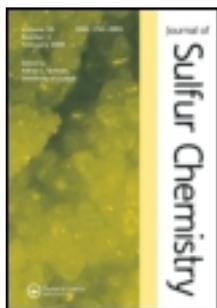


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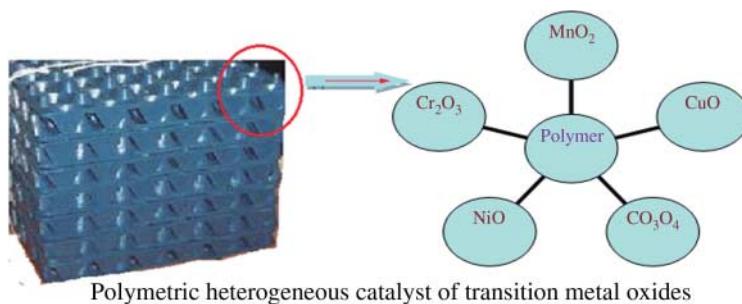
Investigation of factors influencing sodium sulfide oxidation in the presence of polymeric heterogeneous catalysts of transition metal oxides

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The activity of heterogeneous catalysts of transition metal oxides and their mixtures deposited on the polymeric matrix in the oxidation of sodium sulfide was investigated. It is shown that mixtures of manganese oxide and other transition metal oxides have high catalytic activity. It was evident that the positive synergistic effect occurred in the combined action of two or more catalytically active transition metal oxides, and the maximum effect was observed in the mixture of three catalytic agents of transition metal oxides. Catalytic mechanism of transition metal oxides for sulfide oxidation was studied. The kinetics of formation of products of sodium sulfide oxidation was studied in the presence of heterogeneous catalysts based on phthalocyanine cobalt and transition metal oxides. The dependence of the rate of formation of products of sodium sulfide oxidation on alkali concentration was investigated. Some factors influencing the oxidation rate such as sulfide, oxygen and alkaline concentrations, antioxidant and oxidation products were investigated.



Keywords: kinetics; catalysis; transition metal oxides; sodium sulfide oxidation; synergistic effect

1. Introduction

Inorganic and organic sulfides are toxic and stinking pollutants even in low levels of concentration.[1] Many industries like oil refineries, petrochemicals, tanneries, kraft paper mills, dyes and pigments, etc., discharge sulfides containing effluents. From the aspect of pollution control, it is necessary to remove sulfides because of their toxicity and unpleasant odor.[2] Sulfide oxidation by air is one of the ways to remove the sulfide. This reaction is very slow at atmospheric

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pressure and ordinary temperature. The liquid-phase heterogeneous catalytic oxidation of toxic sodium sulfide to safer thiosulfate and sulfate is the most perspective method. The oxidation rate can be accelerated by the presence of transition metals, such as Ni, Mn, Cu, Co, Fe, . . .[3]

Recently, the use of molecular oxygen as terminal oxidant received great attention for both economic and environmental benefits, and many highly efficient systems have been developed for catalytic aerobic sulfide oxidation using rhenium,[4] palladium,[5] ruthenium,[6] copper [7, 8] manganese,[7] iron,[8–10] cobalt [11] and gold-based catalysts.[12] Transition metal phthalocyanines (mainly cobalt phthalocyanine CoPc) are among the most popular and often studied catalysts for sodium sulfide oxidation.[13–15] The majority of the studies, reported in the current literature, have been carried out in a homogeneous phase. Heterogeneous catalysts offer undoubtedly a better technological solution to this problem. A promising group of heterogeneous catalysts are the transition metal oxides, which possess a high activity in the oxidation of gaseous hydrogen sulfide.[16] But these studies are not sufficient both theoretically and experimentally because of the complex dependency of the reaction rate on oxygen and sulfide concentrations as well as on the pH of the liquid. Furthermore, many intermediates and reaction products seem to make this reaction system a very complicated one.

The aim of the present study is to accumulate data on the catalytic activity of a wide range of transition metal oxides and their mixtures deposited on the polymeric matrix in sulfide ion oxidation with air in alkaline aqueous medium. The catalytic mechanism of a heterogeneous multi-component catalyst of transition metal oxides is studied. And in this paper we discuss some factors influencing the rate of sodium sulfide oxidation, such as alkaline concentration and antioxidant, and propose the kinetics of the reaction of sulfide oxidation. The effect of sodium hydroxide concentration on the kinetics of formation of products of sodium sulfide oxidation in the presence of the heterogeneous multi-component oxide catalyst was studied.

