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Low-temperature catalytic decomposition of hydrogen sulfide on metal catalysts under layer of solvent

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ABSTRACT

When hydrogen sulfide decomposition $\{2 \text{H}_2\text{S} \leftrightarrow 2 \text{H}_2 + \text{S}_2^{(\text{gas})}\}$ is carried out in the flow regime at room temperature on metal catalysts placed in a liquid capable of dissolving H_2S and sulfur, the reaction equilibrium can be significantly (up to 100%) shifted to the right yielding the desired product – hydrogen. The process efficiency was demonstrated using aqueous solutions of monoethanolamine (MEA), sodium carbonate, which is widely used in industry for H_2S absorption from tail gases, and aqueous hydrazine as examples. IR and Raman spectroscopy data demonstrated that sulfur obtained in the solutions is in the form of diatomic molecules. DFT calculations showed that diatomic sulfur forms weakly bound coordinative complexes with solvent molecules. Some problems related to sulfur accumulation and recovery from the solvents are discussed.

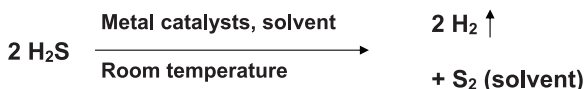
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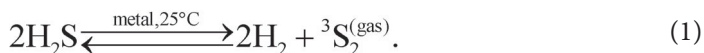
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KEYWORDS

H_2S decomposition; hydrogen production; diatomic gaseous sulfur; triplet and singlet diatomic sulfur; DFT calculations; IR and Raman spectra; sulfur utilization




Experimental evidence of hydrogen sulfide catalytic decomposition to hydrogen and gaseous diatomic sulfur according to reaction (1) has been recently reported.[1–3]

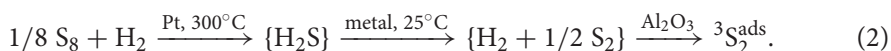


Reaction (1) occurs on metal catalysts in the gas phase at room temperature with H_2S conversion about 15%. To explain the thermodynamics of reaction (1), it was assumed [2,3] that diatomic gaseous sulfur is formed in the catalytic reaction (1) in the triplet ground state. Meanwhile, singlet diatomic sulfur should be obtained by thermal decomposition (dissociation) of hydrogen sulfide in accordance with the spin conservation rule. Singlet diatomic sulfur is metastable under conventional conditions and becomes stable only at

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high temperatures. Experimental evidence for existence of gaseous diatomic sulfur produced in reaction (1) at room temperature has been summarized in [1–4]. This hypothesis was confirmed by simple experiments showing transformation of solid sulfur to diatomic gaseous sulfur via intermediate S_8 hydrogenation with hydrogen to form H_2S followed by its decomposition on the metal surface at room temperature to produce diatomic gaseous sulfur, which is adsorbed on the alumina surface.[4]



Melted sulfur reacts with hydrogen in the presence of Pt to produce H_2S , which decomposes on the surface of the stainless steel chip to produce gaseous diatomic sulfur trapped on alumina. These experiments performed in a closed reactor demonstrated that singlet sulfur can be transformed into the ground triplet state of diatomic sulfur.[4]

Hydrogen sulfide seems to be an inexhaustible source for hydrogen production. Many methods were tested for hydrogen production via H_2S dissociation but none of them achieved commercial success.[5,6] Catalytic reactions (1) open a new perspective to realization of this potential source of hydrogen. A very promising approach to shift the equilibrium of reaction (1) to the right in the direction of hydrogen production is to use a liquid to dissolve H_2S and sulfur formed in the reaction.[1,3,7–10]

However, the second product of reaction (1) diatomic sulfur seems to be of particular interest in the context of its possible involvement in specific chemical reactions. Indeed, diatomic sulfur receives much attention in recent years because of great promise in the synthesis of organic sulfur compounds – model analogues of biological systems.[11–14] Several methods for S_2 generation at mild conditions have been developed. However, all of them use of this molecule *in situ* for synthesis of new chemicals, whereas ‘pure’ form of the S_2 molecule has not been isolated.

In this communication several examples where hydrogen is produced in reaction (1) with H_2S conversion close to 100% are demonstrated, and some properties of diatomic sulfur in aqueous solutions are reported.

