Structure of the Vanadium-Potassium Catalyst during the Oxidation of Sulfur Dioxide and the Oxidation Mechanism

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The structure of vanadium-potassium catalyst in gas mixtures of various compositions of SO_2, SO_3, and O_2 was investigated at 500, 550, and 600°C to elucidate the mechanism of SO_2 oxidation on the catalyst. It was found that in the catalyst 50—70% of V(IV) is in VO^{2+}-form, 10—15% of V(V) in $VO_2{}^+$-form and the rest of the vanadium forms large vanadium-oxygen networks. It was also found that both the reduction of V(V) with SO_2 and oxidation of V(IV) with oxygen are in equilibrium and the desorption of SO_3 from the molten catalyst into gas phase seems to be the rate-determining step in SO_2 oxidation. On the basis of this mechanism, the reaction rate of SO_2 oxidation can be formulated as follows,

$$dSO_3/dt = k'(SO_3) = kP_{SO_2}\cdot P_{O_2}{}^{1/2}.$$

For the sake of confirmation, the kinetics of SO_2 oxidation (below 10% conversion) over vanadium-potassium catalyst was measured by a flow method at 500, 550, and 600°C over gas compositions of $SO_2 = 5\sim24\%$ and $O_2 = 10\sim36\%$. It was found that the rate expression was correct.

It is generally accepted for sulfur dioxide oxidation by vanadium-potassium catalyst that the active component of the catalyst forms a liquid phase under the reaction conditions[1-8], and that the reaction proceeds according to the reduction-oxidation mechanism.[8,9] However, the composition of the active component is not well established and various contradictory rate-determining steps are proposed for the oxidation. Tandy has suggested the reduction of pentavalent vanadium by sulfur dioxide to be the rate-determining step.[4] On the other hand, Mars *et al.* have proposed the following reduction-oxidation mechanism in which (1) is in equilibirum and (2) is rate-determining.[8]

$$2V^{5+} + SO_2 + O^{2-} = 2V^{4+} + SO_3 \qquad (1)$$

$$2V^{4+} + 1/2O_2 = 2V^{5+} + O^{2-} \qquad (2)$$

Simecek *et al.* have recently reported a similar mechanism.[9]

We noted that the reduction and oxidation of vanadium in molten salts are closely related to the basicity (activity of oxide ions) of the melts[7,10]. A quantitative estimation of the basicity of the catalyst is, therefore, necessary to elucidate the reaction mechanism of sulfur dioxide oxidation, although Mars and Simecek treated the reduction and oxidation of vanadium assuming a constant activity of oxide ions. The basicity can be estimated by means of the equilibrium relations for pyrosulfate formation:

$$O^{2-} + S_2O_7{}^{2-} = 2SO_4{}^{2-} \qquad (3)$$

$$\text{or} \quad 2SO_3 + O^{2-} = S_2O_7{}^{2-} \qquad (4)$$

We investigated the structure of potassium-vanadium catalyst under a SO_2-SO_3-O_2 mixture of various compositions, with the emphasis on the determination of the amount of pyrosulfate whose quantitative analyses have never been done. The reaction mechanism of sulfur dioxide oxidation was discussed from the viewpoint based on structural and kinetic investigations.

Experimental

Composition of Catalyst under SO_2-SO_3-O_2 Mixtures. About 0.5 g of V_2O_5–K_2SO_4 mixture was heated in a platinum boat (10×10×30 mm) in the flowing atmosphere of SO_2(2—16%)-SO_3(3—14%)-O_2(5—40%)-N_2. The boat was placed in a 20-mm diameter quartz glass tube heated with an electric furnace. The temperature was controlled to within ±1°C. The gas mixtures were prepared from SO_2–O_2–N_2 mixture by oxidizing SO_2 partially with an industrial catalyst placed immediately before the catalyst sample. The composition of gas phase was determined by measuring SO_2 contents of the entering and outgoing gas mixtures by an iodimetric method with 0.2N iodine and 0.1N sodium thiosulfate solutions. Heating of catalyst sample in a given gas mixture was continued for 15 hr at 500, 550, and 600°C. The composition of catalyst samples was confirmed to be of steady state value after 8 hr. After the treatment of catalyst sample followed by rapid cooling, the weight change and chemical composition of the sample were determined and measurements of IR spectrum and X-ray powder pattern were carried out.