2. Results and discussion

The tested catalysts (MnO_2 , CuO) and some of their characteristics are shown in Table 1. It is shown that the rate of oxidation of sodium sulfide increases: temperature increases up to 60°C , the concentration of the catalyst component in the polymer matrix increases from 0 to 10 wt% and the catalyst amount (mass) increases to 5.0 g. Further increases do not influence the rate of reaction. These results determine the necessary temperature and concentration of transition metal oxides in the polymer matrix and catalyst content for a definite reaction.

The catalyst surface of MnO_2 -10/ CuO -10 was investigated by digital microscope (Figure 1) and Fourier spectrometer (IR spectra, Figure 2). It can be seen that the catalyst surface was not changed after three months of use under relatively vigorous reaction conditions (temperature 60°C , alkaline concentration 5.0% and a strong rotation of solution 1400 rpm). Investigated results

Table 1. Characteristics of oxide catalysts.

Oxides	Initial rate of oxidation of Na_2S ($\text{g}/(\text{l}\cdot\text{s})\cdot 10^2$)				
Temperature ($^\circ\text{C}$)	40	50	60	70	80
MnO_2	0.7	0.81	0.97	0.97	0.97
CuO	0.62	0.75	0.91	0.91	0.91
Oxide concentrations in polymer matrix (wt.%)	0	5	10	15	20
MnO_2	0.67	0.78	0.97	0.97	0.97
CuO	0.67	0.73	0.91	0.91	0.91
Catalyst content (g)	0	2.5	5.0	7.5	10.0
MnO_2	0.67	0.81	0.97	0.97	0.97
CuO	0.67	0.79	0.91	0.91	0.91

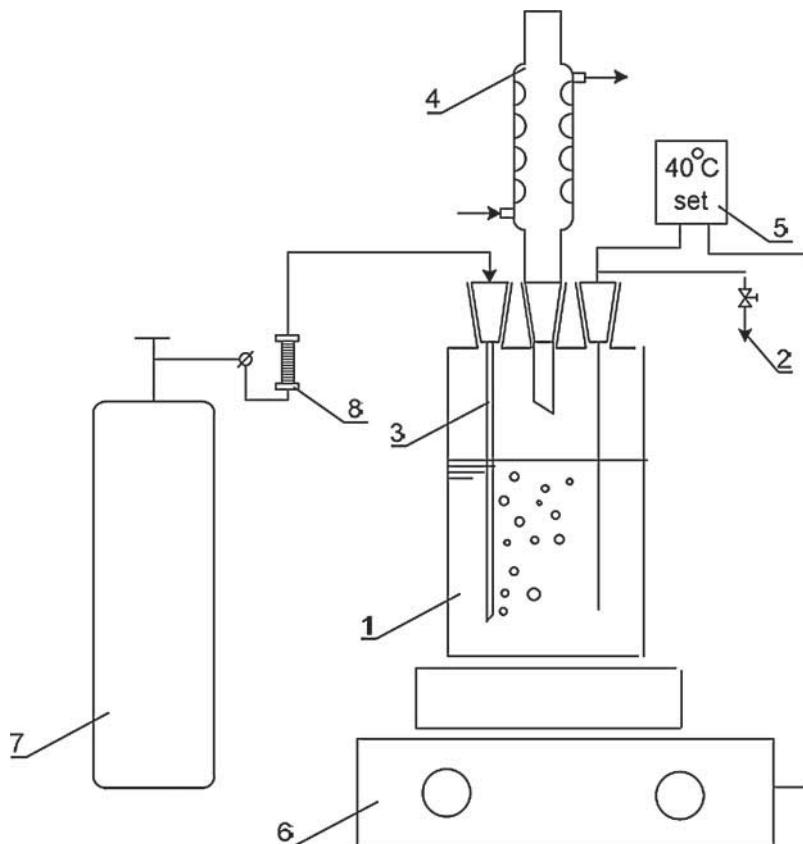


Figure 1. (a) The catalyst surface of $\text{MnO}_2\text{-10/CuO-10}$ before reaction. (b) The catalyst surface of $\text{MnO}_2\text{-10/CuO-10}$ after three months of use.

