

## Liquid-phase oxidation of $\text{Na}_2\text{S}$ to $\text{Na}_2\text{SO}_4$ on graphite-like carbons

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### ABSTRACT

Different types of graphite-like carbons, namely Sibunits, are studied as catalysts in the liquid-phase oxidation of sodium sulfide of high concentrations (28-59 g/l) into sodium sulfate by oxygen, at the temperature range of 90 to 130°C and oxygen pressure of 10 atm. A novel electrochemical mechanism for this liquid phase oxidation by molecular oxygen, which explains most of the experimental data, is suggested.

**KEYWORDS:** liquid-phase oxidation, sodium sulfide, sodium sulfate, carbon catalyst, wet air oxidation

### INTRODUCTION

It is well known that many enterprises produce large amounts of wastewaters containing sulfides in forms of inorganic and organic compounds. The oxidation of sodium sulfide by air in the presence of various catalysts is an important reaction in industry for the creation of a low-cost and effective way of sewage treatment in petrochemistry, pulp-and-paper mills and others. Present technologies of liquid-phase oxidation of sodium sulfide by oxygen are mainly operating in the conditions where the sodium sulfate formed is the only product of oxidation. According to the literature related to the catalytic oxidation of aqueous solutions of metal sulfides, active carbons or the carbon fibers are the most effective

catalysts for the process [1]. The reason is that carbon materials are highly resistant to alkaline media in comparison to conventional oxide supports. Nevertheless, the oxidation of sulfides by molecular oxygen mainly gives thiosulfates and poly-sulfates, and not sulfates. As a result, for  $\text{Na}_2\text{S}$  oxidation (up to 9 g/l) on carbon fiber glasses, the process selectivity towards sodium sulfate does not exceed 50% at 70-80°C [2]. The deposition of phthalocyanine complexes of Fe and Co on carbon supports appeared to be rather an efficient treatment of an aqueous stream containing the water-soluble inorganic sulfide compounds [3]. At temperatures 140-145°C, pH~12 and under pressure of 10 atm of oxygen at LHSV = 0.5 h<sup>-1</sup>, the yield of sulfate was about 95 %.

The above-mentioned publications seem to be the only ones available in the field that are related to  $\text{Na}_2\text{S}$  oxidation into  $\text{Na}_2\text{SO}_4$ . Moreover, the concentrations of  $\text{Na}_2\text{S}$  studied do not exceed 2 wt. %. The subject of current publication is the liquid - phase oxidation of  $\text{Na}_2\text{S}$  of high concentration to  $\text{Na}_2\text{SO}_4$  on different graphite-like carbons, i.e. Sibunits.

### EXPERIMENTAL

#### Catalysts

Sibunits are synthetic graphite-like carbon materials designed by the Boreskov Institute of Catalysis, Novosibirsk. Different commercially available Sibunits (Sibunit 1, Sibunit 2, Sibunit 4, and Sibunit 7) and model systems - Sibunit 8 and Sibunit B vary in texture, strength and particles

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size. Some of their properties are listed in Table 1. The active carbon C-G5-Mizui ( $S_{\text{BET}} = 1050 \text{ m}^2/\text{g}$ ) was also tested.

### Catalysts testing

The experimental setup for sodium sulfide oxidation consists of the reactor, oxygen (air) supply module with pressure regulation and temperature controller. High pressure catalytic reactor is equipped with the removable cap, valves for gas supply (oxygen, air, etc.) and liquid sampling, thermocouples and a jacket for electrical heating. The reactor material is steel,

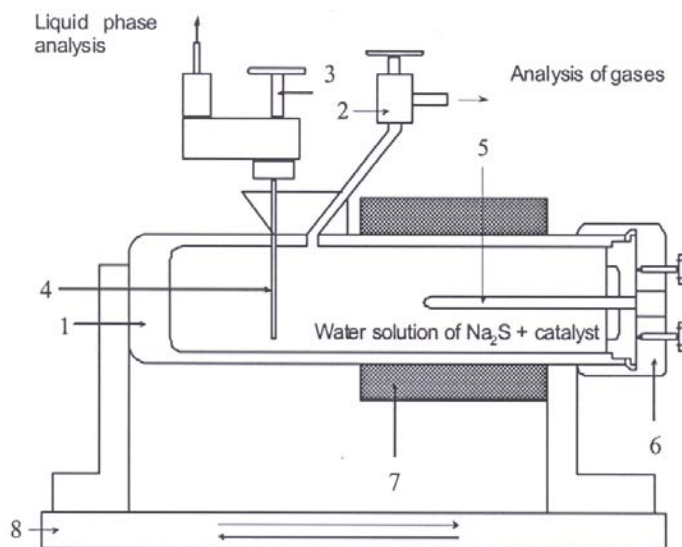
grade 12X18H10T. It is installed horizontally on a vibrator, which provides a high frequency horizontal shaking of three-phase system of liquid-gas-catalyst (Fig. 1). The air (or oxygen) from the cylinder is supplied to the reactor through the SS capillary of  $\frac{3}{4}$  mm diameters and can be isolated by valve 2.