The concentrations of V(IV) and V(V) in the catalyst sample were determined by titration with ferrous sulfate solution using diphenylamine as an indicator. After dissolving the sample into 0.5N sulfuric acid, V(V) was titrated with 0.1N ferrous sulfate solution with one portion and total vanadium was titrated after oxidizing all vanadium to V(V) with potassium permanganate solution with the other portion. The amount of V(IV) was computed from the two values.

The concentration of pyrosulfate was determined as follows. About 200 mg of the catalyst sample ground was allowed to suspend in 60 m*l* of water on a water bath for an hour. By this procedure all the sulfate and pyrosulfate dissolved into water, together with some fractions of V(IV) and V(V). Since pyrosulfate hydrolyses to give $HSO_4{}^-$ ions on dissolu-

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[1] R. Kiyoura, *Nippon Kagaku Zasshi*, **61**, 72 (1940), *Ryusan*, **2**, 223 (1949).

[2] J. H. Frazer and W. J. Kirkpatrick, *J. Amer. Chem. Soc.*, **62**, 1659 (1940).

[3] H. F. Topsoe and A. Nielsen, *Trans. Danish Acad. Tech. Sci.*, No. 1, 3 (1948).

[4] G. H. Tandy, *J. Appl. Chem.*, (London), **6**, 68 (1956).

[5] G. Okamoto, H. Kobayashi, and Y. Kayahara, *Kogyo Kagaku Zasshi*, **63**, 924 (1963).

[6] T. Seiyama, A. Kato, T. Harada, and T. Ishida, *Shokubai*, **5**, 221 (1963).

[7] T. Sakamoto, T. Ishida, A. Kato, and T. Seiyama, *ibid.*, **7**, 338 (1965).

[8] P. Mars and J. G. H. Maessen, *J. Catal.*, **10**, 1 (1968).

[9] A. Simecek, B. Kadlec, and J. Michalek, *ibid.*, **14**, 287 (1969).

[10] M. Nagano, I. Mochida, A. Kato, and T. Seiyama, *Yogyo Kyokai Shi*, **78**, 401 (1970).

tion, the amount of the former contained in the sample can be determined from that of acid formed. After filtration of the solution, a portion of the filtrate was titrated with 0.05N sodium hydroxide solution using phenolphthalein as an indicator. During the course of titration, V(IV) and V(V) ions undergo the following acid-base reactions or oxidation.[11]

$$VO_2^+ + 2H_2O = H_2VO_4^- + 2H^+ \quad (5)$$

$$2VO^{2+} + 3H_2O = HV_2O_5^- + 5H^+ \quad (6)$$

$$HV_2O_5^- + 1/2O_2 + 2H_2O = 2H_2VO_4^- + H^+ \quad (7)$$

In the indicator range of phenolphthalein, $H_2VO_4^-$ and $HV_2O_5^-$ ions are predominant species for V(V) and V(IV), respectively.[11] The amount of acid produced by reactions (5)—(7) during the neutralization can, therefore, be computed from the concentrations of V(IV) and V(V) before and after the titration with the sodium hydroxide solution. The amount of acid was corrected in the calculation of the amount of pyrosulfate from the consumption of the alkali. Most of V(IV) was oxidized to V(V) during titration.

The amount of SO_3 absorbed was calculated from the weight increase of catalyst sample after making a minor correction for the weight decrease due to the reduction of V(V) to V(IV). Sulfate is given as the difference between the total sulfur, the sum of initial potassium sulfate and SO_3 absorbed, and sulfur in pyrosulfate form.

IR spectra were measured by KBr method. Cu-K_α radiation was used for X-ray examination.

Oxidation Rate of Sulfur Dioxide. Catalysts used in the kinetic study were prepared by mixing the hydrochloric solution of V_2O_5 and K_2SO_4 with carborundum powder of 0.3—0.4 mm diameter and drying the mixture under stirring. The mole ratio K_2SO_4/V_2O_5 was 1(catalyst A) and 2(catalyst B). 42 mg of V_2O_5–K_2SO_4 mixture was supported on 1 g of the carborundum in both catalysts. The oxidation rate was measured by a flow method. Catalyst (0.2—0.3 g) was packed in 12 mm diameter quartz glass tube with quartz glass wool. Temperature was measured by a thermocouple inserted in the catalyst bed and controlled to within ±1°C. Analysis of gas phase was carried out by the iodimetric method.