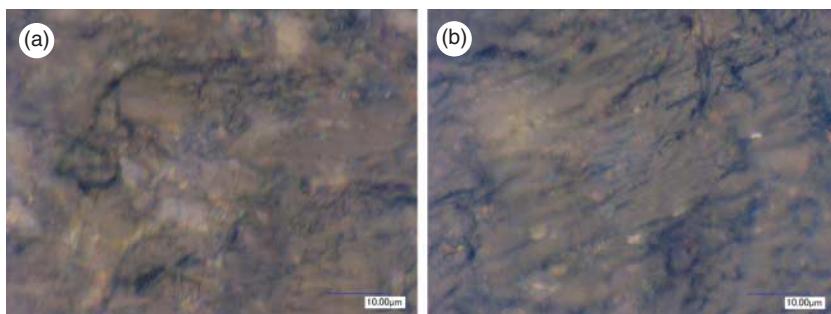


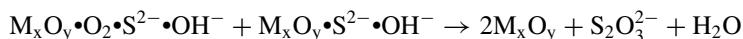
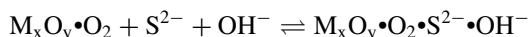
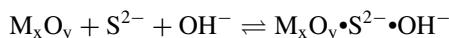
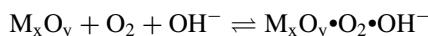
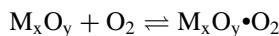
Figure 2. IR spectra of $\text{MnO}_2\text{-10/CuO-10}$ before reaction and after three months of use.

showed that polymeric heterogeneous catalysts of transition metal oxides have high reactivity in a wide range of concentrations of oxidizable compounds and pH, mechanical strength and chemical and hydrolytic stability for three to five years. Polymer-based catalysts can be used under alkaline conditions at temperatures up to 100°C , pressure up to 7.0 kg/cm^2 .

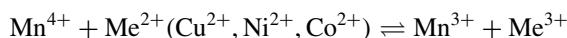
2.1. Catalytic mechanism of mixtures of transition metal oxides

It is well known that two main types of mechanisms are usually assumed for heterogeneous catalytic reactions, *i.e.* the so-called Langmuir–Hinshelwood and Rideal-type or Rideal–Eley-type

mechanisms. In the first case, the reaction is assumed to occur between adsorbed reactant molecules on the catalyst, while in the case of the second mechanism a reactant molecule from the gas phase reacts with another in the adsorbed state.[17] For the heterogeneous oxidation of the sodium sulfide, it is assumed that both oxygen and sulfide ion are adsorbed on the surface of the metal oxide. Adsorbed oxygen may be present as atomic or molecular species with various charges. On transition metal oxides, the most common species are O, O⁻, O₂ and O₂⁻. On some basic alkali and alkaline earth oxides, O₂²⁻ has been reported. On UV-irradiated TiO₂, O₃⁻ species has been observed with EPR.[18] Various review articles discussing these and other species such as O₃⁻ have appeared in recent years.[19–21] In general, atomic oxygen species are adsorbed more strongly than molecular species. This is because strong surface-atomic oxygen bonds are needed to compensate for the energy required to break the double bond of the oxygen molecule. The rate of dissociative adsorption of oxygen to atomic species is expected to be lower than that of molecular adsorption. This is because a pair of neighboring surface sites must be available for the former process. Otherwise, lattice or surface diffusion of mononuclear oxygen ions (or lattice anion vacancies) is needed before dissociation of the oxygen molecule can be achieved. This is consistent with the fact that a saturation coverage of adsorbed atomic oxygen corresponds to a few atoms per square millimeter of surface. On the other hand, molecular adsorption of oxygen can take place on an isolated surface site. This requirement of the availability of a pair of surface sites can be overcome by sulfide ion S²⁻, the oxidation of which would leave an atomic oxygen on the surface. Thus, on different surface sites of the catalyst, the reaction can occur by the following mechanism:



Most of the transition metal ions that are important for the oxidation of sodium sulfide in view of possible catalytic reactivity are only stable in the +2 oxidation state in aqueous solution. In order to exhibit catalytic reactivity, these metal ions probably must be oxidized into a higher oxidation state (+3).[22] Thus, it is reasonable to expect an induction period when a transition metal ion in the oxidation state +2 is used as a catalyst for the oxidation of sulfide ion under the conditions that the oxidation of the metal ion itself is slow. There are several suggestions in the literature to account for the general reaction $M^{2+} \rightarrow M^{3+} + e^-$ and the associated induction period. Coichev and van Eldik [23] suggest a direct oxidation of the metal ion via oxygen $M^{2+} + O_2 \rightarrow M^{3+} + O_2^-$, whereas Anast and Margerum [24] propose a disproportionation reaction $2Cu^{2+} \rightarrow Cu^+ + Cu^{3+}$. Intramolecular electron donor–acceptor systems of heterogeneous multi-component catalyst of transition metal oxides have been observed in which manganese ion (IV) accepts an electron from other transition metal ion in the oxidation state +2.



Higher oxidation state (+3) is always obtained in this system which explains the high catalytic reactivity of mixtures of transition metal oxides with different oxidation states.

Catalytic reactivity of heterogeneous multi-component catalyst of transition metal oxides in the oxidation of sulfur-containing compounds including sodium sulfide (Na₂S), sodium hydrosulfide

Table 2. The catalytic activity of heterogeneous multi-component catalyst of transition metal oxides in the oxidation of sulfur-containing compounds.

Heterogeneous multi-component catalyst (5.0 g)	Sulfur-containing compounds	Initial rate (g/(l•s)•10 ²) (with catalyst)	Initial rate (g/(l•s)•10 ²) (without catalyst)
MnO ₂ -10/CuO-5/Cr ₂ O ₃ -5	Sodium sulfide (Na ₂ S)	2.23	0.67
MnO ₂ -10/Co ₃ O ₄ -5/NiO-5	Sodium hydrosulfide (NaSH)	2.49	0.71
	Ammonium sulfide ((NH ₄) ₂ S)	3.69	1.36

(NaSH) and sulfide ammonium((NH₄)₂S) was investigated. The experimental results shown in Table 2 indicate that this catalyst has high reactivity in the oxidation of all sulfur-containing compounds. In calculating the initial oxidation rate for all experimental runs, it is apparent from Table 2 that the rates of catalyzed reaction are about 3.3, 3.5 and 2.9 times higher than non-catalyzed, corresponding to the oxidation of Na₂S, NaSH and ((NH₄)₂S).

2.2. Investigation of some factors influencing the rate of sodium sulfide oxidation in the presence of a heterogeneous multi-component catalyst of transition metal oxides

In contrast to the homogeneous catalysis by transition metals, it is more difficult to present a general reaction mechanism for the heterogeneously catalyzed oxidation of sodium sulfide, mainly due to the limited information on the adsorption and redox activities of different surface sites. These activities probably depend on the nature of the metal oxide or hydroxide studied.[25] The pH does not show the influence on the rate of adsorption of oxygen on the surface of a heterogeneous catalyst, but it has a significant effect on the rate of adsorption of sulfur compounds and the rate of formation of the complex with sulfur atom.[26] For uncatalyzed reaction, the reaction rate is not influenced by the pH change during the first part of the reaction.[27]

The influence of hydroxyl anions on the oxidation rate of sulfur compounds in the presence of heterogeneous catalysts can be explained as follows:

(1) reduce the number of radicals in the system, which reduces the rate of reaction by increasing concentration of hydroxyl anion;[28]

(2) the hydroxyl ion functioning as a competitive ligand at the metal center, so the rate of complex formation is decreased;[29]

(3) coordinated hydroxyl anion inhibits the rate of recovery of metal ions.[30]

The industrial catalyst (KS catalyst) for the oxidation of sulfur compounds was prepared according to Ac 1041142. The change of alkali concentration from 0 to 1.125 mol/l has no effect on the rate of the sodium sulfide oxidation in the absence of a catalyst. In the case of industrial KS-catalyst or multi-component catalyst, the alkaline concentration has a profound effect on the rate of sodium sulfide oxidation (Figure 3). Increasing more NaOH concentration in aqueous alkaline solution will decrease the rate of sodium sulfide oxidation.