Experimental and theoretical methods

The catalytic experiments were performed at room temperature in a glass absorber equipped with a magnetic stirrer. Bulk catalysts used in this work are chips made of stainless steel. The solid catalyst was placed under a solvent layer. Then, the system was flushed with argon to remove dissolved air, and a mixture of argon with H_2S in definite proportion was passed through the catalytic reactor. Unreacted hydrogen sulfide was trapped at the reactor outlet in an absorber containing zinc acetate solution for quantitative analysis of the H_2S conversion. Reaction products: hydrogen and gaseous sulfur were periodically analyzed with a gas chromatograph.[1,3]

Experimental techniques for analysis by chromatographic, chemical, X-Ray fluorescence, IR and Raman methods were described in a previous publication.[1] To record the IR spectra, a drop of solution was placed between Si metal windows. IR spectra were recorded in the transmission mode using a Shimadzu-8300 spectrometer with 4 cm^{-1} resolution and accumulation of 400 scans per spectrum. The spectra of Si windows and water were subtracted from the spectra of the solution. No bands from OH, NH and CH

absorbance were detected in the region above 2500 cm^{-1} after subtracting the spectrum of water. Bands against background were detected in the region of $1500\text{--}1700\text{ cm}^{-1}$. However, reliability of the band position and their intensity were low. In all other spectral regions the band detection was reliable.

Theoretical calculations were performed using program complex GAUSSIAN09 (version A.02).[15,16] Becke hybrid functional with gradient amendments was used [17,18] in combination with a correlation functional [19] (B3LYP approximation). The basis set 6-311G** was used for sulfur, nitrogen and hydrogen atoms.[20] All calculations were performed for the aqueous solution using the Tomasi polarization continuum model.[21]

Results

Synchronous evolution of hydrogen and diatomic sulfur was observed in the gas phase after passing hydrogen sulfide over the metal catalyst.[1–3] However, the equilibrium H_2S conversion did not exceed 5%. Meanwhile, if the catalyst was immersed into a liquid solvent, H_2S conversion significantly increased even in the case of water (Table 1). This is due to good solubility of H_2S and diatomic sulfur formed in reaction (1) in many solvents, including water.[22] This shifts the equilibrium of reaction (1) to the right because H_2 is removed from the solution. High conversion of hydrogen sulfide was obtained, for example, in the case ethanol. However, the best result (98.5%) was achieved by using a diluted aqueous solution of hydrazine. In all cases reported in Table 1, trace amounts of gaseous sulfur were observed in the gas phase as the reaction product along with hydrogen after passing H_2S over the catalyst under a solvent layer. After the experiments, the absorber was purged with argon to remove unreacted hydrogen sulfide for its quantitative analysis, and the resulting solutions were analyzed with X-ray fluorescence spectroscopy. It turned out that gaseous sulfur was completely evaporated from water. Meanwhile, the residual sulfur concentration was rather high in ethanol and aqueous hydrazine solutions.

The IR spectra of diatomic sulfur in 5% aqueous hydrazine solution exhibited a weak band at 662 cm^{-1} (Figure 1). A similar band at 679 cm^{-1} was detected in the Raman spectra of this solution (Figure 2). The appearance of these bands was attributed to stretching vibrations of sulfur–sulfur bonds. S–O and S–H vibrations were not detected in the spectra. Stretching and bending vibrations of S–S bonds characteristic of solid sulfur dissolved in aqueous hydrazine were not found either.

Table 1. H_2S decomposition at room temperature on stainless steel chips placed in a solvent. Catalyst mass is 5 g.

Solvent	Solvent volume, ml	Time on stream, min	H_2S flow rate, ml/min	Fed H_2S , mmol	Unreacted H_2S , mmol	H_2S conversion, %	Sulfur concentration in solution, wt% ^a	Mass of sulfur in solution, g	Mass of vanished S_2 , g
Gas phase	–	80	3.9	9.23	8.81	4.6			
Water	180	90	2.9	11.8	9.7	17.2	0	0	0.08
Ethanol	100	70	4.07	12.7	6.09	52.2	0.10	0.10	0.13
5% aqueous hydrazine	77	120	3.64	19.5	0.29	98.5	0.60	0.46	0.19

^aX-ray fluorescent analysis data after removal of unreacted H_2S from solution with Ar flow.