TABLE 1. COMPOSITION OF CATALYST SAMPLE

K_2O/V_2O_5 and Temperature	Run	Composition of gas phase (%) (balance: N_2)			Composition of catalyst (reference: 1 mol of V_2O_5)				
		SO_2	SO_3	O_2	$\frac{V(IV) \times 100}{V(IV)+V(V)}$	$S_2O_7^{2-}$	SO_4^{2-} g. ion	$V(V)_{aq}$	$V(IV)_{aq}$
$K_2O/V_2O_5=1$ 500°C	1	3.5	4.7	30.2	32.8	1.08	0.38	0.22	0.43
	2	3.3	5.0	9.9	45.0	1.04	0.48	0.11	0.67
	3	3.4	8.1	30.0	34.6	1.12	0.37	0.30	0.43
	4	4.6	6.8	10.6	47.1	0.94	0.76	0.09	0.69
	5	12.6	4.8	29.8	54.3	0.99	0.61	0.06	0.82
	6	12.1	5.1	9.9	59.9	0.78	1.14	0.08	0.75
	7	12.1	8.0	30.0	55.5	0.94	0.72	0.08	0.73
$K_2O/V_2O_5=1$ 550°C	8	5.0	5.4	7.7	32.3	0.99	0.39	0.24	0.36
	9	11.9	8.9	6.0	40.8	1.13	0.33	0.12	0.53
	10	1.9	3.1	8.7	16.0	0.76	0.63	0.32	0.20
	11	4.4	5.9	5.2	33.4	1.09	0.17	0.13	0.32
	12	1.7	3.5	8.4	19.3	0.99	0.16	0.18	0.16
	13	8.2	13.9	39.8	31.9	1.11	0.31	0.20	0.36
	14	8.4	13.1	25.5	34.3	0.98	0.48	0.19	0.48
	15	10.7	10.4	15.9	38.6	0.85	0.74	0.17	0.61
	16	11.5	10.0	5.4	47.0	0.89	0.71	0.14	0.65
	17	2.2	3.3	9.9	21.8	0.93	0.26	0.17	0.25
	18	6.9	3.2	10.0	30.0	0.86	0.46	0.10	0.40
	19	15.4	5.6	7.9	44.2	0.92	0.57	0.12	0.52
$K_2O/V_2O_5=2$ 550°C	20	3.6	6.4	10.1	33.1	1.27	1.33	0.54	0.45
	21	3.5	6.5	29.2	25.8	1.62	0.55	0.26	0.30
	22	12.2	7.6	30.2	38.2	0.92	1.91	0.57	0.71
	23	12.6	7.4	10.2	44.6	1.44	1.08	0.09	0.62
	24	3.5	8.0	9.8	31.1	1.52	0.91	0.32	0.35
	25	3.2	7.9	29.7	22.5	1.42	0.95	0.49	0.26
	26	12.2	6.3	9.8	43.4	1.41	1.05	0.11	0.56
	27	12.2	6.3	30.0	41.2	1.50	0.85	0.11	0.51
$K_2O/V_2O_5=1$ 600°C	28	2.9	5.4	9.8	15.9	0.93	0.14	0.35	0.13
	29	2.7	5.6	29.9	13.7	0.99	0.02	0.29	0.09
	30	2.9	7.4	30.3	14.7	0.98	0.10	0.32	0.09
	31	12.1	5.9	29.0	22.6	1.02	0.01	0.14	0.19
	32	11.9	5.7	10.0	26.9	0.89	0.35	0.30	0.31
	33	12.1	8.0	10.0	26.3	1.01	0.18	0.12	0.29
	34	12.2	7.7	30.1	22.9	0.93	0.23	0.27	0.22

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[11] M. Pourbaix, "Atlas of Electrochemical Equilibrium in Aqueous Solution", Pergamon Press. (1966) p. 234.

TABLE 2. MELTING OF CATALYST SAMPLE UNDER SO_2–SO_3–O_2 ATMOSPHERE

Run	Temperature (°C)	K_2O/V_2O_5	Composition of gas phase (%) (balance: N_2)			Melting[a]
			SO_2	SO_3	O_2	
35	450	1	8.2	1.2	41.5	incomplete
36	450	1	2.2	3.6	43.2	incomplete
37	470	2	1.8	4.1	42.3	complete
38	470	2	2.4	3.3	19.8	complete
39	470	2	12.2	1.6	33.0	incomplete
40	470	2	5.9	8.4	33.9	incomplete
41	470	2	2.1	3.6	10.8	incomplete

a) complete: glassy and homogeneous appearance.
incomplete: uneven surface, particles differing in colour from surroundings.