It is known that the heterogeneous polymeric catalyst has a high level of chemical stability, mechanical strength and stable catalytic activity. But a problem appeared when polyethylene was changed by polypropylene as a polymeric carrier: the oxidation rate decreased significantly. Based on this, the influence of the antioxidant (Irganox-1010) on the initial rate of sodium sulfide oxidation was investigated (Figure 4). The rate of sodium sulfide oxidation decreased with increasing antioxidant levels in the polymeric matrix. These results can be explained by the following ways: (1) the antioxidant in a polymer decreased the oxygen consumption and therefore decreased the oxidation rate;[31] (2) antioxidation inhibited electron-transfer processes of transition metal oxides in the polymeric matrix which determines the activity of catalysts or the rate of oxidation of sodium sulfide.[32]

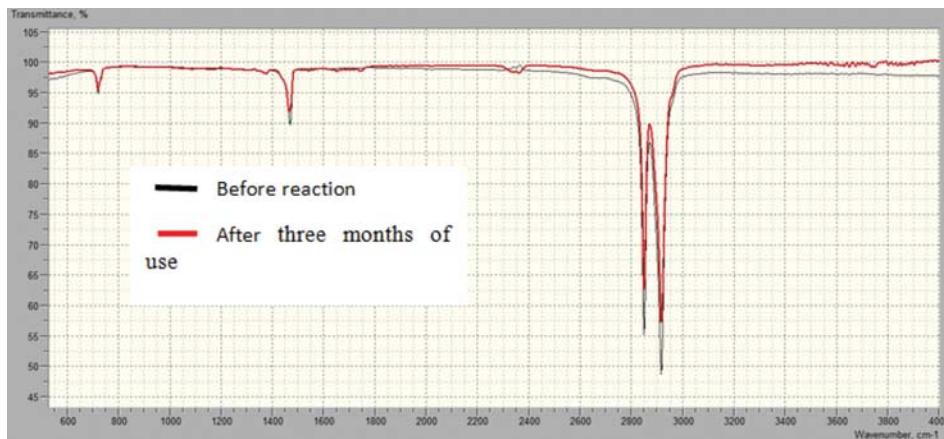


Figure 3. Effect of sodium hydroxide concentration on the rate of the oxidation of sodium sulfide.

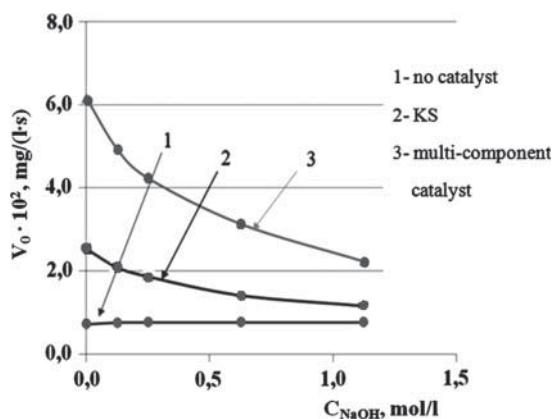
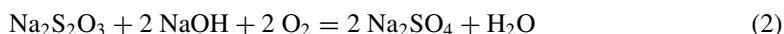
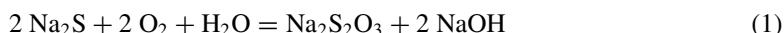


Figure 4. Influence of the antioxidant (irganox-1010) on the initial rate of sodium sulfide oxidation.

The oxidation process proceeds from Na_2S to $\text{Na}_2\text{S}_2\text{O}_3$, Na_2SO_3 or Na_2SO_4 and is expressed by the following equations:



It is known [33] that the reaction of Equation (5) may proceed far more rapidly than that of Equations (3) and (4). As a result, a considerable amount of $\text{Na}_2\text{S}_2\text{O}_3$ is left in the solution together with Na_2SO_4 , which is the final oxidized product. In a weakly alkaline medium ($\text{pH} \approx 12.5$), thiosulfate is rapidly oxidized by the presence of a multi-component catalyst. As can be seen from Figure 5, the initial time of the reaction to 70% of sodium sulfide is oxidized to thiosulfate. Thiosulfate and sulfite were not oxidized until the complete disappearance of sodium sulfide in the solution, then its concentration is decreased and the concentration of the final product (sodium