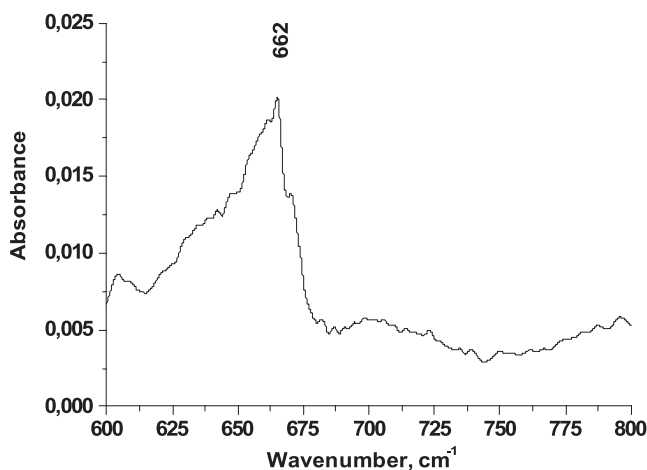


Figure 1. Differential IR spectrum obtained by subtraction of aqueous hydrazine solution from that with dissolved diatomic sulfur.

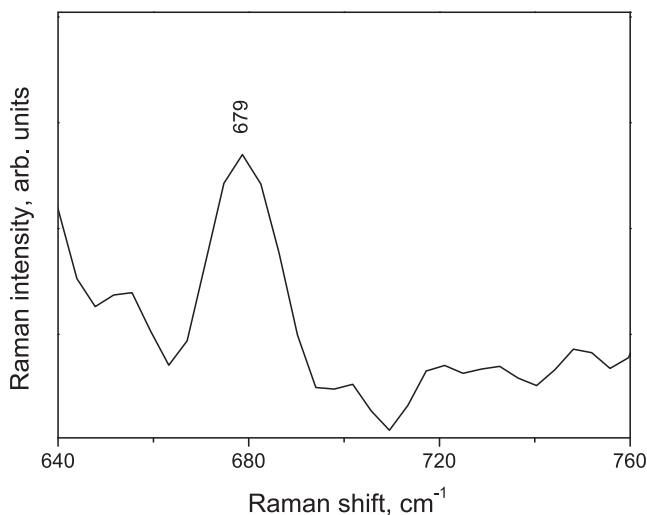


Figure 2. Raman spectrum of diatomic sulfur dissolved in the 5% aqueous hydrazine solution.

For sulfur precipitation, the aqueous hydrazine solution was neutralized with dilute hydrochloric acid to pH = 2. The resulting yellow precipitate was separated using a paper filter, washed with water and dried in air under an IR lamp. The X-ray analysis showed that the precipitate is α -sulfur in orthorhombic modification with the cell parameters of $a = 10.45 \text{ \AA}$, $b = 12.84 \text{ \AA}$, $c = 24.46 \text{ \AA}$. However, the mother solution contained sulfur as well. In a few days a yellowish precipitate was formed on the glass walls of the vessel.

It is well known that monoethanolamine (MEA) is widely used in industrial processes for extraction of hydrogen sulfide from sour gases. Therefore, aqueous MEA solutions were used as solvents for carrying out hydrogen sulfide decomposition in the three-phase regime. Continuous hydrogen evolution was observed in the gas phase when hydrogen

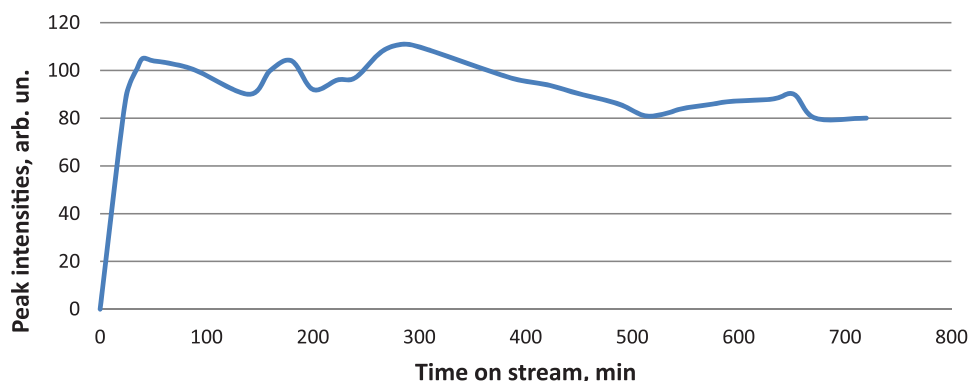


Figure 3. Hydrogen evolution on passing H_2S through the stainless steel chip placed into the 5% MEA aqueous solution.

Table 2. H_2S decomposition over stainless steel chips placed in aqueous solutions.