Results and Discussion

Composition and Structure of Catalys tunder SO_2-SO_3-O_2 Mixture. The compositions of gas phase and catalyst are shown in Table 1. $V(V)_{aq}$ and $V(IV)_{aq}$ are water-soluble pentavalent and quadrivalent vanadiums, respectively, extracted into water phase. The amount of SO_3 absorbed can be obtained from the relation, $(SO_3) = 2(S_2O_7^{2-}) + (SO_4^{2-}) - (K_2O/V_2O_5)$ (in mol).

Some remarks are given on the melting of catalyst. Experiments were carried out at 450 and 470°C under the conditions given in Table 2. In runs 35 and 36, only a part of the sample appeared to melt. Even at 470°C, indication of incomplete melting was observed on samples treated under gas mixture of high SO_2/O_2 ratio as in runs 39—41. This casts a doubt on the homogeneity of the molten catalyst over 380—500°C at which the previous kinetic studies were carried out.[8,9] Above 500°C, all the samples had a glassy appearance and showed only a broad diffraction effect around $2\theta=28°$ in X-ray examinations, indicating the complete melting of catalyst sample. The following discussions are restricted to the results on completely molten catalysts.

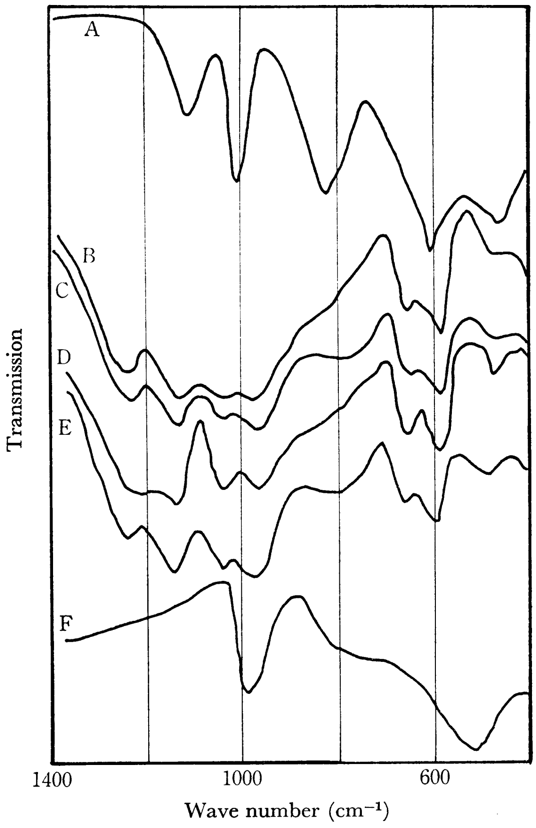

Fig. 1. IR spectra of catalyst samples.
A: Initial $2K_2SO_4$-V_2O_5 mixture, B: Run 7, C: Run 18, D: Run 24, E: Run 34, F: Water-insoluble residue in Run 32.

IR spectra of catalyst samples are shown in Fig. 1. As compared with the initial mixture of V_2O_5 and K_2SO_4 the sample treated under gas mixture showed complex spectra. IR spectra of the catalyst samples in other runs were very similar to the illustrated spectra of respective temperatures. Absorptions at 1050, 1150, and 1250 cm^{-1} in the spectra B to E can be assigned to ν_3 of SO_4^{2-} and SO_4-groups in $S_2O_7^{2-}$. There is a weak band near 800 cm^{-1}. The frequency coincides with that of asymmetric SOS stretching in $S_2O_7^{2-}$[12], indicating the presence of pyrosulfate ions. Bands at 600—700 cm^{-1} are considered to be ν_4 vibration of SO_4-groups. Spectrum F of the insoluble residue of water-extraction has a band at 990 cm^{-1} which is assigned to the stretching vibration of double V–O bond.[13] The residue has a compsoition of $K_2O\cdot 1.2V_2O_4\cdot 7.7V_2O_5$ which is close to that of a vanadium bronze $K_2O\cdot V_2O_4\cdot 8V_2O_5$ found in $V_2O_5\cdot K_2SO_4$ system[6]. Spectrum F is also similar to that of the bronze. Water-insoluble residue in other runs showed very close spectra to F. Thus it seems that the insoluble vanadiums in the catalyst formed a network structure similar to those in vanadium bronzes.[14]

