Catalyst Activity and Selectivity for Liquid-Phase Oxidation of Sodium Sulfide catalyzed by various Materials

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The liquid-phase oxidation of sodium sulfide catalyzed by various materials such as 4 sulfur dyes, 6 vat dyes, $CuSO_4$, $MnSO_4$, $CoSO_4$, $FeSO_4$, pyrocatechol, and sulfate lignin have been studied, and catalyst activity and selectivity for this oxidation of the employed catalysts have been investigated.

Measurement of time-course of concentration of liquid compounds was carried out with a stirred vessel under aeration, while that of a absorption rate of oxygen was performed in a batchwise operation.

Oxidation products were Na_2S_2, Na_2SO_3, and mainly $Na_2S_2O_3$. At first, Na_2S_2, Na_2SO_3 and $Na_2S_2O_3$ were formed by oxidation of Na_2S simultaneously, and $Na_2S_2O_3$ was also formed by the reaction of Na_2S_2 with Na_2SO_3 subsequently.

In general, catalyst activity of sulfur dyes was higher than that of vat dyes, and that of metal sulfates such as $MnSO_4$, $CuSO_4$, and $CoSO_4$ was particularly high. Metal sulfates had a high selectivity for the formation of $Na_2S_2O_3$.

A presumption of reaction mechanism was somewhat described.

1. INTRODUCTION

The waste water from dye-works[1] and the black liquor in the digestion of kraft pulp process[2] contain sodium sulfide which has a toxicity and a high reduciblity. These strongly alkaline solutions cause a lowering of the dissolved oxygen in water, increase in chemical oxygen demand, evolution of hydrogen sulfide as the solution becomes acidic, and corrosion of metals. Therefore, it is preferable that sodium sulfide is recovered as sodium thiosulfate, having a high additional value for chemicals, produced by the oxidation of it or is converted to harmless substances by the oxidation to prevent water pollution.

In the previous paper[3] of authors, the liquid-phase oxidation of sodium sulfide with oxygen catalyzed by sulfur dye Sulfur Black B has been studied kinetically on the basis of the characteristics of this reaction obtained experimentally.

In the present paper, we shall discuss on catalyst activity and selectivity for this oxidation reaction catalyzed by some sulfur dyes and redox catalysts such as metal sulfates.

2. EXPERIMENTAL

Measurement of the rate of oxidation with respect to liquid compounds was carried out with a stirred vessel under aeration, while that of absorption rate of oxygen was performed in a batchwise operation. Only the outlined experimental procedure using the stirred vessel under aeration will hereinafter be descrided.

The weighted sodium sulfide and catalyst* were charged together with distilled water in the stirred vessel under purified nitrogen atmosphere. After the solution temperature in the vessel reached a desired level with agitation, oxygen gas was introduced to the bottom of reactor through a ring sparger at the predetermined rate of gas flow. Thus, the oxidation reaction started.

Aliquots of reaction solution were then withdrawn at regular intervals, and zinc carbonate powder as a reaction-stopping reagent was immediately added in the sampled solution to precipitate soluble sulfides. Sodium sulfide and sulfur compounds formed by this oxidation were determined by means of iodometry and high-performance liquid chromatography. For futher details of experimental procedures and analytical techniques the previous paper[3] should be reffered to.

3. RESULTS AND DISCUSSION

3.1 Time-course of concentration of liquid compounds

With regard to the liquid-phase oxidation of sodium sulfide catalyzed by sulfur dyes or metal sulfates, the time-course of concentration of liquid compounds was followed. The typical representations which illustrate the obtained results are shown in Figs. 1 to 4. From these figures, it was proved that sodium sulfide was simultaneously changed to