Solution	Volume, ml	Fed H_2S , mmol	Decomposed H_2S , mmol (g)	H_2S conversion, %	Sulfur content in solution ^a ,		Ratio S:MEA (Na)
					wt%	g	
5% MEA	200	110.6	108.3 (3.69)	97.9	1.62	3.24	1.7
1% MEA	200	88.45	31.75 (1.08)	35.9	0.69	1.38	0.75
Na_2CO_3 [Na] = 0.84%	100	53.4	42.5 (1.33)	79.6	1.30	1.30	1.17

Note: Catalyst mass is 5 g. Reaction temperature is ambient, Ar flow rate is 10 ml/min, H_2S flow rate is 3 ml/min.

^aX-ray fluorescent analysis data after removal of unreacted H_2S from solution with Ar flow.

sulfide was passed through the reactor containing stainless steel chips placed in a dilute aqueous MEA solution (Figure 3). The hydrogen concentration reached a constant level after ~ 30 min and did not change after 12 h (Figure 3). Gaseous sulfur was not detected by chromatography, whereas the solution turned intense yellow. After stopping the hydrogen sulfide feed, the solution was purged with argon to remove unreacted hydrogen sulfide for its quantitative analysis. As it follows from Table 2, the H_2S conversion was about 98% in the case of the 5% MEA solution resulting in the formation of more than 3 g of sulfur in the solution.

No new bands were observed in the Raman spectrum of this solution compared with the spectrum of the original solution. The absence of S–H and S–S vibrations clearly indicates that the molecule is diatomic in the solution. Vibrations of diatomic gases are active in the Raman spectra. However, in some cases they have relatively small cross-sections of Raman scattering. Therefore, the sensitivity of a standard Raman spectrometer is often not sufficient to observe lines related to such fluctuations. For example, in our case Raman spectra of the aqueous solutions or water never exhibited the bands of dissolved oxygen and nitrogen from the air. In the case of the S_2 molecule, the Raman spectrum can be measured only using excitation with certain lines of some lasers.[23] Apparently, one can observe the effect of resonance Raman scattering but not the regular spectra.

It is well known that diatomic molecules are inactive in the IR spectra due to the lack of a dipole moment. However, a weak band at 660 cm^{-1} was detected in the IR spectrum of the solution containing 1.62% sulfur and 5% MEA (Figure 4). It was assigned to stretching

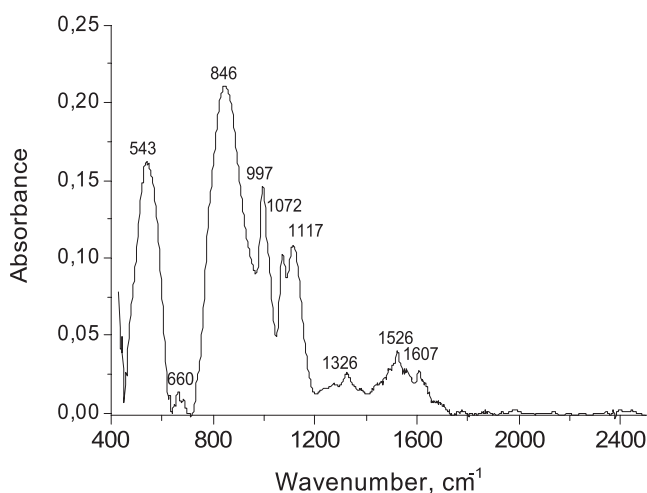


Figure 4. Differential IR spectrum of the 5% MEA solution containing 1.62% of sulfur after subtracting spectrum of water.

vibrations of sulfur–sulfur bonds. It is obvious that this band appears due to the induced dipole moment of diatomic sulfur resulting from its coordination to the solvent molecule. If the solution was stored in a closed vessel in the presence of air for a long period of time (several weeks), no visible change of color was not observed. However, two weak bands that belong to vibrations of the S–O bond appeared in the IR spectra in the region of 1000–1100 cm^{-1} . Apparently, slow oxidation of dissolved sulfur takes place. Neutralization of the solution with dilute hydrochloric acid to $\text{pH} = 2$ also results in the precipitation of orthorhombic α -sulfur with parameters $a = 10.45 \text{ \AA}$, $b = 12.84 \text{ \AA}$, $c = 24.46 \text{ \AA}$. Hydrogen sulfide conversion significantly decreased when 1% MEA solution was used (Table 2).

The industrial vacuum-carbonate method for H_2S extraction from coke-oven gas is well known. So, a diluted aqueous solution of sodium carbonate was used as a solvent in decomposition of hydrogen sulfide on stainless steel chips at room temperature (Table 2). It turned out that even in very dilute solutions the H_2S conversion reached 80%. In the gas phase only hydrogen was detected as a reaction product, while sulfur was accumulated in the solution. When unreacted hydrogen sulfide was removed, no new bands were observed in the Raman spectra in comparison with the spectrum of the initial solution. This result also clearly indicates that the dissolved gas is diatomic. It is very important that no precipitate was formed after neutralization of the solution with hydrochloric acid to $\text{pH} = 2$ and the Raman spectra still exhibited no bands attributed to stretching vibrations of dissolved substances.