The oxygen atoms in the catalyst should be bound to either a vanadium or a sulfur atom. The compositions of the catalyst sample shown in Table 1 enable us to evaluate the limiting number of oxygen atoms bound to a vanadium atom. The lower limit is given when all sulfur atoms are assumed to be in the form of SO_4^{2-}. The calculated values for the limiting O/V ratio fall in the range 1.3—1.9. This means that each vanadium atom in the catalyst was bound with oxygen atoms on an average of more than 1.3—1.9 atoms. Although Mars *et al.* assumed V^{5+} or V^{4+} ions for vanadiums in vanadium-potassium catalysts under SO_2 oxidation, the present finding appears to be more reasonable considering high ratio of charge to radius of both ions.

The number of oxygen atoms bound a water-soluble vanadium atom is also of interest and can be estimated in a similar way. It was assumed that the ratio of oxygen atom to water-insoluble vanadium atom was 2.5 since the insoluble materials had a composition close to $K_2O\cdot V_2O_4\cdot 8V_2O_5$, and that all sulfur atoms were in the form $S_2O_7^{2-}$. The second condition gives the upper limit of the ratio O/V_{aq} for water-soluble vanadiums. Caluculations revealed that the limiting O/V_{aq} ratio was in the range 1.3—1.7 for most catalyst samples with $K_2SO_4/V_2O_5=1$. Based on this value

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[12] A. Simon and H. Wagner, *Z. Anorg. Chem.*, **311**, 102 (1961).
[13] J. Selbin, *Chem. Rev.*, **65**, 153 (1965).
[14] H. G. Bachman and W. H. Barnes, *Z. Krist.*, **115**, 215 (1961).

for O/V_{aq} ratio and the analogy in the forms of vanadium atoms in acidic solution,[11] the water-soluble vanadiums in the catalyst are most likely to be present as VO^{2+} and VO_2^+ ions which will be coordinated with SO_3^{2-} or $S_2O_7^{2-}$ ions. Compounds consisting of K^+, SO_4^{2-}, and VO^{2+} or VO_2^+ ions such as $K_2SO_4\cdot 2VOSO_4$, $K_2SO_4\cdot VOSO_4$, and $K(VO_2)(SO_4)$ are highly water-soluble.[15] In the above pyrosulfate determination, the water-soluble vanadiums were thus assumed to be in VO^{2+} or VO_2^+-forms in the catalysts.[16]

From the above findings and compositions in Table 1, it might be concluded on the structure of vanadiums in vanadium-potassium catalysts under reaction conditions that 50 to 70% of V (IV) is in VO^{2+}-form, 10—15% of V(V) in VO_2^+-form and the rest of the vanadium forms large vanadium-oxygen networks.

Rate-determining Step in Sulfur Dioxide Oxidation. Sulfur dioxide oxidation proceeds by the reptition of the reduction of V(V) with sulfur dioxide and oxidation of V(IV) with oxygen. From the conclusions on the structures of vanadiums, the reduction and oxidation can be expressed as follows:

$$2(VO_2^+) + SO_2 = 2(VO^{2+}) + (SO_3) + (O^{2-}) \tag{8a}$$

$$(V(V)_nO_m) + SO_2 = (V(V)_{n-2}V(IV)_2O_{m-2}) + (SO_3) + (O^{2-}) \tag{8b}$$

$$2(VO^{2+}) + 1/2O_2 + (O^{2-}) = 2(VO_2^+) \tag{9a}$$

$$(V(V)_{n-2}V(IV)_2O_{m-2}) + 1/2O_2 + (O^{2-}) = (V(V)_nO_m) \tag{9b}$$

where, $V(V)_nO_m$ and $V(V)_{n-2}V(IV)_2O_{m-2}$ represent the V-O networks, and (8b) and (9b) show their reduction and oxidation, respectively. The desorption of sulfur trioxide formed in molten catalyst according to (8a) or (8b) completes sulfur dioxide oxidation.

$$(SO_3) = SO_3 \tag{10}$$

From the compositions of catalyst and gas phase given in Table 1, the rate-determining step in sulfur dioxide oxidation was examined as follows, where the reaction in molten phase

$$(SO_3) + (SO_4^{2-}) = (S_2O_7^{2-}) \tag{11}$$

$$[SO_3] = \frac{[S_2O_7^{2-}]}{K_{11}[SO_4^{2-}]} \tag{12}$$

was assumed to be in equilibrium and the equilibrium relation was used for the estimation of the concentration of (SO_3). We first examine whether reaction (10) is in equilibrium. If this is so, the ratio $[S_2O_7]/[SO_4^{2-}]$ should be proportional to P_{SO_3}. The observed value, however, was not in agreement with this expectation so that reaction (10) is considered to be not in equilibrium. When reaction (10) is rate-determining, reactions (8a) to (9b) are supposed to be in equilibrium. In this case, the following reaction should necessarily be in equilibrium.

