

The Reduction-Oxidation Mechanism of Sulfur Dioxide Oxidation on Vanadium Catalysts

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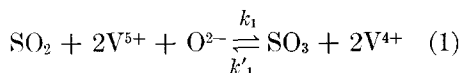
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In continuation of a previous study, it is shown that the oxidation of SO₂ on vanadium catalysts proceeds according to the reduction-oxidation mechanism. The validity of this mechanism has been verified by means of a study of the oxidation rate dependence on the vanadium concentration and kinetic measurements on two different types of industrial catalysts.

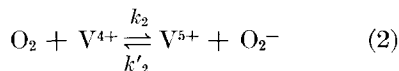
I. INTRODUCTION

From the results of the papers published recently dealing with the study of the kinetics and the mechanism of sulfur dioxide oxidation on vanadium catalysts it follows that the active component of the catalyst forms a liquid phase under the reaction conditions (1-6) and that this reaction occurs according to the reduction-oxidation mechanism (4, 5, 7).

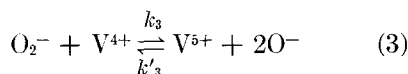
Considering this mechanism we supposed that the oxidation proceeds in two or more consecutive elementary stages. The oxidation proper proceeds by oxygen from the catalyst molecules. The next process consists of supplementing the oxygen bound by the catalyst with oxygen from the gas phase. On the basis of the analysis of the results of our previous measurements (7-9) we can conclude that probable reaction mechanism consists of the following steps (see List of Symbols).



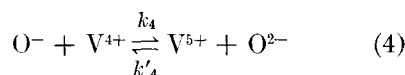
$$K_1 = p_{\text{SO}_2} c_{\text{V}^{5+}}^2 / p_{\text{SO}_3} c_{\text{V}^{4+}}^2 \cdot c_{\text{O}^{2-}} \quad (1a)$$



$$K_2 = c_{\text{V}^{5+}} c_{\text{O}_2^-} / c_{\text{V}^{4+}} p_{\text{O}_2} \quad (2a)$$



$$K_3 = c_{\text{V}^{5+}} c_{\text{O}^{2-}} / c_{\text{V}^{4+}} c_{\text{O}_2^-} \quad (3a)$$



$$K_4 = c_{\text{V}^{5+}} c_{\text{O}_2^-} / c_{\text{O}^-} c_{\text{V}^{4+}} \quad (4a)$$

with the reaction (3) as rate-determining step.

In proposing this mechanism, we started from the results of the measurements of Mars (4). According to them the reaction of sulfur dioxide with the oxidized active component of the catalyst [reaction (1)] is always in equilibrium under experimental conditions.

If the assumptions of Mars—(a) $a_{\text{O}^{2-}}$ is independent of the activity of the other components, and (b) the activity coefficients of V⁴⁺ and V⁵⁺ are equal—are fulfilled, then it is possible to express K_1 by K_M according to the relation $K_1 = K_M / c_{\text{O}^{2-}}$.

The temperature dependence of the equilibrium constant K_M is given by the equation:

$$K_M = 2.3 \times 10^{-8} \exp(27\,200/RT) \quad (5)$$

The mechanism mentioned above is in accord with the kinetic expression

$$r = C_2 \frac{K_M p_{\text{SO}_2} / p_{\text{SO}_3}}{1 + (K_M p_{\text{SO}_2} / p_{\text{SO}_3})^{1/2}} \times \left(p_{\text{O}_2} - \frac{p_{\text{SO}_3}^2}{K_p p_{\text{SO}_2}^2} \right) \quad (6)$$

where $C_2 = k_3 K_2 c_{V,t}$.

In a previous publication (7) we calculated the values of K_M and C_2 from the kinetic data by the least-squares method.

The calculated K_M values were in very good agreement with those measured by Mars. Therefore, in the present publication, we used directly the K_M values given by the Mars Eq. (5).

The aim of the present work was to verify the validity of the reduction-oxidation mechanism formerly proposed based on the study of the dependence of the sulfur dioxide oxidation rate on the total concentration of vanadium in the catalyst. The proposed mechanism has also been tested using kinetic data obtained for two different types of catalysts.

