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Use of Tracers in Study of Catalytic Oxidation of Sulfur Dioxide

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This study describes the employment of ^{35}S and ^{18}O to assess the importance of individual steps in the catalytic oxidation of sulfur dioxide over a commercial vanadium oxide based catalyst. It is found that oxygen adsorption is always the slowest step. Desorption of sulfur trioxide also exerts a significant effect on the overall rate, especially close to equilibrium.

The use of tracers for study of this system has been reviewed by Happel (1972). Experimental studies using a vanadium based catalyst were reported by Happel et al. (1971) employing ^{35}S. Preliminary studies using ^{18}O were reported by Happel et al. (1972). This note presents further data using ^{18}O as well as results with simultaneous tracing with ^{18}O and ^{35}S.

The reactor employed is of the recirculating type (Happel et al., 1971). Feed and product streams are analyzed by chromatography. ^{35}S is determined by scintillation counting and ^{18}O is determined by mass spectroscopy.

The catalyst employed is a commercial vanadium pentoxide type (typical analysis V_2O_5—9.1%; K_2O—10.1 wt. %) supplied by American Cyanamid Company. The pellets were crushed and screened to a size range of 0.35 to 0.71 mm. Previous studies (Happel et al., 1971) indicate that diffusional effects due to particle size are not important at the temperatures employed.

RESULTS

The data are interpreted on the basis of a generalized mechanism which allows for slow steps considered by most previous investigators. With the overall reaction written as $2SO_2 + O_2 = 2SO_3$, the following steps are assumed:

$$\begin{array}{ccc} \text{Step no.} & \text{Partial reaction} & \text{Stoichiometric number, } \nu \\ 1 & O_2 + 2l \underset{v_{-1}}{\overset{v_{+1}}{\rightleftharpoons}} 2\,Ol & 1 \\ 2 & SO_2 + l \underset{v_{-2}}{\overset{v_{+2}}{\rightleftharpoons}} SO_2l & 2 \\ 3 & SO_2l + Ol \underset{v_{-3}}{\overset{v_{+3}}{\rightleftharpoons}} SO_3l + l & 2 \\ 4 & SO_3l \underset{v_{-4}}{\overset{v_{+4}}{\rightleftharpoons}} SO_3 + l & 2 \end{array} \tag{1}$$

The symbol l refers to any site associated with the catalyst that interacts with the chemical species involved to form intermediates. Since the steady state is maintained for the overall reaction being studied by tracing, the amount of each intermediate associated with a given quantity of catalyst remains constant. The velocities $v_{\pm i}$ will also be constant and can be measured by tracers provided that diffusional resistances are not important so that the sites involving intermediates are equally accessible to reacting species. In the case of reactions involving only gases and solids, it is customary to use effectiveness factors to assess the importance of gaseous diffusion and to identify the intermediates as chemisorbed reactants and

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TABLE 1. VELOCITY RATIOS USING ^{18}O TRACER