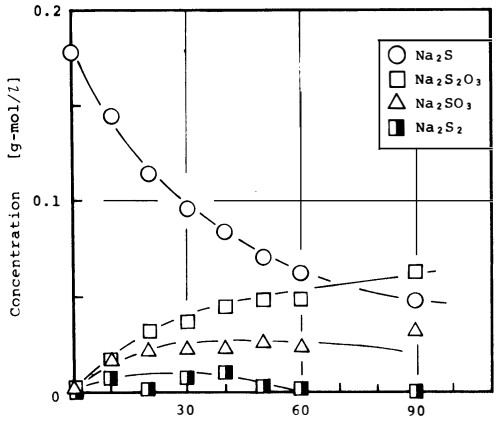


Fig. 1 The course of oxidation of sodium sulfide catalyzed by Sulfur Red Brown 6RN
Reaction conditions; Na_2S: 0.2 g-mol/l, Oxygen partial pressure: 1.0 atm, Sulfur Red Brown 6RN (Catalyst): 0.1 g/l, pH in reaction solution: 12.88, Reaction temp.: 25 °C, Rate of stirring: 1120 rpm, Rate of oxygen gas flow: 1000 ml/min

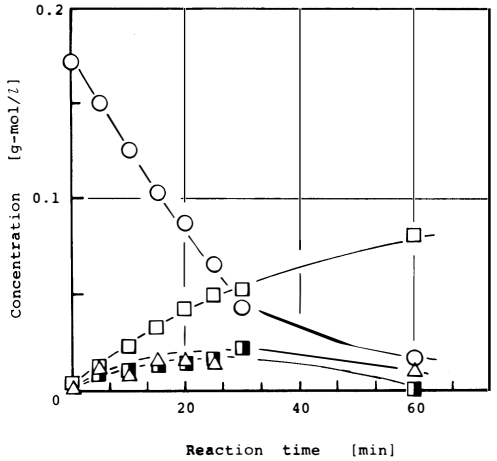


Fig. 2 The course of oxidation of sodium sulfide catalyzed by Vat Brilliant Blue 4G pdr.
Reaction conditions are the same as those of Fig. 1.

*Dye manufactured by Mitsui Toatsu Chemicals Inc. were employed.

sodium sulfite, sodium disulfide, and sodium thiosulfate, and sodium thiosulfate was also consecutively formed by reaction of sodium sulfite with sodium disulfide regardless of kinds of catalyst.

Although Cu(II), Co(II), Mn(II), and Fe (II) ions are well-known catalysts[4] which have been employed in the reaction of sulfites with oxygen to form sulfates, these metal ions didn't almost promote the oxidation of sodium sulfite until a considerable decrease in concentration of sodium sulfide.

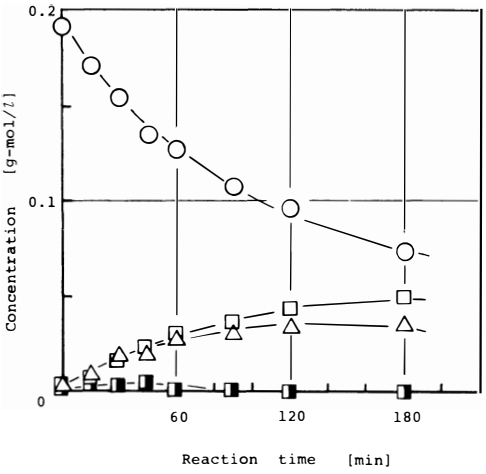


Fig. 3 The course of oxidation of sodium sulfide catalyzed by Threne Black BBN pdr.
Reaction conditions are the same as those of Fig. 1.

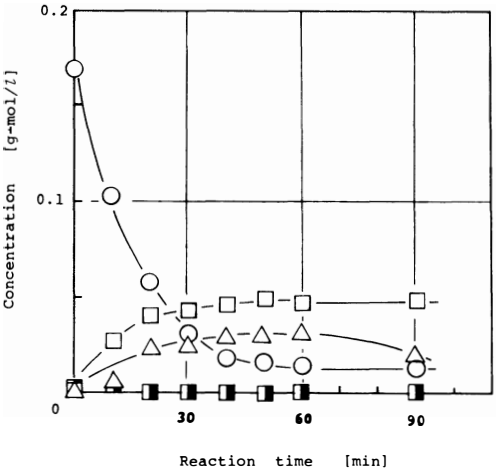


Fig. 4 The course of oxidation of sodium sulfide catalyzed by $MnSO_4$
Reaction conditions are the same as those of Fig. 1 except concentration of catalyst.
Concentration of $MnSO_4$ (Catalyst): 7.0×10^{-5} g-mol/l