The reactor temperature is controlled by the thermocouple (temperature range of 0-600°C, accuracy 0.25°C), and continuously monitored by a recorder.

The catalyst sample of known weight is inserted into reactor, and the reactor cap is sealed.

**Table 1.** Properties of Sibunits.

	Basic characteristics of commercially available carbon supports of the Sibunit family				Some characteristics of new carbon supports of the Sibunit family prepared for commercialization	
	Sibunit 1	Sibunit 3	Sibunit 4	Sibunit 7	Sibunit 8	Sibunit B
Predominant size of granules, mm	1.6÷3.2	1.6÷3.2	1.0÷1.6	0.2÷1.0	0.0003	1.0-1.6
Specific BET surface area, $\text{m}^2/\text{g}$	440±40	360±80	380±80	520±80	30÷5	20÷5
Total pore volume (from water adsorption) $\text{cm}^3/\text{g}$	0.7÷0.05	0.5±0.05	0.7±0.05	0.3±0.7	-	0.4÷0.05
Volume of pores < 5000Å in size, $\text{cm}^3/\text{g}$	0.68±0.05	0.42±0.05	0.55±0.05	0.40±0.05	-	-
Volume of pores < 15 Å in size, $\text{cm}^3/\text{g}$	0.015	0.13	0.04	0.05	-	-
Average pore size, Å ( $4V/S_{\text{BET}}$ )	64	40	45	35	-	-
Substructural parameters of graphite-like phase	Degree of crystallinity: 65±5% Coherent scattering region $L_a \times L_c = (35 \pm 5) \times (35 \pm 5)$ Interlayer distance $d/n = 3.47 \pm 0.02$ E Degree of 3D azimuth disordering 0.4±0.1					
Ash content, wt %	3.5±0.2 for all samples					
Crushing strength, $\text{kg}/\text{cm}^2$ , no less	50	140	50	50	-	-
Concentration of carboxylate groups on surface, $\mu\text{mol}/\text{g}$	100	60	150	20	40	60



**Fig. 1.** The reactor for oxidation of the sodium sulfide: 1 - reactor body; 2 - gas sample valve; 3 - liquid sample valve; 4 - capillary; 5 - thermocouple; 6 - cover; 7 - heater; 8 - vibrator.

Then solution of  $\text{Na}_2\text{S}$  (100 ml) is loaded, the reactor is heated to the desired temperature, oxygen is supplied, and the shaking is started (this moment is considered to be  $t = 0$ ). All tests are performed at constant oxygen pressure (if not mentioned otherwise), and the liquid is periodically sampled for the analysis. The sampled volume is 1 ml. The concentrations of sulfide, sulfite and thiosulfate ions are determined. The concentrations of sulfate ions are calculated based on the reaction balance. Using the above concentrations, the conversions of sodium sulfide ( $X_{\text{Na}_2\text{S}}$ ) and sodium sulfate selectivities ( $S_{\text{Na}_2\text{SO}_4}$ ) are calculated.

#### Analysis of $\text{Na}_2\text{S}$ , $\text{Na}_2\text{S}_2\text{O}_3$ , $\text{Na}_2\text{SO}_3$ , $\text{Na}_2\text{SO}_4$

Ions were analyzed for their combined concentration. In addition, the presence of sulfide ions was monitored with the Pb paper indicator. The sulfate ions were tested with  $\text{BaCl}_2$  according to the reaction of precipitation of  $\text{BaSO}_4$ .

The iodometric measurements were used for the determination of the total concentration of sulfur. Then sulfide ions were removed by the precipitation with salts of Zn and Cd and filtration [4]. The procedure of chemical analysis is described elsewhere [5]. The filtrate was first analyzed for the combined concentrations of sulfite and thiosulfate ions. Then, the formalin

solution is introduced to bind sulfite in the complex inert to iodine. Then the filtrate was analyzed for the concentration of thiosulfate only. The sulfite concentration was calculated as the difference between the sulfur content in the filtrate and the thiosulfate concentration. Finally, the precipitated sulfide was the difference between the total concentration of sulfur and combined concentrations of sulfite and thiosulfate. The accuracy of the analysis for individual ions ( $\text{SO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ) was 0.002 g/l.

To ensure the correctness and suitability of the above "balance" approach and suitability of the balance, the following experiments were performed. The chemical composition of the reaction mixtures at different reaction times and also mixtures containing certain ions ( $\text{S}^{2-}$ ,  $\text{S}_2^{2-}$ ,  $\text{S}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_6^{2-}$ ,  $\text{S}_3\text{O}_6^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ) were studied using UV spectroscopy over 200-370 nm range. (Note that the solution of  $\text{SO}_4^{2-}$  does not absorb in this range). The data obtained by the UV spectroscopy showed clearly that no intermediate ions, except for  $\text{SO}_3^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  were present.