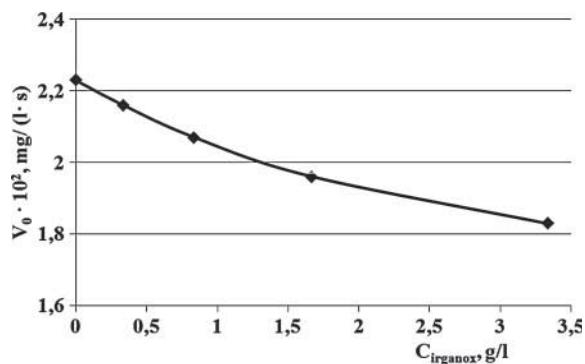


Figure 5. The kinetics of formation of products of sodium sulfide oxidation in the presence of the multi-component oxide catalyst.

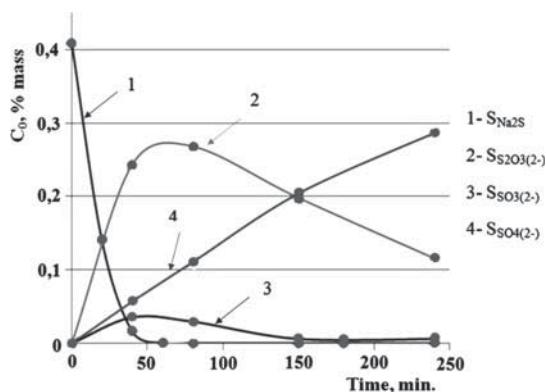


Figure 6. Effect of NaOH concentration on the rate of sodium sulfate formation.

sulfate) is increased. The rate of sulfate formation does not depend on the alkaline concentration in the absence of catalysts. The dependence of the rate of sodium sulfate production on the NaOH concentration (Figure 6) in the presence of a heterogeneous multi-component oxide catalyst shows that increasing the NaOH concentration from 0 to 1.125 mol/l led to drastic reduction in the rate of sodium sulfate production about 8.0 times. In addition, at a NaOH concentration of 1.125 mol/l,

Table 3. The concentration of thiosulfate and sodium sulfite formation at different NaOH concentrations in the absence of catalysts.

C_{NaOH} (mol/l)	C_{products} (mg/l)	Time (min)				
		0	80	150	240	330
0	$\text{S}_{\text{S}2\text{O}3}^{2-}$	0	1749	2595	2551	2551
	$\text{S}_{\text{SO}3}^{2-}$	0	368	651	687	687
0.125	$\text{S}_{\text{S}2\text{O}3}^{2-}$	0	1760	2450	2461	2403
	$\text{S}_{\text{SO}3}^{2-}$	0	449	720	768	645
0.25	$\text{S}_{\text{S}2\text{O}3}^{2-}$	0	1560	2237	2514	2434
	$\text{S}_{\text{SO}3}^{2-}$	0	424	710	834	897
0.625	$\text{S}_{\text{S}2\text{O}3}^{2-}$	0	1560	2350	2556	2479
	$\text{S}_{\text{SO}3}^{2-}$	0	499	746	784	680
1.125	$\text{S}_{\text{S}2\text{O}3}^{2-}$	0	2182	2584	2538	2488
	$\text{S}_{\text{SO}3}^{2-}$	0	520	716	782	672

Table 4. The concentration of thiosulfate and sodium sulfite formation at different NaOH concentrations in the presence of KS.

0	S_{S2O3}^{2-}	0	2749	2648	2373	2217
	S_{SO3}^{2-}	0	592	309	163	102
0.125	S_{S2O3}^{2-}	0	2835	2795	2565	2467
	S_{SO3}^{2-}	0	683	585	437	338
0.25	S_{S2O3}^{2-}	0	2652	2502	2370	2258
	S_{SO3}^{2-}	0	738	517	430	367
0.625	S_{S2O3}^{2-}	0	2632	2587	2519	2519
	S_{SO3}^{2-}	0	720	696	647	605
1.125	S_{S2O3}^{2-}	0	2660	2769	2769	2769
	S_{SO3}^{2-}	0	706	693	667	607

Table 5. The concentration of thiosulfate and sodium sulfite formation at different NaOH concentrations in the presence of a multi-component catalyst.

