomposition on the surface is possible [22].

The calculated energy profile of the sequence of the elementary events described above is shown in Fig. 8, and the corresponding thermodynamic parameters for every stage are listed in Table 8. As follows from Table 8 and Fig. 8, the first three stages are the stoichiometric reaction and can occur spontaneously at room temperature. Only the removal of the second hydrogen molecule from surface intermediates requires energy expenditures from the outside. The most energy-consuming stage is the removal of the  $S_2$  surface intermediate into the gas phase in the molecular form. It would require considerable energy consumption (the hypothetical stage  $2Co(III) + S_2(g)$ , Fig. 8). There is, however, a strongly exothermic process of the surface recombination (oligomerization) of molecular sulfur  $S_2(ads)$  into cyclooctasulfur  $S_8(ads)$ .

The energy released in the recombination (oligomerization) of sulfur is quite sufficient for balancing energy expenditures for the removal of the second hydrogen molecule. For this reason, the final surface state of the system (stage V in Fig. 8) is much lower in energy ( $\Delta G = -7.2$  kcal/mol) than the initial state and

the decomposition of hydrogen sulfide as a whole can occur as early as at a low temperature.

Indeed, we experimentally substantiated the existence of the new reaction that included the stoichiometric reaction on the surface of the catalyst and the directly catalytic stage in the adsorption layer,



where M is the surface transition metal ion. This reaction occurs on solid catalysts at a low temperature under nonisothermal conditions with a 100% conversion and selectivity with respect to hydrogen sulfide [22].

To summarize, we theoretically substantiated the thermodynamic possibility of the occurrence of the new catalytic reaction of low-temperature decomposition of hydrogen sulfide to hydrogen and elemental sulfur. The reaction occurs already at low temperatures under nonisothermal conditions. The thermodynamic driving force of the decomposition of hydrogen sulfide, which ensures the possibility of the process, is the stoichiometric surface reaction of S-S bond formation at the stage of conjugated chemisorption of two hydrogen sulfide molecules on two adjacent metal ions having a certain electronic configuration with the release of the first hydrogen molecule into the gas phase. The closure of the catalytic cycle involves the surface recombination of molecular sulfur  $S_2(ads)$  into cyclooctasulfur

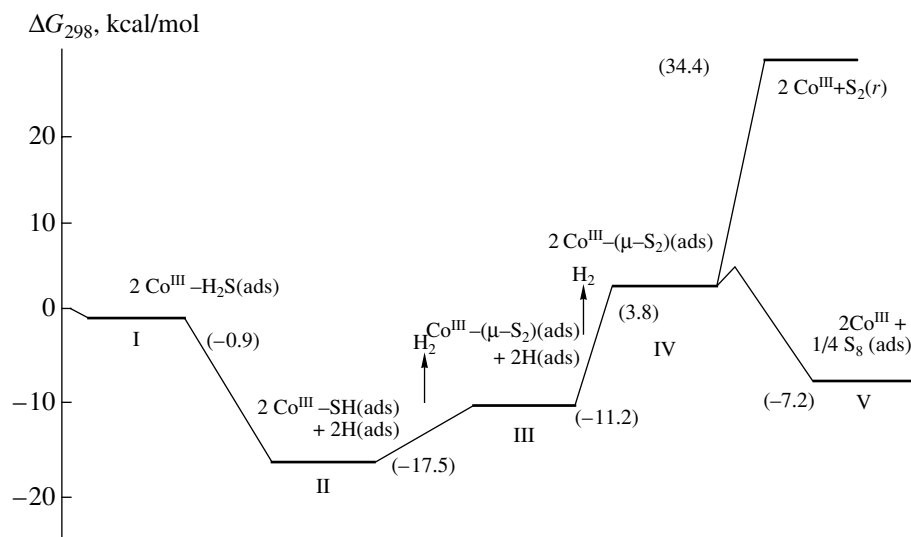


Fig. 8. Density functional theory calculations: the Gibbs energy profile of sequential hydrogen sulfide decomposition stages on Co(III) ions with the  $d^6$  electronic configuration. The energy profile for the IV  $\Rightarrow$  V stage of the surface reaction  $S-S(ads) \Rightarrow (1/4)S_8(ads)$  was approximated using the thermodynamic data on the gas-phase reaction  $S_2 \Rightarrow (1/4)S_8$ . The Gibbs energies (kcal/mol) with respect to the initial state  $[(Co^{III}-H_2O)_2S_2(SH_2)_4 + 2H_2S]$  are given in parentheses.

**Table 8.** Quantum-chemical calculations of the thermodynamic parameters ( $\Delta H_{298}$  and  $\Delta G_{298}$ , kcal/mol, and  $\Delta S_{298}$ , cal/(mol K)) of sequential stages of the catalytic decomposition of hydrogen sulfide at room temperature

Stage	Reaction	$\Delta H_{298}$	$\Delta S_{298}$	$\Delta G_{298}$
I	Molecular adsorption: $2M + 2H_2S(g) \longrightarrow 2M - H_2S(ads)$	-12.7	-39.6	-0.9
II	Dissociative chemisorption: $2M - H_2S(ads) \longrightarrow 2M - SH(ads) + 2H(ads)$	-16.0	2.2	-16.6
III	The removal of the first hydrogen molecule: $2M - SH(ads) + 2H(ads) \longrightarrow 2M - (\mu - S_2)(ads) + 2H(ads) + H_2(g)$	-0.2	-21.9	6.3
IV	The removal of the second hydrogen molecule: $2M - (\mu S_2)(a) + 2H(ads) \longrightarrow 2M - (\mu - S_2)(ads) + H_2(g)$	25.5	35.1	15.0
V	Recombination: $2M - (\mu S_2)(ads) \longrightarrow 2M + (1/4)S_8(ads)$	-19.6	-29.0	-11.0
	Overall catalytic reaction: $2H_2S(g) \longrightarrow 2H_2(g) + (1/4)S_8(ads)$	-23.0	-53.2	-7.2
	Gas-phase reaction: $2H_2S(g) \longrightarrow 2H_2(g) + (1/4)S_8(g)$	15.8	10.3	18.9

Note: The thermodynamic parameters for the gas-phase reaction were taken from [34, 36].

$S_8(ads)$ , the release of the second hydrogen molecule into the gas phase, and the removal of sulfur  $S_8$  from active centers under nonisothermal conditions of conducting the catalytic reaction.

#### ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research, project no. 04-03-32188.

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