Run no.	4	7	11	12	13	14	15	16	16*	23	24	23*	24*	25*
Temp.	745	749	749	753	748	748	750	753	753	750	750	750	750	751
Pressure	1.05	1.05	1.04	1.04	1.08	1.08	1.06	1.06	1.06	1.05	1.06	1.05	1.06	1.06
p_{N_2}	0.818	0.823	0.945	0.941	1.038	1.035	1.017	1.015	1.02	1.01	1.02	1.01	1.02	1.02
p_{O_2}	0.200	0.181	0.0585	0.0620	0.0183	0.0192	0.0215	0.0222	0.0222	0.0223	0.0216	0.0223	0.0216	0.0239
p_{SO_2}	0.00320	0.00342	0.00347	0.00430	0.00441	0.00454	0.00414	0.00403	0.00402	0.00579	0.00456	0.00579	0.00456	0.00151
p_{SO_3}	0.0422	0.0417	0.0369	0.0373	0.0145	0.0158	0.0175	0.0189	0.0189	0.0121	0.0136	0.0121	0.0136	0.0120
$V \times 10^7$	4.10	7.17	3.08	3.08	3.98	5.08	5.51	4.55	4.55	3.41	4.05	3.41	4.05	0.606
$(V_+/V_-)^{1,3,4}$	4.45	4.45	2.14	2.14	6.79	6.79	3.52	3.52	3.74	24.8	24.8	24.2	13.6	1.57
$(V_+/V_-)^{2,3,4}$	1.43	1.43	1.36	1.36	1.55	1.55	1.30	1.30	1.52	1.47	1.47	1.39	1.32	1.28
v_{+1}/v_{-1}	4.60	4.10	1.86	2.62	5.09	3.84	4.65	3.44	3.84	15.6	7.43	17.4	9.12	1.90
v_{+2}/v_{-2}	1.48	1.32	1.18	1.66	1.16	0.88	1.72	1.27	1.56	0.92	0.44	1.00	0.89	1.18
v_{+3}/v_{-3}	0.59	0.94	0.96	0.67	1.09	0.94	0.58	0.91	0.81	1.13	2.29	1.02	1.28	0.85
v_{+4}/v_{-4}	1.65	1.16	1.19	1.22	1.22	1.87	1.30	1.12	1.21	1.41	1.46	1.37	1.16	1.27
$(v_{+2}/v_{-2})\,(v_{+3}/v_{-3})$	0.87	1.25	1.14	1.11	1.27	0.83	1.00	1.16	1.26	1.04	1.01	1.02	1.14	1.00
$\exp(-\Delta G/RT)$	9.42	0.38	3.42	4.82	12.2	9.18	7.89	5.84	5.84	33.6	16.0	33.6	16.0	2.36

* ^{35}S tracer used simultaneously.

products. For the SO_2 oxidation reaction studied here, the working condition of the catalyst involves a molten $K_2S_2O_7$-V_2O_5 phase, so that diffusional effects in the liquid must also be considered. Such problems are discussed in a number of recent experimental studies (Livjberg and Villadsen, 1972). A complete description of these phenomena seems complicated since liquid phase diffusion of both catalyst components and reaction components and blocking of pore passages may have to be taken into consideration as well as the conventional gas phase diffusion limitation. The latter can be minimized, as in this study, by use of sufficiently small catalyst granules. Transport of reactants and products within a molten film of salt has been considered by Kenny and Shah (1973). They conclude on the basis of rough estimates that with industrial SO_2 oxidation catalysts liquid diffusional effects could begin to assume importance for films over 10,000 Å in thickness. Calculations indicate film thicknesses of 100-1000 Å for catalysts of the type employed in this study. In other studies (Kadlec et al., 1973) the effect of molten salt is considered in terms of blocking catalyst pores and thus reducing effective gas diffusivity. Such effects, if present, will not introduce complications in data interpretation for sufficiently small particles. Thus, it is believed that interpretation on the basis of sufficient access of reactants and products to the liquid melt so that diffusional effects can be neglected is reasonable in this study. Whether the actual reaction occurs in the liquid phase, or precipitated compounds in the melt (Mastikhin et al., 1970), or at the silica solid is still an open question.

The reaction sequence given in Equation (1) may be drawn schematically as follows to show the holdup of intermediates:

$$\left.\begin{array}{l} O_2 \underset{v_{-1}}{\overset{v_{+1}}{\rightleftharpoons}} Ol \\ \\ \\ SO_2 \underset{v_{-2}}{\overset{v_{+2}}{\rightleftharpoons}} SO_2l \end{array}\right\} \underset{v_{-3}}{\overset{v_{+3}}{\rightleftharpoons}} SO_3l \underset{v_{-4}}{\overset{v_{+4}}{\rightleftharpoons}} SO_3 \qquad (2)$$

The theory for interpretation of data by this model has been developed by Happel et al. (1972, 1973). Atomic transfer of sulfur which is traced by ^{35}S occurs through steps 2, 3, and 4 of Equation (2). Atomic transfer of oxygen, traced by ^{18}O, can occur either through steps 1, 3, and 4 or steps 2, 3, and 4 and is therefore said to occur in a branched path. This makes it more difficult to employ ^{18}O as a tracer.