0	S_{S2O3}^{2-}	0	2682	1985	1156	475
	S_{SO3}^{2-}	0	293	61	61	61
0.125	S_{S2O3}^{2-}	0	2600	2050	1540	1080
	S_{SO3}^{2-}	0	480	271	215	126
0.25	S_{S2O3}^{2-}	0	2727	2057	1792	1463
	S_{SO3}^{2-}	0	469	328	273	209
0.625	S_{S2O3}^{2-}	0	3243	2938	2780	2581
	S_{SO3}^{2-}	0	613	591	496	492
1.125	S_{S2O3}^{2-}	0	3365	3261	3261	3261
	S_{SO3}^{2-}	0	448	432	432	432

the rate of sulfate formation in the presence of a heterogeneous multi-oxide catalyst even lowers the rate of sulfate formation in the absence of catalysts.

The investigation results (Tables 3–5) show that the thiosulfate concentration in the system is increased sharply at the initial time of the oxidation reaction of sodium sulfide. The concentration of sodium sulfite formed was 5–10 times lower in comparison with sodium thiosulfate, which is explained by the higher rate of oxidation of sulfite to sulfate. The thiosulfate concentration

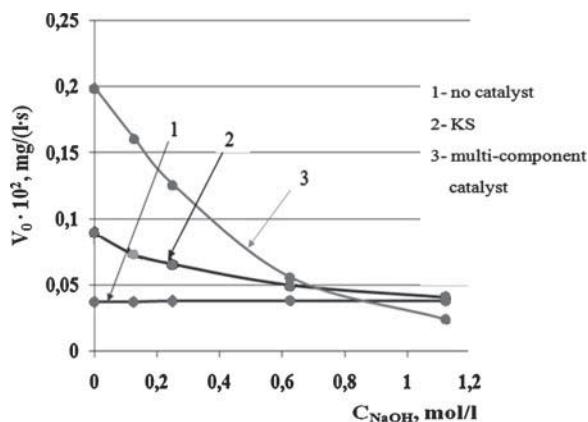


Figure 7. Influence of oxidation products on the initial rate of sodium sulfide oxidation.

of subsequent oxidation decreased slightly. The stability of the thiosulfate ion in the absence of catalysts and in high alkaline concentration is due to its stable tetrahedral structure, which is similar to that of the sulfate ion.[34]

The influence of products on the initial rate of sodium sulfide oxidation in the presence of a multi-component catalyst is shown in Figure 7. It can be seen that thiosulfate and sulfite have led to an increase in the rate of sulfide oxidation; in this case, sulfate inhibits the oxidation rate. As shown in Figure 6, the combined influence of all products on the rate of sodium sulfide oxidation is always zero; this result provides previous evidence that the reaction order does not depend on sulfide concentration, but has the first order with respect to oxygen concentration.

3. Conclusion

In this paper the effectivity of different transition metal oxides deposited on the polymeric matrix in the oxidation of sodium sulfide was studied. For a comparison of the catalytic activity, one should keep in mind that if the metal ions are present in different oxidation states, *e.g.* +2 and +3, the metal ion with the lower oxidation state must first be oxidized into the higher oxidation state in order to show catalytic activity.

Manganese oxide and its mixtures with other transition metal oxides are the most effective catalysts in the oxidation of sodium sulfide in aqueous alkaline solution. The synergistic effect of two or three catalytically active transition metal oxides is positive; mixtures of three transition metal oxides show the maximum synergistic effect in the oxidation of sodium sulfide.

The kinetics of formation of the products of sodium sulfide oxidation in the presence of a multi-component oxide catalyst was studied. It is shown that the reduction of alkaline concentration increases the rate of sodium sulfide oxidation and the rate of sodium sulfate formation in the presence of a multi-component oxide catalyst and KS, and with the non-catalytic reaction, the rate stays constant. Sodium thiosulfate in a weakly alkaline medium is oxidized to sulfate solution only in the presence of catalysts. The reaction order was defined, which has zero order with respect to sulfide concentration and first order with respect to oxygen concentration.