II. LIST OF SYMBOLS

C_2	Overall rate constant (g mole/hr at. mg catalyst)
$c_{V^{+4}}, c_{V^{+5}}$	Concentration of vanadium in oxidation state +4 or +5
$c_{V,t}$	Analytical (total) concentration of vanadium in catalyst
k_i, k'_i	Rate constants of forward and back reactions
K_i	Equilibrium constant of the elementary process
K_p	Equilibrium constant of sulfur dioxide oxidation defined by partial pressures ($\text{atm}^{-1/2}$)
p_i	Partial pressures of species i [atm]
r	Reaction rate (g mole/hr g catalyst)
R	Gas constant (kcal/mole grad)
T	Absolute temperature ($^{\circ}\text{K}$)
y	Conversion

III. EXPERIMENTAL

A differential reactor with gas recirculation was used in the measurements of the oxidation rate. The scheme of the experimental equipment and the description of the method of the measurements has been presented in previous publication (9).

The dependence of the reaction rate on the concentration of vanadium was studied on six model catalysts. The amount of vanadium pentoxide and the mole ratio $\text{K}_2\text{O}/\text{V}_2\text{O}_5$ in the catalysts used are given in Table 1. The support of all the catalysts was kieselguhr.

TABLE 1
COMPOSITION OF THE MODEL CATALYSTS

Catalyst	Vanadium oxide V_2O_5 (% by wt.)	Mole ratio $\text{K}_2\text{O}/\text{V}_2\text{O}_5$
1	1.0	4.0
2	2.0	3.9
3	3.1	3.9
4	5.2	4.0
5	6.3	3.9
6	7.3	4.1

Preparation of catalyst. Finely milled kieselguhr catalyst support was mixed with the calculated quantity of ammonium metavanadate and of potassium bisulfate. After thoroughly mixing both components in the dry state, the mixture was kneaded and granulated. Finally the granules were crumbled into grains with the desired sizes.

Catalyst particles of approx. 0.8 mm in diameter were used in the measurements proper. The influence of transport processes on the oxidation rate was eliminated by this choice of particle size.

In the second part of this study the oxidation rate was measured on the industrial catalyst ICI-33-2. Its active component also contains sodium, unlike catalyst SVD (7-9), and is supported on the silica. Diameters of the catalyst particles were approx. 0.8 mm. For temperatures below 490°C the diffusion does not influence the reaction rate either.

IV. RESULTS AND DISCUSSION

The measured reaction rate values for a composition of the inlet gas of 10% SO_2 , 11% O_2 , 79% N_2 (by volume) are plotted against conversion for the model catalysts in Figs. 1-3 and for the commercial catalyst ICI-33-2 in Fig. 4.

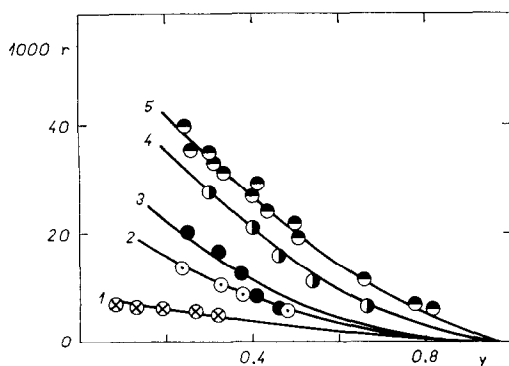


FIG. 1. Dependence of reaction rate r on conversion y at 460°C; concentration of V_2O_5 : 1, 1; 2, 2; 3, 3.1; 4, 5.2; 5, 6.3% by wt.

1. The Influence of the Concentration of Vanadium on the Reaction Rate

In order to investigate the influence of the vanadium concentration on the oxidation rate the measured data have first been correlated with Eq. (6). The calculated average values of the overall rate constant C_2 for single catalysts are summarized in Fig. 5. This figure shows that the experimental points of all three isotherms lie on straight lines starting from origin. Hence, the oxidation rate of sulfur dioxide can be considered (for catalysts containing less than 7% V_2O_5 and of mole ratio $K_2O/V_2O_5 = 4$) as a first order one with respect to

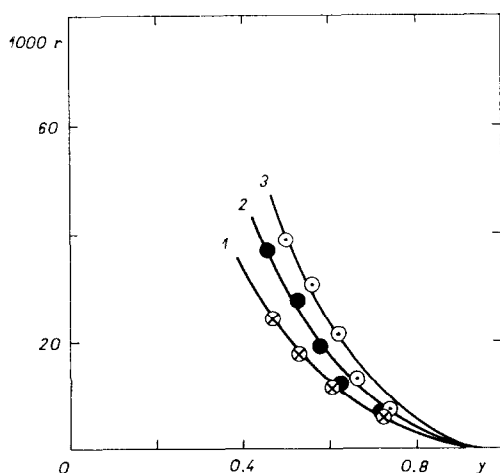


FIG. 2. Dependence of reaction rate r on conversion y at 480°C; concentration of V_2O_5 : 1, 3.1; 2, 5.2; 3, 6.3% by wt.