The concentrations of sulfate ions were confirmed by the direct weighing of the precipitated barium sulfate. This method showed a higher concentration of  $\text{SO}_4^{2-}$  by ca. 5-10% compared to that calculated assuming ion balance as described above.

The amounts of  $\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  solutions required for the complete oxidation of sulfur compounds to sulfates were also verified. In this case, the sulfate selectivities found by two methods agreed within 1.15%.

Sodium sulfide conversion ( $X_{\text{Na}_2\text{S}}$ ) and sulfate selectivity ( $S_{\text{SO}_4^{2-}}$ ) were calculated using the equations:

$$X_{\text{Na}_2\text{S}} = \frac{C_{\text{Na}_2\text{S}}^0 - C_{\text{Na}_2\text{S}}}{C_{\text{Na}_2\text{S}}^0} \times 100\%$$

$$S_{\text{SO}_4^{2-}} = \frac{M[\text{S}^{2-}]^0 - M[\text{S}^{2-}] - 2M[\text{S}_2\text{O}_3^{2-}] - M[\text{SO}_3^{2-}]}{M[\text{S}^{2-}]^0 - M[\text{S}^{2-}]} \times 100\%$$

where M is molarity, and the concentrations with "o" stand for the initial concentrations.

The sulfate yield is equal to  $Y = X_{\text{Na}_2\text{S}} \cdot S_{\text{SO}_4^{2-}}$ .

## RESULTS

### Catalysts testing

The different types of Sibunits were tested at  $100^\circ\text{C}$ , at the reaction time of 1 hour (Table 2). Apparently, for all Sibunits, both  $\text{SO}_3^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  were found among the products of sulfide oxidation, while Sibunit B is the only exception, since it did not produce a significant amount of  $\text{SO}_3^{2-}$ . On other Sibunits, the sodium sulfide oxidation always generates  $\text{SO}_3^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$ .

Figure 2 shows the conversion of  $\text{Na}_2\text{S}$  (in 5 min) and  $\text{Na}_2\text{SO}_4$  selectivity (in 60 min) for different Sibunits used. Sibunit 3 was found to be the most active in sodium sulfide oxidation and also the most selective one. Its  $\text{Na}_2\text{SO}_4$  selectivity can run as high as 98-100%. The Sibunit 3 generates the least amount of thiosulfate comparing to other Sibunits (Fig. 3).

### Temperature effect

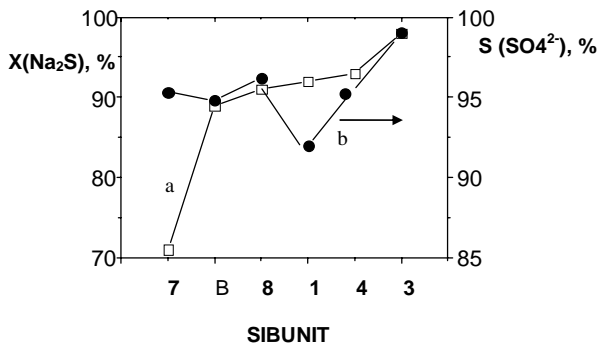
It is well known that the rate of the chemical reaction increases with the increase of temperature. Since the sodium sulfide oxidation involves at least two intermediates, it is important to understand the temperature dependencies of the reaction selectivity of these intermediates and sulfide conversion. It is significant that the temperature threshold was observed around  $100^\circ\text{C}$ , because below this temperature the sulfate selectivity remains low at relatively high sulfide conversion (Fig. 4).

Figure 5 shows the dependence of the concentration of the  $\text{S}_2\text{O}_3^{2-}$  ions versus the reaction time at different temperatures for Sibunit 8 catalyst and reaction mixture containing different ratios of sulfide and thiosulfate.

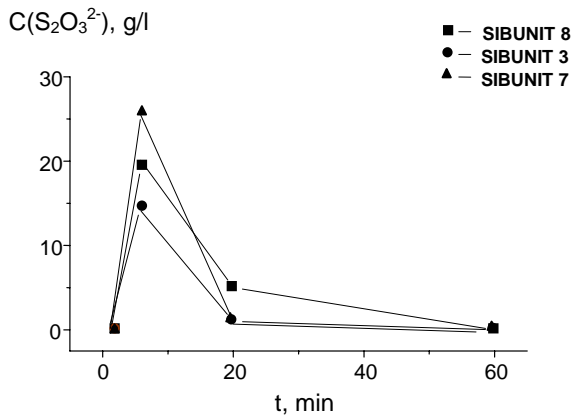
Fig. 6 shows time dependence of the concentration of  $\text{SO}_3^{2-}$  at the following temperatures, 110, 130 and  $150^\circ\text{C}$ , on the same catalyst in the mixtures of sulfide and thiosulfate.