Theoretical calculations

DFT calculations were performed for two possible cases – gas phase and aqueous solution with the account of the solvent effect.[21] It turned out that all parameters in the hydrated state were only slightly different from the gas phase. Therefore, all obtained data refer to the dissolved state.

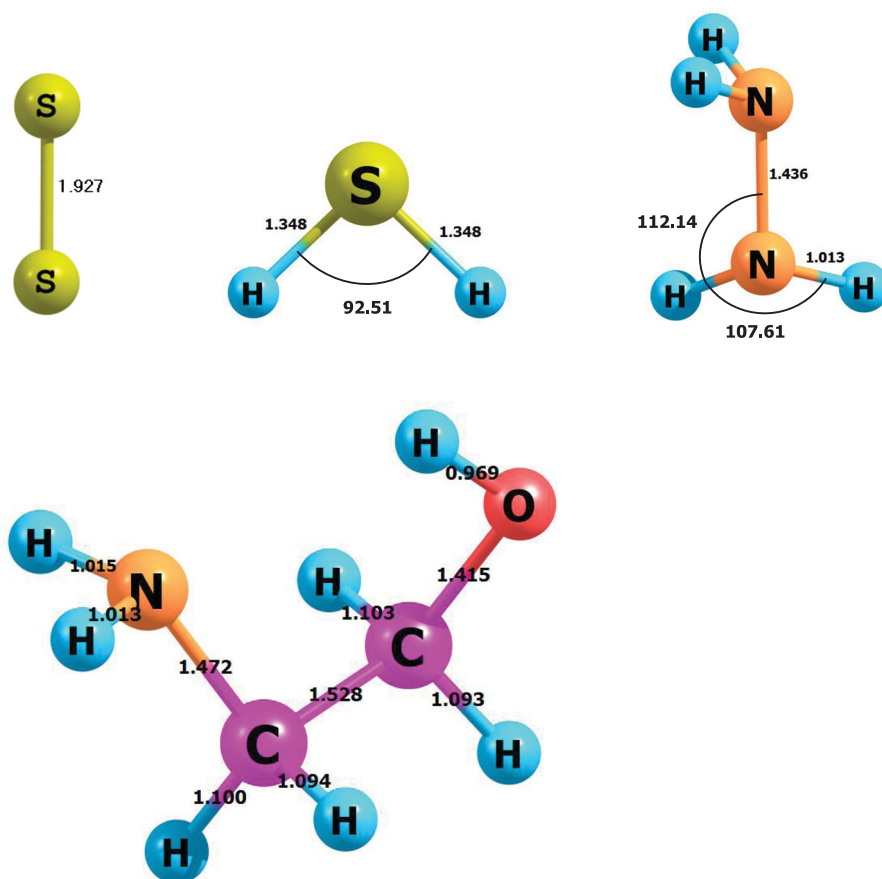


Figure 5. Optimized structures of isolated molecules of S_2 , H_2S , hydrazine and mono ethanoamine.

Table 3. DFT calculations of free triplet diatomic sulfur, hydrogen sulfide and their coordinative complexes with aqueous hydrazine and MEA.

Structure	Interatomic distances S-S, Å	Charges on S atoms (coordinated/terminal)	ν_{S-S} (cm^{-1}) (intensity, a.u.),	Δ_{st}^b , kcal/mol
S_2	1.927	0.0/0.0	682 (0.0)	
H_2S			1195 (1.85) 2684 (0.02) 2698 (0.07)	
HYD ^a + S_2	1.933	-0.01/-0.04	669 (5.6)	-1.6
HYD ^a + H_2S			1238 (2.6) 2172 (1619.0) 2681 (2.4)	-5.6
+ S_2	1.930	-0.02/-0.03	672 (4.1)	-1.2
+ H_2S			1237 (2.2) 2109 (1891.5) 2681 (1.5)	-3.3

^aHYD, hydrazine.

^b Δ_{st} , Stabilization energy of coordinative complexes, kcal/mol.

As it was shown by calculations, the optimized sulfur–sulfur distance in the triplet diatomic molecule is 1.927 Å with the stretching vibration frequency $\nu_{S-S} = 682\text{ cm}^{-1}$, and the dissociation energy of the molecule is equal to 90.6 kcal/mol (Figure 5, Table 3).