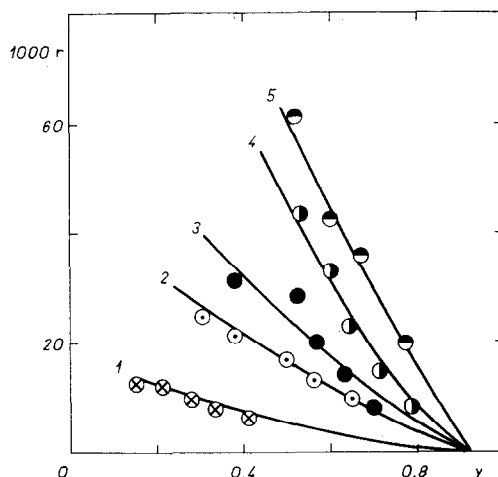


FIG. 3. Dependence of reaction rate r on conversion y at 500°C; concentration of V_2O_5 : 1, 1; 2, 2; 3, 3.1; 4, 5.2; 5, 6.3% by wt.

the total concentration of vanadium in catalyst.

This finding is in agreement with the dependence following from kinetic formula (6), derived on the assumption that oxidation proceeds according to the mechanism mentioned above. The temperature dependence of the overall rate constant C_2 for single measured catalysts is plotted in Fig. 6 ($E = 52$ kcal/mole).

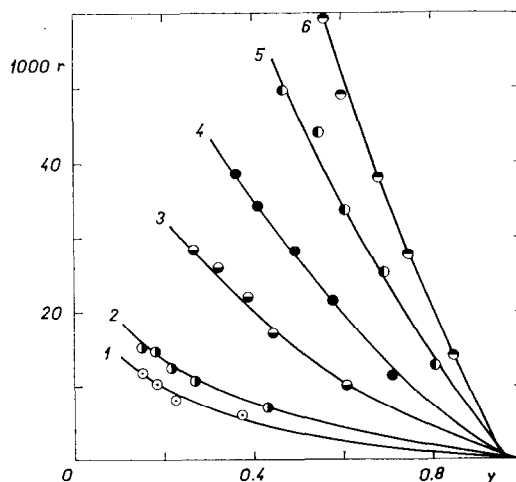


FIG. 4. Dependence of reaction rate r on conversion y for catalyst ICI-33-2; 1, 380°; 2, 400°; 3, 420°; 4, 440°; 5, 460°; 6, 480°C.

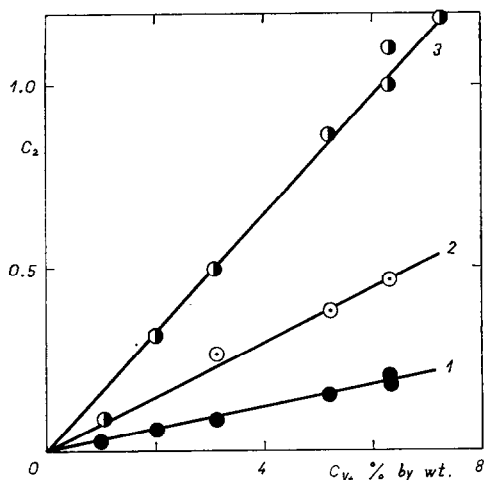


FIG. 5. Dependence of overall rate constant C_2 on concentration of vanadium $c_{v,t}$ (calculated as V_2O_5); 1, 460°; 2, 480°; 3, 500°.

2. Correlation of Data Measured on Two Different Types of Catalysts with Equations Derived for the Reduction-Oxidation Mechanism

The measured reaction rate values for ICI-33-2 catalyst at 380–480°C were correlated with the rate Eq. (6) as well as with Eq. (7) recommended by Mars (5)

$$r = k p_{O_2} \frac{K_M p_{SO_2} / p_{SO_3}}{[1 + (K_M p_{SO_2} / p_{SO_3})^{1/2}]^2} \quad (7)$$

where K_M is expressed by Eq. (5).