$$SO_2 + 1/2O_2 = (SO_3) \tag{13}$$

The equilibrium conditions of reactions (12) and (13) lead to

$$\frac{[SO_4^{2-}]}{[S_2O_7^{2-}]}\cdot P_{SO_2}P_{O_2}^{1/2} = \frac{1}{K_{11}\cdot K_{13}} \tag{14}$$

When this relation is compared with the observed quantities, $1/K_{11}\cdot K_{13}$ shows no constant value. Flood *et al.*, however, have reported that the polarizing power of cations affects the stability of $S_2O_7^{2-}$ ions in molten state.[17] The inconstancy of $K_{11}\cdot K_{13}$ may be due to a similar effect of cations present. In the present study, correlations among observed quantities are found to be as shown in Fig.2 when $1/K_{11}\cdot K_{13}$ was assumed to vary in proportion to the square of V(IV)/V(V). It should be noted that quantities observed on both catalyst samples with ratios $K_2SO_4/V_2O_5=1$ and 2 could be correlated by a common line. The dependence of $1/K_{11}\cdot K_{13}$ values on the ratio [V(IV)]/[V(V)] means the decrease in the stability of $S_2O_7^{2-}$ ions with increasing the ratio. This is presumably due to the polarizing effect of VO^{2+} ions on $S_2O_7^{2-}$ ions. The linear relations in Fig. 2 may be considered to support the view that reaction (13) is in equilibrium, although the ratio [V(IV)]/[V(V)] is introduced as a parameter. The effect of the ratio [V(IV)]/[V(V)] was also taken into account in the examination of equilibrium of reaction (10), but no reasonable correlation could be found between the ratio $[S_2O_7^{2-}]/[SO_4^{2-}]$ and P_{SO_3}.

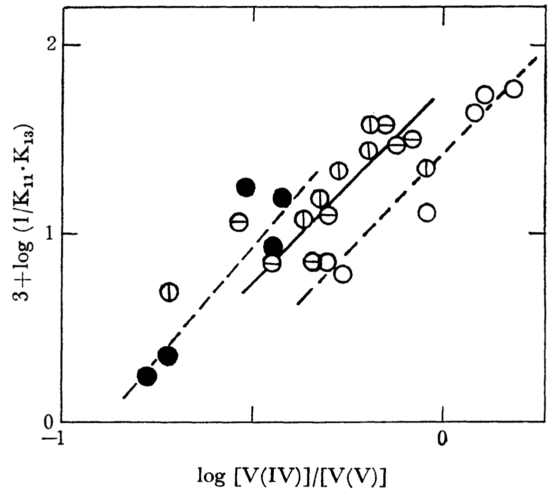

Fig. 2. Dependence of equilibrium constant $1/K_{11}K_{13}$ on the ratio V(IV)/V(V).
○: 500°C, $K_2O/V_2O_5=1$, ⦶: 550°C, $K_2O/V_2O_5=1$, ⊖: 550°C, $K_2O/V_2O_5=2$, ●: 600°C, $K_2O/V_2O_5=1$.

When (SO_3) in the molten catalyst is formed by reactions (8a) to (9b), establishment of equilibrium of reaction (13) means that both reduction and oxidation of vanadiums are in equilibrium as described above. Accordingly, reaction (10) might be considered to be the rate-determining step for sulfur dioxide oxidation with respect to the catalyst at 500—600°C. In this

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[15] J. W. Mellor, "A Comprehensive treatise on Inorganic and Theoretical Chemistry". Vol. IX, Longmans, London. (1960) p. 818.

[16] Although the upper-limit value of V/O_{aq} for catalyst samples with $K_2SO_4/V_2O_5=2$ was in the range 1.9—2.3, VO^{2+} or VO_2^+-forms were assumed in the pyrosulfate determination. A somewhat higher value for the ratio will be due to the relatively higher concentration of sulfate, all of which was assumed to be $S_2O_7^{2-}$ in the calculation.