3.2 Comparison of characteristics of catalysis

The characteristics of catalysis of catalysts such as 4 sulfur dyes, 6 vat dyes, $CuSO_4$, $MnSO_4$, $CoSO_4$, $FeSO_4$, pyrocatechol, and sulfate lignin will be considered in some detail. We take up both catalyst activity and selectivity as the characteristics.

At first, the results obtained on catalyst activity are shown in Tables 1 and 2. In general, catalyst activity of sulfur dyes was higher than that of vat dyes. Sulfur Brilliant Green 4GF and Sulfur Red Brown 6RN which contained $CuSO_4$ added in thionation

Table 1. Comparison of catalyst activity of sulfur dyes and vat dyes

	Dye	Absorption rate of oxygen* V_{O_2} [ml-stp/l·min]	Initial rate of disappearance of sodium sulfide** $r_{(Na_2S)} \times 10^4$ [g-mol/l·min]
Sulfur dye	Sulfur Black B	33	23
	Sulfur Brilliant Green 4GF	70	42
	Sulfur Red Brown 6RN	41	27
	Vat Brilliant Blue 4G pdr.	68	44
Vat dye	Threne Blue BCS pdr.	9.2	2.4
	Threne Black BBN pdr.	16	12
	Threne Brilliant Violet RR pdr.	27	10
	Threne Yellow GCN pdr.	7.4	1.2
	Threne Brilliant Pink R pdr.	6.1	0.75
	Threne Blue RSN pdr.	10	3.2

Reaction conditions
Na_2S:0.2 g-mol/l, Oxygen partial pressure:1.0 atm, Dye:0.1 g/l, Reaction temp.:25 °C, pH in reaction solution:12.88, Rate of stirring:1120 rpm, Rate of oxygen gas flow:1000 ml/min

* Measurement of absorption rate of oxygen was performed in a batchwise operation.
** Measurement of this rate was carried out with a stirred vessel under aeration.

Table 2. Comparison of catalyst activity of metal sulfates and the other catalysts

	V_{O_2} [ml-stp/l·min]	$r_{(Na_2S)} \times 10^4$ [g-mol/l·min]
Sulfur Black B	75	45
$MnSO_4$	360	72 *
$FeSO_4$	12	8
$CuSO_4$	108	36 *
$CoSO_4$	44	11 *
Pyrocatechol	32	unobserved
Sulfate lignin	18	14
Without catalyst	1.7	0.78

Reaction conditions are the same as those of Table 1 except concentration of catalyst.
Concentration of catalyst: 7.0×10^{-4} g-mol/l or 7.0×10^{-5} g-mol/l (*mark)

process, and Vat Brilliant Blue 4G which contained phthalocyanine Blue ($C_{32}H_{16}Cu$) added in the same process, had particularly high activity. The order of catalytic activity of metal sulfates and the other redox catalysts was obtained as follows: $MnSO_4 > CuSO_4 > CoSO_4 >$ Pyrocatechol > Sulfur lignin > $FeSO_4$. Particularly, catalyst activity of $MnSO_4$ was extremely high.

Next, for these catalysts the ratio of formation of oxidation products estimated on the basis of sulfur amounts were determined at 25, 50, and 75% conversion of sodium sulfide to the oxidation products. The obtained results are shown in Table 3. It was

Table 3. Ratio of the oxidation products on the basis of sulfur amounts for various catalysts