**Table 2.** Sodium sulfide oxidation ( $T = 100^\circ\text{C}$ ,  $C(\text{S}^{2-}) = 24 \text{ g/l}$ , reaction time = 1 h, size of catalyst's particles  $< 100 \mu\text{m}$ , except Sibunit-8 ( $0.3 \mu\text{m}$ )).

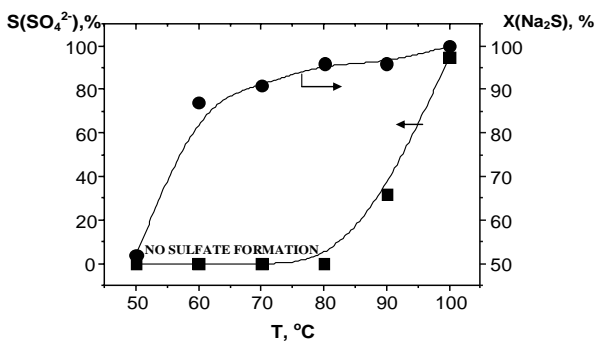
Catalyst	$X(\text{Na}_2\text{S})$ , %			$C(\text{S}_2\text{O}_3^{2-})$ , g/l			$C(\text{SO}_3^{2-})$ , g/l			$S(\text{SO}_4^{2-})$ , %		
	5 min	20 min	60 min	5 min	20 min	60 min	5 min	10 min	60 min	5 min	20 min	60 min
Sibunit 1	92	-	100	19.5	-	0.5	11.2	-	4.1	29.2	-	92
Sibunit 3	98	100	100							60	96	99
Sibunit 4	93	100	100	7.9	1.0	0	2.5	3.6	2.7	75.3	91.5	95.5
Sibunit 7	71	100	100	26.9	1.0	0	17	3.2	2.8	30.1	92.3	95.3
Sibunit 8	91	100	100	21	0.5	0	4.8	2.3	2.3	36.3	95	96.2
Sibunit B	89	100	100	15	3.1	2.2	0	0	0	59.9	92.6	94.8
AC C-G5-Mizui	71	95.8	99.7	28.4	11.5	1.0	8	4.1	3.9	14	64.3	91.1



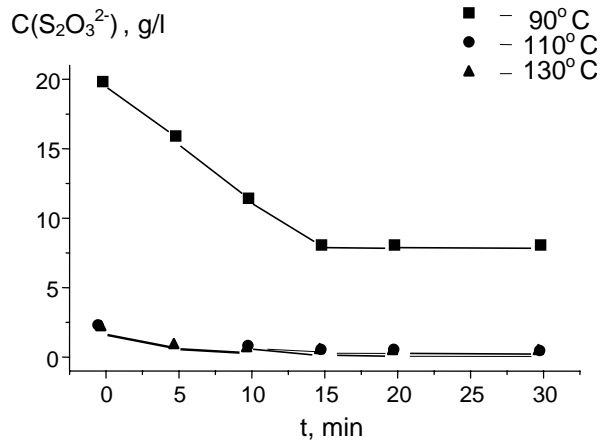
**Fig. 2.** Sodium sulfide conversion 5 min after reaction start depending on Sibunit type ( $T = 100^\circ\text{C}$ ,  $C(\text{S}^{2-}) = 24 \text{ g/l}$ ) (a); and Selectivity of Sibunits towards sodium sulfate formation in 1 hour after reaction start ( $T = 100^\circ\text{C}$ ,  $C(\text{S}^{2-}) = 24 \text{ g/l}$ ) (b).



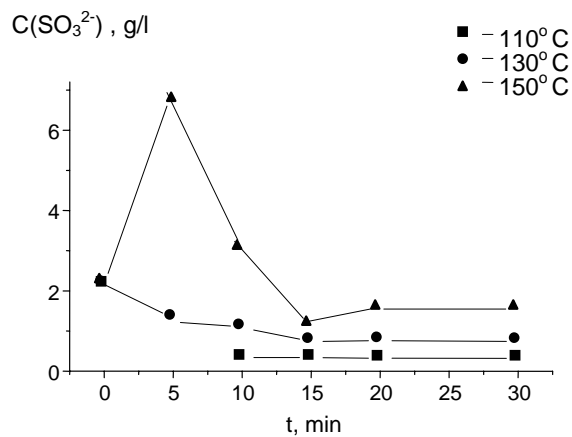
**Fig. 3.** Sodium thiosulfate generation in oxidation of sodium sulfide ( $T = 100^\circ\text{C}$ ,  $C(\text{S}^{2-}) = 24 \text{ g/l}$ ).