Velocity ratios in the 2, 3, 4 path can be computed directly by material balances, assuming steady state conditions and employing ^{35}S marking. The forward and reverse overall path velocities determined by tracing are related to the individual step velocities by the following:

$$\frac{V_+^{2,3,4}}{V_-^{2,3,4}} = \frac{v_{+2}\,v_{+3}\,v_{+4}}{v_{-2}\,v_{-3}\,v_{-4}} \qquad (3)$$

To determine $V_+^{1,3,4}/V_-^{1,3,4}$ two methods are available. One may perform two experiments, each at the same overall velocity V but with two different levels of ^{18}O marking. Two simultaneous equations result. They may be solved to obtain $V_+^{1,3,4}/V_-^{1,3,4}$ and v_{+4}/v_{-4}. In the case of the path through steps 1, 3, and 4 a relationship similar to Equation (3) may be written.

$$\frac{V_+^{1,3,4}}{V_-^{1,3,4}} = \frac{v_{+1}\,v_{+3}\,v_{+4}}{v_{-1}\,v_{-3}\,v_{-4}} \qquad (4)$$

A second method for establishing the value of $V_+^{1,3,4}/V_-^{1,3,4}$ is to simultaneously use ^{35}S and ^{18}O in a single experiment. With $V_+^{2,3,4}/V_-^{2,3,4}$ determined from the ^{35}S data, it is possible to solve directly for $V_+^{1,3,4}/V_-^{1,3,4}$ and v_{+4}/v_{-4}.

One additional relationship among the step velocities is necessary to determine the individual ratios. This is obtained from basic assumptions of thermodynamics and transition state theory (Happel, 1972).

$$\exp\frac{-\Delta G}{RT} = \frac{v_{+1}}{v_{-1}}\left(\frac{v_{+2}\,v_{+3}\,v_{+4}}{v_{-2}\,v_{-3}\,v_{-4}}\right)^2 \qquad (5)$$

$\exp(-\Delta G/RT)$ is computed from thermodynamic data for the overall reaction.

These relationships enable the individual step velocities to be determined. Reaction conditions and calculated velocity ratios are presented in Table 1. Further details of data and methods of calculation are given by Rodriguez (1973).

Figure 1 gives a graph of velocity ratios plotted vs. exp $(-\Delta G/RT)$. In this figure steps 2 and 3 are combined and shown as the velocity ratio $(v_{+2}v_{+3})/(v_{-2}v_{-3})$. This product is less sensitive to error because its computation does not require the use of Equation (5). It appears that steps 2 and 3 are close to equilibrium for the test conditions employed. Near equilibrium for the overall reaction the velocity ratios for all steps approach unity. Under all conditions the data show that step 1 (oxygen chemisorption) is the slowest. Step 4 (sulfur trioxide desorption) is also significantly slow as equilibrium for the overall reaction is approached.