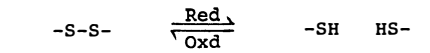
	Product ratio [%]								
	at 0.25 conversion of Na_2S			at 0.5 conversion of Na_2S			at 0.75 conversion of Na_2S		
	Na_2SO_3	Na_2S_2	$Na_2S_2O_3$	Na_2SO_3	Na_2S_2	$Na_2S_2O_3$	Na_2SO_3	Na_2S_2	$Na_2S_2O_3$
Sulfur Black B	37.2	6.4	56.4	30.0	4.6	65.4	—	—	—
Sulfur Brilliant Green 4GF	31.2	12.4	56.4	27.8	2.0	70.2	16.4	0.0	83.6
Sulfur Red Brown 6RN	25.2	16.4	58.4	20.6	10.6	68.8	—	—	—
Vat Brilliant Blue 4G pdr.	16.4	26.8	56.8	12.0	19.6	68.4	15.9	21.6	62.5
Threne Blue BCS pdr.	39.2	2.4	58.4	—	—	—	—	—	—
Threne Black BBN pdr.	32.0	8.0	60.0	27.6	1.0	71.4	—	—	—
Threne Brilliant Violet RR pdr.	34.0	10.8	55.2	27.0	1.0	72.0	—	—	—
Threne Yellow GCN pdr.	31.2	5.6	63.2	—	—	—	—	—	—
Threne Brilliant Pink R pdr.	35.6	0.4	64.0	—	—	—	—	—	—
Threne Blue RSN pdr.	36.0	3.2	60.8	—	—	—	—	—	—
$MnSO_4$	6.8	15.2	78.0	10.2	4.8	85.0	19.6	0.0	80.4
$FeSO_4$	30.4	7.2	62.4	—	—	—	—	—	—
$CuSO_4$	17.2	3.2	79.6	18.6	2.6	78.8	—	—	—
$CoSO_4$	23.2	2.4	74.4	15.8	1.6	82.6	19.6	0.5	79.9
Sulfate lignin	32.4	5.6	62.0	26.8	0.0	73.2	—	—	—

found that product ratios were about 55 to 85% for sodium thiosulfate, about 10 to 35% for sodium sulfite, and about 0 to 25% for sodium disulfide, respectively, without regard to kinds of catalyst. The chief product was therefore sodium thiosulfate, and the yield of sodium thiosulfate increased with an increase in conversion of sodium sulfide.

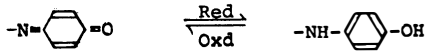
The following features of the selectivity for this oxidation were also proved. Sulfur dyes were superior to the formation of sodium disulfide than the other catalysts, vat dyes were excellent in the formation of sodium sulfite than that of sodium disulfide, and metal sulfates had a high selectivity for the formation of sodium thiosulfate.

3.3 Presumption of reaction mechanism

In general, sulfur dyes have the structure of polysulfides together with the fundamental ring structure made up of thiazole ring or thiazine ring which acts as a chromophore. It seems that as shown in Eqs. (1) and (2)



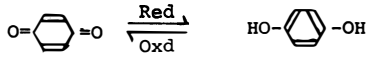
(1)



(2)

polysulfides and the part of indophenol in the fundamental ring structure would participate in a oxidation-reduction reaction.

Whereas vat dyes have a quinon type ring and the part of catalysis of the dyes may be represented by a oxidation-reduction reaction as shown in Eq. (3).



(3)

Sodium sulfide is oxidized by the dyes and metal ions to form oxidation products, and the dyes and metal ions reduced at that time are reoxidized by oxygen to produce their's original forms.

On the basis of the kinetic study reported in the previous paper[3], it could also presumed that this reaction has a complex reaction mechanism involving a chain reaction step.

4. CONCLUSION

With regard to the liquid-phase oxidation of sodium sulfide catalyzed by various materials such as sulfur dyes, vat dyes, metal sulfates, and the other redox catalysts, the characteristics of catalysis of the employed catalysts were considered.

The obtained informations were as follows.

(1) In general, catalyst activity of sulfur dyes was higher than that of vat dyes.
(2) Catalyst activity of metal sulfates such as $MnSO_4$, $CuSO_4$, and $CoSO_4$ was particularly high.
(3) Metal sulfates had a high selectivity for the formation of sodium thiosulfate.

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