From the results of the correlations summarized in Table 2 it follows that Eq. (6) fits experimental data better than Eq. (7). Since our measurements were also

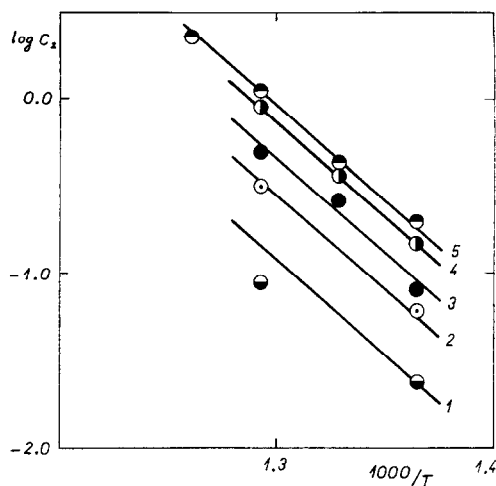
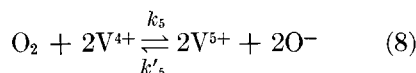
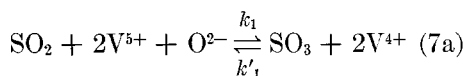


FIG. 6. Dependence of overall rate constant C_2 for catalysts with different contents of V_2O_5 : 1, 1; 2, 2; 3, 3.1; 4, 5.2; 5, 6.3% by wt V_2O_5 .

carried out for high conversions, the different accuracy in fitting of the data by Eqs. (6) and (7) could be explained by the fact that the rate Equation (7) is probably the equation for the forward reaction only. Therefore, in the evaluation of the data according Eq. (7) the backwards reaction was taken into account.

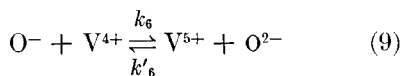
If the following mechanism is assumed:



$$K_5 = k_5/k'_5 = K_2 K_3 \quad (8a)$$

TABLE 2
AVERAGE RATE CONSTANTS C_2 , k , AND C AND MEAN RELATIVE DEVIATIONS, Δ , OF THE CONSTANTS FROM THEIR AVERAGE VALUES

t (°C)	Equation (6)		Equation (7)		Equation (11)	
	C_2	Δ (%)	k	Δ (%)	C	Δ (%)
380°	0.010	6.6	0.103	14.5	0.111	14.5
400°	0.019	5.0	0.153	14.8	0.153	14.8
420°	0.074	4.9	0.349	15.0	0.349	15.0
440°	0.194	4.9	0.631	16.1	0.632	16.1
460°	0.494	4.5	1.165	13.8	1.170	13.4
480°	1.048	4.9	1.980	15.3	2.019	13.6
Average		5.1		15.0		14.6



$$K_6 = c_{V^{5+}}c_{O^{2-}}/c_{V^{4+}}c_{O^-} \quad (9a)$$

and if the reaction (8) is rate-determining, the reaction rate is given by

$$r = k_5c_{V^{4+}}^2p_{O_2} - k'_5c_{V^{5+}}^2c_{O^-}^2 \quad (10)$$

After expressing c_{O^-} from Eqs. (4a) and (9a) and $c_{V^{4+}}$ from (4a), the kinetic equation takes the form

$$r = C \frac{K_M p_{SO_2}/p_{SO_3}}{[1 + (K_M p_{SO_2}/p_{SO_3})^{1/2}]^2} \times \left(p_{O_2} - \frac{p_{SO_3}^2}{K_p^2 p_{SO_2}^2} \right) \quad (11)$$

The average values of the constants C and their mean relative deviations from the average values are also summarized in Table 2. From this table it follows that the constants C and their deviations are practically the same as the values of constant k . Both these constants show a systematic variation with conversion at all measured temperatures (see Table 3). Analogously, this is also true for the constants C and k of the SVD catalyst (7).

The dependence of the overall rate constant C_2 in the plot of $\log C_2$ against $1/T$ (Fig. 7) is described by the straight lines

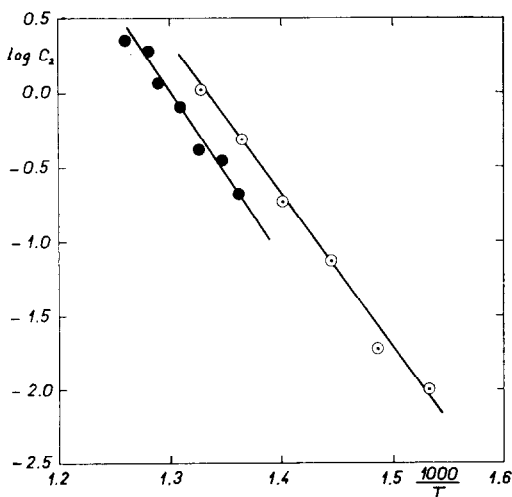


Fig. 7. Dependence of overall rate constant C_2 on temperature: O, catalyst ICI-33-2; ●, catalyst SVD.