[17] H. Flood and T. Forland, *Acta Chem. Scand.*, **1**, 781 (1947).

this case, the following expression may be expected for the oxidation.

$$dSO_3/dt = k'[SO_3] = kP_{SO_2}\cdot P_{O_2}^{1/2} \qquad (15)$$

Oxidation Rate of Sulfur Dioxide as a Function of P_{SO_2} *and* P_{O_2}. In order to examine the proceeding conclusion on the reaction mechanism, the rate of SO_2 oxidation was measured at 500, 550, and 600°C on vanadium-potassium catalysts. Conversion of SO_2 is shown as a function of contact time in Fig. 3, where the contact time is expressed in terms of the ratio of weight of catalyst to the flow rate of reaction mixture (g·min/m*l*). The oxidation rates are constant up to almost 10% conversion of SO_2. We determined the oxidation rates as a function of P_{SO_2} and P_{O_2} below 10% conversion of SO_2.

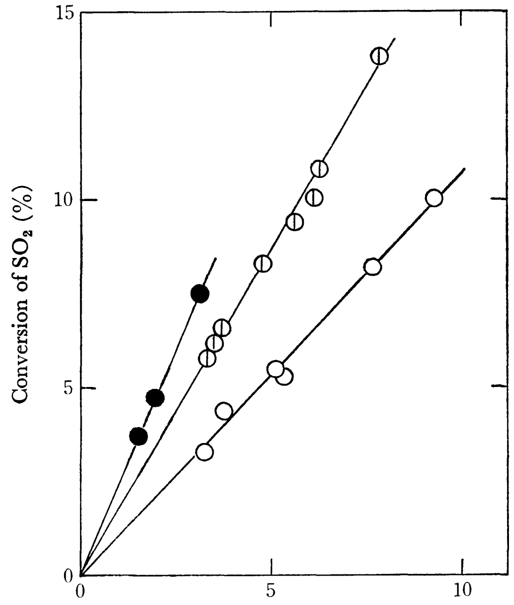

Fig. 3. Conversion of SO_2 as a function of contact time. Catalyst A. Initial gas composition: 10% SO_2, 10% O_2, 80% N_2. ○: 500°C, ⦶: 550°C, ●: 600°C.

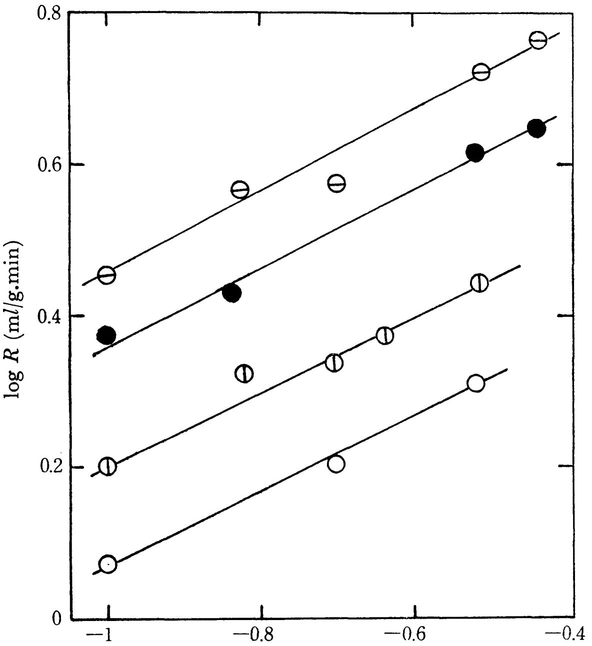

Fig. 4. Influence of the partial pressure of oxygen on the oxidation rate (P_{SO_2}=0.1 atm).
○: 500°C, catalyst A, ⦶: 550°C, catalyst A, ●: 600°C, catalyst A, ⊖: 600°C, catalyst B.