Investigation of factors influencing the oxidation rate led to the following results: (1) a high oxidation rate is observed with respect to the weakly alkaline solution; (2) the antioxidant (irganox-1010) inhibited the oxidation rate and (3) the combined action of all oxidation products had no influence on the reaction rate.

4. Experiments

4.1. Materials

All reagents were obtained from KAZPELEN and were of the highest grade available and used without further purification. During experiments, the following oxides of the metals with variable valence were used: MnO₂ (Russia, GOST 4470-79), CuO (Russia, GOST 16539-79), NiO (Russia, GOST 4331-78), TiO₂ (Russia, GOST 9808-84), V₂O₅ (Russia, MRTU 6-09-6594-70), Cr₂O₃ (Russia, GOST 2912-79), MoO₃ (Russia, TU 2611-002-469133-2002), Fe₂O₃ (Russia, GOST 4173-77), cobalt oxide (II, III) (Russia, GOST 4467-79) and cobalt phthalocyanine (Russia, TU 6-07-1135-78). The polymer used was a type of high polymer made from polyethylene, known commercially as KAZPELEN no. 15313-003. Stock sulphide solutions were made by dissolving the 9-watered sodium sulfide in deionized water and used within 1 h of preparation to minimize losses due to aerial oxidation. Deionized water was used in all experiments. All other solvents used were of analytical grade.

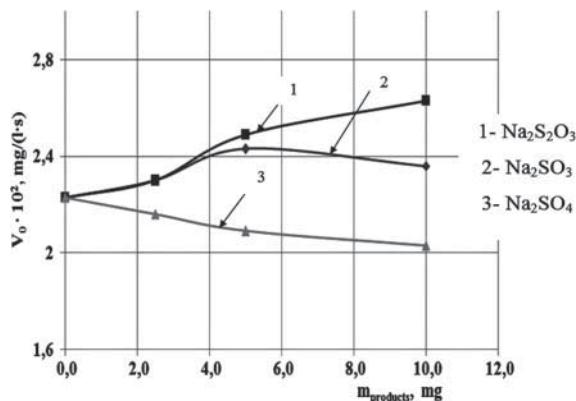


Figure 8. Oxidation tower apparatus.

4.2. Catalyst preparation

Laboratory samples of the heterogeneous catalysts were prepared by roll-mixing the catalytically reactive component (transition metal oxides or phthalocyanine cobalt) with the molten polymer at 150°C until a uniform mass was obtained, after which shavings with a thickness of 0.25 mm were formed (specific surface area of about 150 cm²/g). These catalysts can be prepared in the form of granules (particle size 2 × 2 × 2 mm), with the same equipment used to obtain carbon black concentrates or dye concentrates in polyethylene or polypropylene production. Packing elements can be prepared from the catalyst granules in casting machines.[35] The metal oxide content, expressed as wt.% of metal oxide in the catalyst samples, was determined by means of chemical analysis (example CuO-5 – the heterogeneous catalyst contains 5.0% cuprum oxide by mass). After washing the catalyst with distilled water for 10 h at 60°C, it was used in labs for testing.

4.3. Experimental procedures and analytical methods

Na₂S oxidation in aqueous NaOH solution was made in an air bubbling vessel of oxidation tower. The oxygen was fed into the reaction solution with the exact concentration of Na₂S in the presence of the catalytic agent which was being tested at a speed of 30 l/h. The solution inside the reactor was stirred at a speed of 1400 rpm. The temperature of the reaction solution was maintained at 60°C with a thermally controlled magnetic mixer (Figure 8).

The concentration of Na₂S in the solution was measured using the potentiometric titration method with an aqueous AgNO₃ solution.[36] The concentration of Na₂SO₄ was determined using spectrophotometry (SS1207UV regime A, λ = 450 nm, L = 50.0 mm), and the concentration of Na₂S₂O₃ and Na₂SO₃ including Na₂S was determined using iodometry.[37]

4.4. Catalyst characterization

The catalysts based on copper and manganese oxides (MnO₂, CuO) were used for testing. Characterization of the catalyst surface before and after three months of use was done by digital microscope (Keyence-VH-Z500R) and Fourier spectrometer (Infracium-FT-08).

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