TABLE 3
DEPENDENCE OF THE RATE CONSTANTS OF
EQS. (7) AND (11) ON CONVERSION

Temperature (°C)	y	k	C	C_2
380°	0.144	0.131	0.131	0.009
	0.187	0.123	0.123	0.010
	0.228	0.102	0.102	0.009
	0.383	0.087	0.088	0.011
400°	0.145	0.181	0.181	0.017
	0.178	0.180	0.180	0.019
	0.215	0.157	0.157	0.018
	0.267	0.136	0.136	0.018
420°	0.432	0.114	0.114	0.021
	0.267	0.421	0.421	0.072
	0.320	0.414	0.414	0.078
	0.388	0.386	0.386	0.082
440°	0.443	0.315	0.315	0.073
	0.611	0.248	0.248	0.074
	0.248	0.380	0.380	0.062
	0.304	0.385	0.385	0.071
460°	0.374	0.366	0.366	0.076
	0.444	0.316	0.316	0.074
	0.617	0.253	0.253	0.076
	0.360	0.738	0.738	0.185
480°	0.414	0.712	0.712	0.195
	0.496	0.677	0.677	0.208
	0.580	0.595	0.595	0.205
	0.712	0.427	0.428	0.177
460°	0.374	0.786	0.786	0.202
	0.413	0.709	0.709	0.194
	0.496	0.677	0.677	0.208
	0.570	0.573	0.574	0.195
480°	0.708	0.421	0.422	0.173
	0.469	1.326	1.327	0.469
	0.546	1.383	1.385	0.540
	0.606	1.209	1.212	0.508
480°	0.687	1.110	1.116	0.517
	0.804	0.832	0.850	0.459
	0.479	1.382	1.383	0.496
	0.531	1.303	1.305	0.499
480°	0.601	1.186	1.189	0.495
	0.686	1.106	1.111	0.514
	0.799	0.808	0.822	0.441
	0.570	2.483	2.493	1.152
480°	0.610	2.236	2.249	1.085
	0.677	2.074	2.095	1.087
	0.726	1.766	1.796	0.984
	0.847	1.448	1.572	1.001
480°	0.563	2.412	2.421	1.110
	0.601	2.154	2.166	1.035
	0.673	2.039	2.059	1.064
	0.726	1.766	1.796	0.984
480°	0.844	1.422	1.539	0.976

whose slope was calculated by the least-squares method and corresponds to the apparent activation energy $E = 48$ kcal/mole.

For comparison with the values of C_2 for SVD catalyst earlier published (7, 9) these are also plotted in Fig. 7 ($E = 52$ kcal/mole).

Therefore, it can be concluded that the measurements carried out and the results of their correlations can be considered as further evidence for the reduction-oxidation mechanism of sulfur dioxide oxidation previously proposed.

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REFERENCES

1. FRAZER, J. H., AND KIRKPATRICK, W. J., *J. Am. Chem. Soc.* **62**, 1659 (1940).
2. TOPSOE, H. F., AND NIELSEN, A., *Trans. Danish Acad. Tech. Sci.* No. 1, p. 3 (1948).
3. TANDY, G. H., *J. Appl. Chem. (London)* **6**, 68 (1956).
4. MARS, P., AND MAESSEN, J. G. H., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* **1**, 266.
5. MARS, P., AND MAESSEN, J. G. H., *J. Catalysis* **10**, 1 (1968).
6. BAZAROVA, Z. G., BORESKOV, G. K., KEFELI, L. M., KARAKCIEV, L. G., AND OSTANKOVIČ, A. A., *Dokl. Akad. Nauk USSR* **180**, 1132 (1968).
7. REGNER, A., AND ŠIMEČEK, A., *Coll. Czech. Chem. Commun.* **33**, 2540 (1968).
8. ŠIMEČEK, A., MICHÁLEK, J., AND REGNER, A., *Coll. Czech. Chem. Commun.* **33**, 2709 (1968).
9. ŠIMEČEK, A., REGNER, A., AND VOSOLSOBĚ, J., *Coll. Czech. Chem. Commun.* **33**, 2162 (1968).