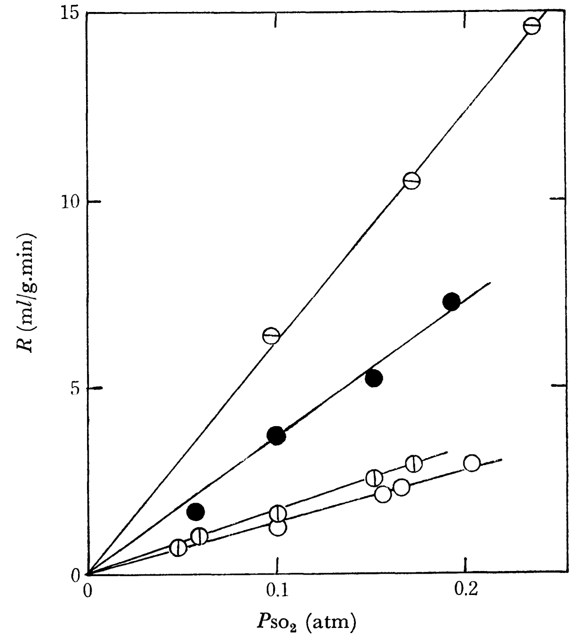

Fig. 5. Influence of the partial pressure of sulfur dioxide on the oxidation rate (P_{O_2}=0.1 atm).
○: 500°C, catalyst A, ⦶: 550°C, catalyst A, ●: 600°C, catalyst A, ⊖: 600°C, catalyst B.

The influence of P_{O_2} on the rate is shown in Fig. 4, where the rate R is expressed in m*l*. SO_3(stp)(*g*-catalyst)$^{-1}$ min^{-1}. All the correlations, at three different temperatures on catalyst A and at only one temperature on catalyst B, gives straight lines with a common slope. From the slope, the values 0.50±0.05 can be obtained for the order of the reaction with respect to oxygen. The influence of P_{SO_2} on the rate is shown is Fig. 5, where the oxidation rate is first order with respect to sulfur dioxide.

In summary, the oxidation rate of sulfur dioxide on vanadium-potassium catalyst at 500, 550, and 600°C fits the rate expression (15), showing that the preceeding reaction mechanism concluded from the compositional consideration of catalysts under SO_2–SO_3–O_2 mixture may be valid.

It should be noted that catalyst B showed higher catalytic activity than catalyst A as seen in Figs. 4 and 5. The concentration of vanadium in catalyst A is 1.5 times larger than that in catalyst B. Since the ratio [V(IV)]/[V(V)] for both catalysts is supported to be close to each other from Table 1 and Fig. 2, concentrations of both V(IV) and V(V) will also be about 1.5 times larger in catalyst A than in catalyst B. If the rate-determining step is either the oxidation of V(IV) or reduction of V(V), the catalytic activity should be higher on catalyst A than on catalyst B. This is not the case in the present study. When the desorption of sulfur trioxide from the molten catalysts is rate-determining, a higher activity may be expected for catalyst B, because the lower concentration of vanadium will give less viscous molten phase and make the desorption of sulfur trioxide from catalyst melt easier. Thus, the higher activity of catalyst B could be taken as another support of the conclusion on the rate-determining step.

Comparison of the Present Kinetics with the Literatures. The present rate expression $R=k P_{SO_2} \cdot P_{O_2}$ for the initial stage of SO_2 oxidation differs from the kinetics found in literature,[8] most of which were measured below 500°C. The difference may perhaps be due to that in the reaction temperatures. The lowering of reaction temperature may give two effects.

One is the variation of reaction mechanism. The temperature dependences of oxidation rate in Figs. 3, 4, and 5 give 6—10 kcal as the activation energy. This value is smaller than those obtained at lower temperatures.[8,9] The difference in activation energy suggests the change of the oxidation mechanism with temperature.

The second is the change in the solubility of vanadium component in the molten catalyst. $V_2O_5 \cdot K_2SO_4$ mixture is not always a homogeneous melt below 500°C. The appearance of precipitates will influence the observed reaction kinetics and activation energy. This is true especially when the rate-determining step consists of the oxidation or reduction of vanadium. The phase diagram of $V_2O_5 \cdot K_2SO_4$ system[6] and the present finding in Table 2 show that the limiting temperature at which the active component of catalyst changes from a homogeneous to a heterogeneous molten phase will depend upon the ratio V_2O_5/K_2O of catalyst and the composition of reacting gas phase. It should be noted that the temperature of the discontinuity in the Arrhenius plot depends on the composition of reaction mixture.[18]

The two effects may be partially responsible for the discrepancies between the present and other works and also for the discontinuity in the Arrhenius plot. To elucidate the reaction mechanism at lower temperatures, it is desirable to investigate the structure of catalyst and oxidation kinetics on catalysts with low V_2O_5/K_2O ratio. A low ratio is necessary to obtain a homogeneous molten catalyst.

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[18] E. V. Gerburt-Geibovich and G. K. Boreskov, *Zh. Fiz. Khim.*, **30**, 1801 (1956).