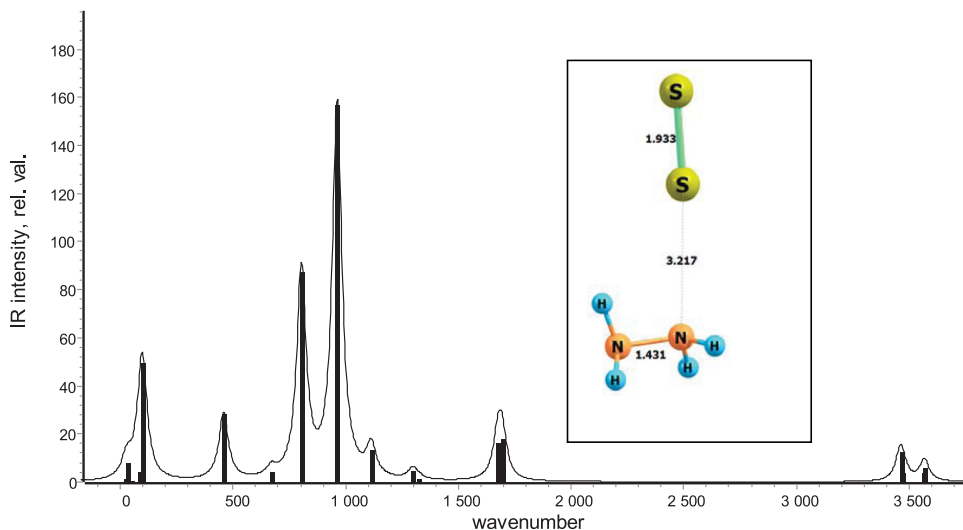


Figure 6. DFT calculation of the vibrational spectrum of the coordination complex S_2 – hydrazine (right). Width FWHM 50, Lorentz broadening. The intensity of the line at $\nu_{S-S} = 669\text{ cm}^{-1}$ is $I = 5.6$ arb. units (Table 3).

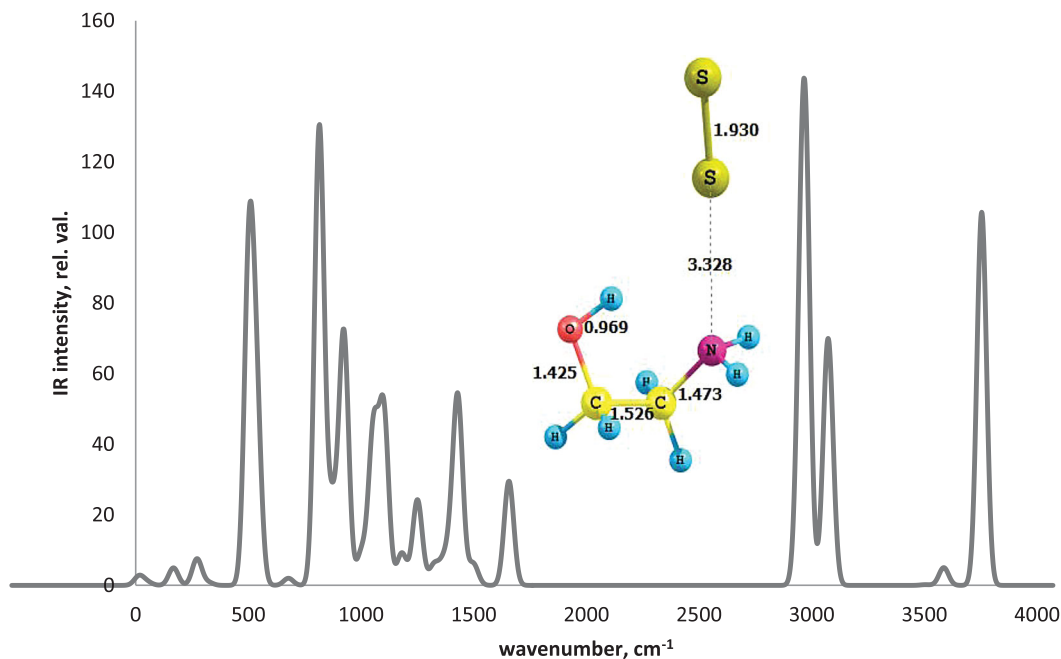


Figure 7. DFT calculation of the vibrational spectrum of the coordination complex S_2 – MEA (upper). Width FWHM 50, Lorentz broadening. The intensity of the line at $\nu_{S-S} = 672\text{ cm}^{-1}$ is $I = 4.1$ arb. units (Table 3)

The calculated frequency of the stretching vibrations is in good agreement with the data obtained by IR and Raman spectroscopy. The calculated structures of hydrogen sulfide, hydrazine, and MEA are shown in Figure 5.