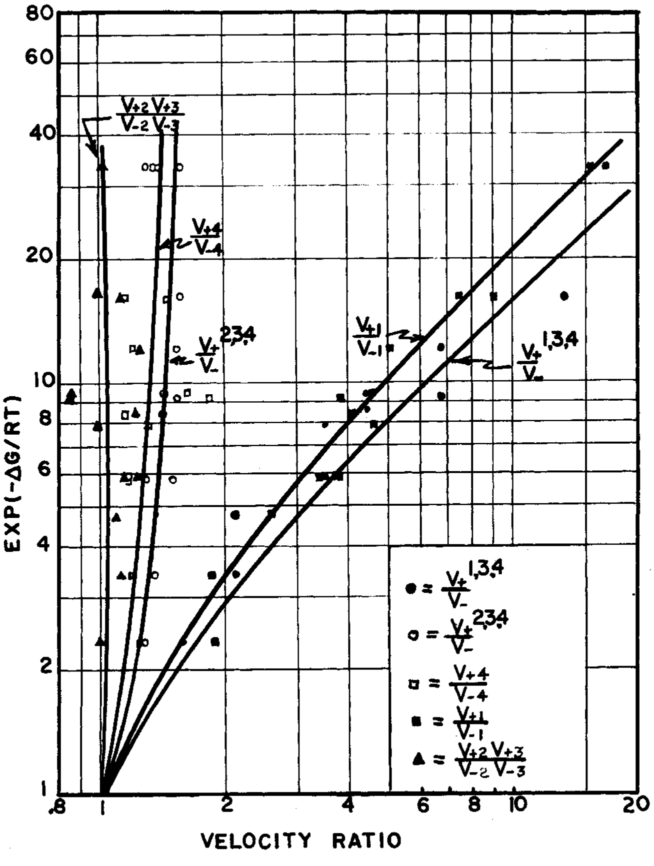
Velocity diagrams of this type are discussed by Happel et al. (1973). Velocity ratios shown in Figure 1 are not necessarily a unique representation because equilibrium can be approached by various systematic changes in partial pressures of terminal species. In the experiments reported here the partial pressure of SO_2 was only varied from approximately 0.003 to 0.005 atm. The major change to approach equilibrium was obtained by employment of increasing ratios of p_{SO_3}/p_{O_2}. It was not possible to trace oxygen accurately at lower partial pressures of SO_2. Even at these fairly low partial pressures of O_2 it appears that the chemisorption of SO_2 is close to equilibrium.

A question which arises in using tracers is whether the tracer follows the same mechanistic path as the overall reaction being studied. Experiments were conducted (Runs 23 and 24) in which double tagging with ^{35}S and ^{18}O were conducted simultaneously with double level ^{18}O experiments. The resulting velocity ratios obtained independently compare favorably with each other providing evidence that ^{18}O and ^{35}S transfer in the same manner in the path following steps 2, 3, and 4.

Experiments were also conducted by Rodriguez (1973) to determine the extent to which ^{35}S and ^{18}O were transferred under reaction conditions (same partial pressures and temperatures as in actual runs) in the apparatus containing only catalyst support. In the case of ^{35}S such transfer is very small. It occurs to a greater extent in the case of ^{18}O, but is still a small fraction of that which occurs under reaction conditions in the presence of catalyst.

DISCUSSION

There have been a large number of studies of the catalytic oxidation of sulfur dioxide in which overall rate data were determined. A recent study by Livjberg and Villadsen (1972) reviews a number of these and presents new data. Some 12 rate expressions are critically examined and shown to predict rates which vary considerably especially when they are applied outside the ranges of the underlying individual experimental studies. There are some characteristic features common to the majority of expressions. Thus the reaction is generally found to be first order in oxygen partial pressure, indicating the probable importance of oxygen adsorption. The influence of SO_2 and SO_3 is more conflicting, but a product inhibition by SO_3 is found in most cases, even far from equilibrium. These findings are consistent with those obtained in the present study using a quite different approach.



This study must be considered only a beginning in establishing the behavior of vanadium catalysts for SO_2 oxidation. Additional studies at different temperatures and partial pressures of reactant gases (including other diluents than nitrogen) will be necessary. The results obtained are sufficient to indicate that this method of tracer study has considerable promise.

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NOTATION

ΔG = Gibbs free energy change
l = active catalyst site; Ol, SO_2l, SO_3l are intermediate species
R = gas constant
T = temperature, K
V = overall reaction velocity, oxygen reacted per unit mass of catalyst per s, kg mol/kg s
v_{+i} = forward reaction velocity of a step, $i = 1, 2, 3, 4$
v_{-i} = backward reaction velocity of a step, $i = 1, 2, 3, 4$
p_i = partial pressure of a species, atm., $i = SO_2, O_2, SO_3$
ν = stoichiometric number, the number of times each elementary step occurs for a single occurrence of the overall reaction as written

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