**Fig. 4.** Conversion of  $\text{Na}_2\text{S}$  and selectivity of  $\text{Na}_2\text{SO}_4$  formation vs. temperature (catalyst - Sibunit B,  $C(\text{Na}_2\text{S}) = 58.5 \text{ g/l}$ ).



**Fig. 5.** The concentration of  $\text{S}_2\text{O}_3^{2-}$  ions vs. reaction time at different temperatures (catalyst - Sibunit 8, initial concentration of oxidative mixture: a) ( $42 \text{ g/l Na}_2\text{S} + 2.5 \text{ g/l Na}_2\text{S}_2\text{O}_3$ ) -  $110, 130^\circ\text{C}$ ; b) ( $14 \text{ g/l Na}_2\text{S} + 28 \text{ g/l Na}_2\text{S}_2\text{O}_3$ ) -  $90^\circ\text{C}$ ).



**Fig. 6.** The concentration of  $\text{SO}_3^{2-}$  ions vs. reaction time at different temperatures (catalyst - Sibunit 8, initial concentration of oxidative mixture - ( $42 \text{ g/l Na}_2\text{S} + 2.5 \text{ g/l Na}_2\text{S}_2\text{O}_3$ )).

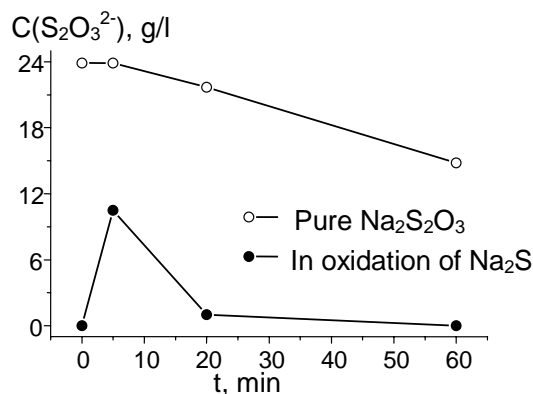
It was found that at low temperatures the sodium sulfate generation is complicated due to the formation of sodium thiosulfate as an intermediate product. At higher temperatures the other product, sodium sulfite  $\text{Na}_2\text{SO}_3$ , forms in larger quantities.

When the reaction temperature increase, the rate of thiosulfate oxidation also increases, and as a result, temperature does not have any effect on the oxidation of sulfite ions. According to the

literature [6], ions of  $\text{SO}_3^{2-}$ , formed during oxidation of  $\text{S}^{2-}$  as intermediate products, are oxidized rather slowly, though the rate of their oxidation in the absence of  $\text{S}^{2-}$  ions is quite high. For  $\text{S}_2\text{O}_3^{2-}$  ions, the tendency seems to be opposite. Our experiments show that under the same experimental conditions pure  $\text{Na}_2\text{S}_2\text{O}_3$  is oxidized better if  $\text{S}^{2-}$  ions are present. Figure 7 demonstrates the change of the  $\text{S}_2\text{O}_3^{2-}$  concentration during the oxidation of pure  $\text{Na}_2\text{S}_2\text{O}_3$  in solution and also when  $\text{S}_2\text{O}_3^{2-}$  forms as an intermediate product during sodium sulfide oxidation on Sibunit 3.

### Effect of Sibunit pretreatment with $\text{H}_2\text{O}_2$

In order to improve the catalytic performance, one of the Sibunits used, Sibunit 8, was first treated with hydrogen peroxide. This procedure changes the number of carboxyl groups on the Sibunit's surface, and was done in order to provide support for the view of a dominating role of carboxylate groups in the sulfide oxidation to sulfate on Sibunits. Table 3 demonstrates both the activity



**Fig. 7.** The concentration of  $\text{S}_2\text{O}_3^{2-}$  ions vs. reaction time in oxidation of: a) pure solution of  $\text{Na}_2\text{S}_2\text{O}_3$  ( $C = 24$  g/l) and b)  $\text{Na}_2\text{S}$  ( $C = 58.5$  g/l); catalyst - Sibunit 3.

and selectivity of non-treated and peroxide-treated Sibunit 8.

According to the experimental data, the higher the number of carboxylate groups on the Sibunit surface, the higher is the initial reaction rate, and  $\text{SO}_4^{2-}$  selectivity is doubled in 5 min after the beginning of the reaction. However, the effect will disappear with time.

Therefore, the catalytic performance (more correctly, selectivity) of Sibunits does not depend on the surface carboxylate groups or the dependency is more complex and not obvious.