Triplet diatomic sulfur molecule forms a weakly bound complex with a hydrazine molecule with stabilization energy of $\Delta E_{(\text{N}_2\text{H}_4-\text{S}_2)} = -1.6$ kcal/mol (Figure 6, Table 3). S_2 molecule is coordinated to the nitrogen atom of the hydrazine molecule with the bond length of 3.217 Å, resulting in the formation of an induced dipole by partial electron density transfer from the nitrogen atom of the hydrazine molecule to the sulfur atoms (Table 3). This results in lengthening of the sulfur–sulfur interatomic distance to 1.933 Å and change in the frequency of stretching vibrations to 669 cm^{-1} (Table 3). Calculation of the vibrational spectra of coordination complexes shows that the intensity of the sulfur–sulfur vibrations is very small compared with the main lines of the vibrational spectrum (Figure 6). However, this line could be discerned at the background of intense overlapping neighboring spectral lines. Apparently, that is the reason for the appearance of weak bands in the IR spectra (Figure 1).

Coordination of the triplet diatomic sulfur molecule to the MEA molecule happens farther away 3.328 Å (Figure 7) compared with hydrazine. This leads to a small change of the sulfur–sulfur distance compared with the free molecule. The charge redistribution between the sulfur atoms significantly decreases (Table 3). The calculation of the vibrational IR spectrum of the coordination complex $\text{S}_2 - \text{MEA}$ (Figure 7) showed that the intensity of S–S stretching vibrations is very small at the background of overlapping neighboring intense lines. So this band has very low intensity in the IR spectra (Figure 4). There is very good agreement between the experimental and calculated IR spectrum (Figures 4 and 7).

Hydrazine and MEA form more stable complexes with the hydrogen sulfide molecule $\Delta E_{\text{st}} = -5.6$ and -3.3 kcal/mol, respectively (Figure 8, Table 3). The formation of hydrogen bond between the hydrogen sulfide molecule and the nitrogen atom of the solvent molecules results in a decrease in the stretching vibration frequency of the coordinated

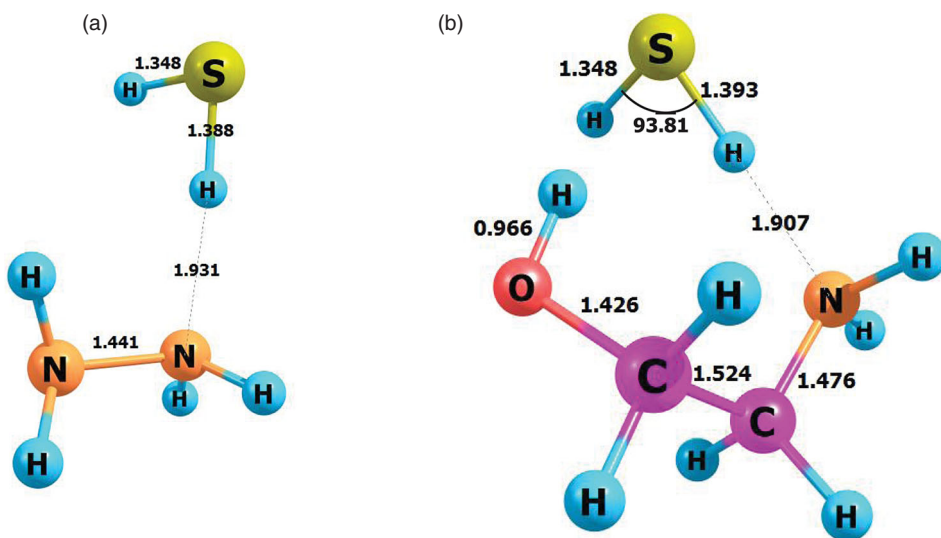


Figure 8. H_2S coordination to the molecule of hydrazine (A) and MEA (B).

S–H bond by $\sim 500\text{ cm}^{-1}$ and a sharp increase in the intensity of these lines at 2172 and 2109 cm^{-1} (Table 3). The absence of these bands in the IR spectra of the solvents definitely shows the absence of unreacted H_2S after blowing absorbers with argon after the catalytic experiments.