### Effect of Sibunit particles size on the catalyst performance

Using the Sibunit 3 as an example, the dependence of its fraction composition on the activity and selectivity of sulfide oxidation was studied (Table 4). According to Table 4, the smaller the Sibunit particles, the higher is the reaction selectivity. Thus, in 20 min  $\text{SO}_4^{2-}$  selectivity over 5 micron catalyst fraction is 97%, while it is 94% over 3 mm fraction. According to Fig. 8, the size of the Sibunit particles decreases and the oxidation selectivity to  $\text{SO}_4^{2-}$  increases. However, in 5 min the conversion of  $\text{Na}_2\text{S}$  is almost constant for the particles ranging from 5 micron to 1 mm in size.

## DISCUSSION

### Performance comparison of different catalysts

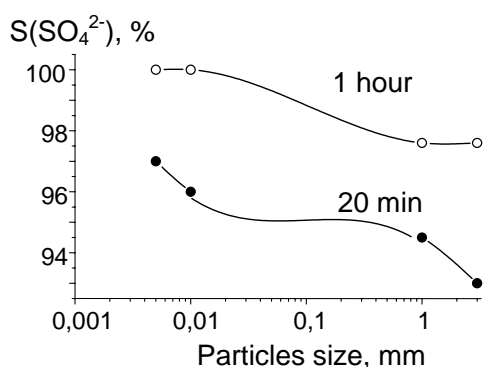
It was observed that sodium sulfide oxidation occurs on all Sibunits studied. Carbon materials used varied by the specific surface (8-1000  $\text{m}^2/\text{g}$ ), by nature and concentration of functional groups on their surfaces (concentration of carboxyl groups varied from 20 to 150  $\mu\text{mol}/\text{g}$ ), and by the particle size (5 micron - 3mm). The effect of the above factors on the catalytic performance will be discussed below.

**Table 3.** Catalytic performance of peroxide-treated Sibunit 8 ( $T = 100^\circ\text{C}$ ).

Sibunit 8	N(COO <sup>-</sup> ), $\mu\text{mol}/\text{g}$	X( $\text{Na}_2\text{S}$ ), %			S( $\text{SO}_4^{2-}$ ), %		
		5 min	20 min	60 min	5 min	20 min	60 min
non-treated	40	91	100	100	36.3	95	96.2
treated with $\text{H}_2\text{O}_2$	50	99.5	100	100	95	93.8	95.7

**Table 4.** Sulfide conversion and oxidation selectivity towards Na<sub>2</sub>SO<sub>4</sub> versus reaction time for various fractions of Sibunit 3 (T = 100°C, C(S<sup>2-</sup>) = 24 g/l).

fraction	X(Na <sub>2</sub> S), %			S(SO <sub>4</sub> <sup>2-</sup> ), %		
	5 min	20 min	60 min	5 min	20 min	60 min
5 μm	98	100	100	63.8	97	100
<100 μm	98	100	100	60	96	99
1 mm	98.5	100	100	71.6	94.5	97.6
3 mm	94	100	100	55.3	93.1	97.6

**Fig. 8.** Effect of Sibunit-3 particles size on catalyst performance (T = 100°C, C(S<sup>2-</sup>) = 24 g/l).

According to Tables 1 and 2, there is no relation between porous structure of Sibunits and reaction selectivity. For example, at a 100% Na<sub>2</sub>S conversion Sibunit 8 with the surface area of 8 m<sup>2</sup>/g and Sibunit B with the surface area of 24 m<sup>2</sup>/g both show rather higher Na<sub>2</sub>SO<sub>4</sub> selectivity than Sibunits 1, 4 and 7 with surface areas of 670, 510 and 600 m<sup>2</sup>/g, respectively. At the same time, Sibunit 3 with a similar surface area (760 m<sup>2</sup>/g) is far more selective than all other carbon supports including those with small surface areas. Note that the active carbon C-G-5 Mizui with a high surface area (>1000 m<sup>2</sup>/g) is the least active and selective carbon support.

No relation was observed between the catalyst performance and the total pore volume, volume of macropores and substructural parameters such as crystallinity degree, coherent scattering region, interlayer distance, etc. (Table 2). The only correlation is the one that occurs between the SO<sub>4</sub><sup>2-</sup> selectivity and the volume of super-micro-pores

(size of 10-15Å). Indeed, the volume of super-micro-pores of the most selective catalyst, Sibunit 3, is 3 to 9 times greater than that of other Sibunits.

Tables 2 and 3 show no obvious relationship between the Sibunit performance and the concentration of carboxylate groups on their surfaces. For example, less selective Sibunits 1 and 4 have 2-2.5 times more carboxylate groups (100-150 μmol/g) than the best Sibunit 3 (60 μmol/g). At the same time, the concentration of carboxylate groups on the low selective Sibunit 7 is 3 times lower. Early in the study, the carboxylate groups were presumed to activate molecular oxygen and oxidize S<sup>2-</sup> ions into S<sup>6+</sup> ions through S<sup>2+</sup> intermediates.