Discussion

Purification of exhaust gases from hydrogen sulfide begins with its extraction from the waste gas stream in an absorber with solvents to the required sanitary standards of the purified gas. Concentrated solutions of the absorbers are thereupon directed to the regeneration stage where sulfur is recovered primary with the Claus method or is used to obtain sulfuric acid. Many solvents are used in industrial processes for hydrogen sulfide extraction from gas streams of different origins. The choice of these solvents depends on many parameters and, primarily, on the chemical composition of gas emissions and technological problems of processing enterprises. The main idea of our study was to carry out reaction (1) at the stage of hydrogen sulfide extraction from tail gases to obtain hydrogen, thus eliminating subsequent high-temperature hydrogen sulfide processing.

Indeed, the aqueous MEA solution, a well known and widespread hydrogen sulfide absorber, was one of the most suitable solvents for reaction (1). Decomposition of hydrogen sulfide on stainless steel as one of the simplest and readily available catalysts [1–4] occurs at room temperature with hydrogen evolution to the gas phase (Figure 3) and sulfur accumulation in solution (Table 2). More than 3 g of sulfur with the atomic ratio S:MEA = 1.7 at the sulfur concentration of 16 g per liter of solution was accumulated after 12 h of the experiment (Table 2). This value is comparable with the mass of the catalyst (5 g) that has very low specific surface area. DFT calculations showed that the resulting triplet diatomic sulfur forms a weak coordination complex with MEA, in which the S_2 molecule experiences very slight distortion of the electronic structure. Therefore, weak lines corresponding to vibrations of sulfur–sulfur valence bond are observed in the IR spectra due to the induced dipole moment (1 and 4). A similar situation is apparently observed for aqueous solutions of hydrazine and sodium carbonate (Tables 1 and 2).

Recovery of sulfur formed in reaction (1) from solutions presents a very complicated technological challenge. It can undermine the economic feasibility of implementing reaction (1) at the industrial scale due to potential high cost of produced hydrogen and the need for disposal of solutions. A simple technological method to recover sulfur from the solutions demonstrated in this paper is not optimal and requires additional research. Neutralization of the solutions with hydrochloric acid to $\text{pH} = 2$ does not result in complete sulfur recovery, and the mother solution requires further processing.

However, a very important conclusion can be made from the experiments on sulfur recovery from solutions. It is well known that hydrazine and MEA are strong bases. Therefore, very large neutralization energy is liberated during titration of the solutions with hydrochloric acid. Apparently, the released neutralization energy is sufficient to convert triplet diatomic sulfur formed in reaction (1) into the excited singlet state that requires 13.4 kcal/mol . [24] As it was shown in [3,4] with CASSCF and Hartree–Fock methods, singlet diatomic sulfur cannot exist at room temperature in the free state because it spontaneously ($\Delta_r G^\circ_{298} < 0$) transforms into thermodynamically most stable cyclooctasulfur by reaction: $\{4\ ^1\text{S}_2 \rightarrow \text{S}_8\}$. It is obvious that acidification of a sodium carbonate solution

with hydrochloric acid is not accompanied by triplet – singlet sulfur transition. So, sulfur remains in solution in the form of diatomic molecules even at low pH values.

However, there are alternative processes for sulfur recovery from solutions formed in reaction (1). Sulfur can be used, for example, to synthesize new chemical compounds or composite materials with different functional purposes. Chemistry of diatomic sulfur attracted attention of researchers over the past 30 years due to the prospect of its use for synthesis of organic sulfur compounds – analogs of biological objects, in which sulfur plays a critical role. No less attractive is the prospect of using solutions of diatomic sulfur in agriculture to replenish the sulfur deficiency in soils and in the industry to produce new composite materials, which can find wide application in construction, road-paving, etc.

Conclusions

Thus, in this study we demonstrated the principal possibility of a technological solution for producing hydrogen from hydrogen sulfide at room temperature with H_2S conversion close to 100%. It is obvious that the process can be profitable only if sufficiently cheap hydrogen can be obtained. This can be achieved by using diatomic sulfur formed in reaction (1) for the synthesis of new chemicals or composites of various functional purposes, which could significantly improve the economic indicators of the hydrogen sulfide decomposition to produce hydrogen. This work demonstrates principal feasibility of shifting the equilibrium of reaction (1) to the right by placing the catalyst under a solvent layer. This approach seems to be very promising for handling the problem of hydrogen recovery from hydrogen sulfide at room temperature. However, many problems are related to extracting sulfur from solutions. Therefore, the search for appropriate solvents to obtain high hydrogen yield seems to be the key to solve this problem.

Disclosure statement

No potential conflict of interest was reported by the authors.

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