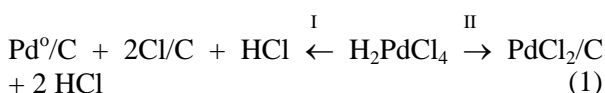
There is a slight effect observed that the reaction selectivity increases from 98 to 100% with the Sibunit particle size decrease from 3 mm to 5 micron (see Fig. 8 and Table 4). Note that the sulfide conversion remains constant even at the beginning. Available data show that there is no diffusion limitation in the pores of the support. Moreover, Sibunit 8 exhibits the worst selectivity while it does not have porous structure, since it consists of spherical particles 3000 Å (0.3 micron in size). Nevertheless, it is too premature to make final conclusions on a size effect. The major reason is that it is hard to collect the reaction kinetics data using the CSTR batch reactor, especially because it is problematic to make reliable measurement of the initial catalytic activity (within 5 min).

Therefore, we assume that the catalytic performance of Sibunits does not depend on their pore structure and surface chemical composition,

but weakly depends on the particle size. Most likely, the sodium sulfide oxidation does not proceed through a classical reaction mechanism of the oxygen catalyst surface activation by oxygen followed by the oxidation of sulfide to sulfate and regeneration of reduced surface sites. In fact, the hydrogen peroxide pretreatment of Sibunit 8 provides a sharp increase of the initial reaction rate. This effect disappears with time (Table 3), because Sibunit is incapable to reactivate molecular oxygen, and, therefore, the catalytic cycle is not completed.

### Possible mechanism of Na<sub>2</sub>S oxidation over Sibunit based catalysts

Early data showing that Sibunit may act as an electrochemical cell, were reported in [7]. It was found that when H<sub>2</sub>PdCl<sub>4</sub> solution contacts with Sibunit 2 the following processes spontaneously occur:



The driving force of the process I is the electric double layer formation (Fig. 9).

As a result, the excessive negative charge is generated at the opposite part of the microcrystal (L<sub>a</sub>·L<sub>c</sub> in size) surface, which is able to reduce Pd<sup>2+</sup> to Pd<sup>0</sup> or oxygen molecule (O<sub>2</sub>) to O<sup>2-</sup>.

The facts in support of Na<sub>2</sub>S oxidation by electrochemical mechanism are listed below:

- catalytic activity is independent on the chemical composition of Sibunit surface, and of the O-containing functional groups in particular;
- catalytic activity does not depend on the specific surface area, which varies within a wide range;
- catalyst performance depends on the nature of carbon material. In contrast to active carbons, Sibunits have the optimum size of microcrystals L<sub>a</sub>·L<sub>c</sub> (Table 1);
- according to Figs. 3, 6, 7 and Table 2, the reaction seems to consist of two stages. At first (within 5 min), it is so fast that Na<sub>2</sub>S conversion is almost complete. At the same time, sulfide selectivity reaches up to 60-90%, and, therefore, sodium sulfide is immediately oxidized to Na<sub>2</sub>SO<sub>4</sub>

without the intermediate stage. At the second stage (1 hour), there are almost no sulfide anions, and slower oxidation of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> into SO<sub>4</sub><sup>2-</sup> takes place. The experiments using pure thiosulfate or thiosulfate/ sulfate mixtures clearly show that this process occurs very slowly even on the most active Sibunits. Therefore, during the oxidation of pure sodium sulfide we should anticipate high concentrations of thiosulfate and low concentration of sulfate early in the reaction. In reality, the situation is quite opposite (with the exception of low active Sibunits 1 and 7, and active carbon). In order to explain observed kinetic dependencies it is assumed that sulfide is oxidized to sulfate in one stage, and therefore, we have the transfer of 8 electrons (S<sup>2-</sup> to S<sup>6+</sup>). Such process can be only electrochemical rather than chemical.

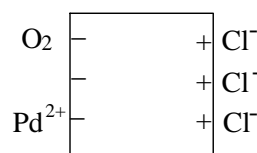


Fig. 9. The electric double layer formation in reaction (1).

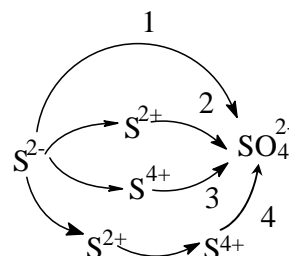


Fig. 10. The kinetic scheme of Na<sub>2</sub>S oxidation.

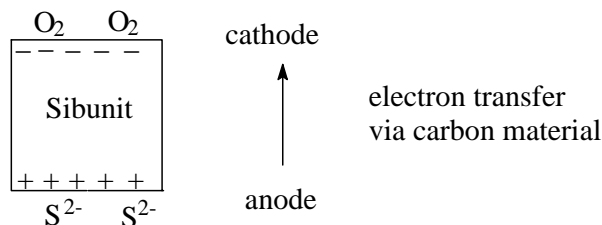


Fig. 11. Scheme of electrochemical cell - C|Na<sub>2</sub>S||OH<sup>-</sup>O<sub>2</sub>|C+.



All the above arguments allow us to suggest the mechanism of Na<sub>2</sub>S oxidation (Fig. 10). Here, the contribution of the route 1 to the total reaction rate is the largest, while the contributions of the route 2, and routes 3 and 4, in particular, are the least.

Electrochemical cell element may be presented as (Fig. 11).

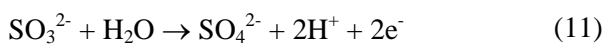
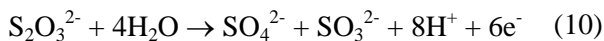
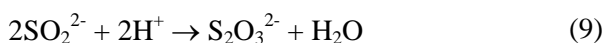
Electrochemical reactions by route 1 are:



Reactions by route 2 are:



Reactions by route 3 and 4 are:



At the present stage of investigation reactions (2)-(12) may be considered as rather conditional. Nevertheless, they allow us to explain the observed kinetic dependencies. First, in the presence of S<sup>2-</sup> the reactions (2)-(7) may go essentially faster than the reactions (8)-(12), because it is easier to transfer electrons from the sulfide ions than from thiosulfate or particularly sulfite ions. As a result, we have fast initial oxidation of sulfide to sulfate, and then further slow oxidation of thiosulfate and sulfite.

An active and selective catalyst is expected to execute a process primarily via 1 and 2 paths (reactions (2)-(7)) to avoid the problems with the further oxidation of the by-products. Nevertheless, it is almost impossible to avoid the side processes. Therefore, it is reasonable oxidizing thiosulfates and especially sulfites through the activation of O<sub>2</sub> on the catalytic sites.

According to the thermodynamics of the liquid phase sodium sulfide oxidation by molecular oxygen, in alkaline media the multi-electron mechanisms of the redox reactions (S<sup>2-</sup> → S<sup>6+</sup> + 8e<sup>-</sup>, S<sup>2-</sup> → S<sup>4+</sup> + 6e<sup>-</sup> and S<sup>2-</sup> → S<sup>2+</sup> + 4e<sup>-</sup>) are the most feasible. In neutral and acidic media, one- and two-electron mechanisms are the most possible and resulting in polysulfides and elementary sulfur. Multi-electron mechanisms provide the redox reactions involving S-containing anions in various redox states, and, as a result, the variety of reaction products. The observed data of sulfide oxidation agrees with the process thermodynamics. At the beginning of the reaction when the reaction medium is alkaline (pH~12), sulfide totally converts to sulfate, thiosulfate and sulfite. Then, with the decrease of pH to 8-9, the rate of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> oxidation into SO<sub>4</sub><sup>2-</sup> significantly decreases. Therefore, there are two requirements for the efficient sodium sulfide oxidation to sulfate:

- 1) the catalyst should provide the multi-electron redox processes;
- 2) the reaction rate should not be limited by the supply of molecular oxygen to the catalyst surface.

The first requirement can be easily implemented, since Sibunit is the electrocatalyst, and is able to oxidize sulfide to sulfate via the electrochemical mechanism. In this case, the typical times of sulfide oxidation via a slow outer sphere mechanism of the electron transfer are within the milliseconds (the inner sphere mechanism of electron transfer is much faster).

Apparently, the rate of Na<sub>2</sub>S oxidation in the gas-liquid-solid system is controlled by oxygen transport to the surface of the Sibunit particles. In other words, the second requirement can hardly be fulfilled because of the high reaction rates of S<sup>2-</sup> oxidation. The oxygen shortage near the Sibunit's surface, as well as the unfavorable thermodynamics due to a low pH are the main reasons for the accumulation of sodium thiosulfate and sulfite, and, as a result, low sulfate selectivity. Therefore, it is hard to build up any kinetic model since the apparent reaction rate is determined by the reactor design, liquid and gas supply, a pressure drop (e.g. by the oxygen mass exchange

factors in the gas-liquid-solid system, rather than by kinetic factors such as the reagent concentrations and temperature).

In conclusion, the sodium sulfide oxidation to sulfate occurs according to electrochemical mechanism, and the reaction rate is controlled by oxygen mass exchange in the gas-liquid-solid catalyst system. It is important to note that Sibunit-3 was found to be an active and selective catalyst, and also a rather stable one.

### CONCLUSIONS

In summary, the following conclusions can be reached:

1. Different types of graphite-like carbons, namely Sibunits, were studied as catalysts in the liquid-phase oxidation of sodium sulfide of high concentrations (28-59 g/l) into sodium sulfate by oxygen, at the temperature range between 90 to 130°C and oxygen pressure of 10 atm.

2. A novel electrochemical mechanism of a liquid phase oxidation of sodium sulfide to sodium sulfate

by molecular oxygen, which explains most of the experimental data, is suggested.

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