

Comparison of Kinetic Data for K/V and Cs/V Sulfuric Acid Catalysts

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Intrinsic kinetics of SO₂ oxidation were measured on K/V and Cs/V catalysts to determine the differences for the two catalysts. An external recirculation reactor was used to obtain differential reaction rates as a function of SO₂ and O₂ concentrations, temperatures, and catalyst properties at conversions above 90%. To eliminate effects of the support, an inert controlled pore glass silica supported the active vanadium composition. Experimental results showed significantly higher oxidation activity below 425°C for the Cs/V catalysts than for the K/V catalysts. Catalysts with higher ratios of Cs/V had lower activation energies below 400°C. Distinct breaks in the Arrhenius plots occurred at 425°C for K/V = 3 and at 400°C for Cs/V = 3. The kinetic results indicate that a V⁴⁺ species is crystallizing out of the molten salt solution more readily for the K/V catalyst and for the lower Cs/V ratios. A kinetic model based on a proposed reaction mechanism is shown to fit the kinetic data very well. © 1987 Academic Press, Inc.

INTRODUCTION

Many papers have been published on the oxidation of SO₂ to SO₃ with vanadium catalysts (1). At reaction temperatures the commercial catalyst for sulfuric acid production is a molten salt of V₂O₅ in potassium pyrosulfate dispersed on a silica support. A major problem with the vanadium catalyst is the sudden drop of oxidation activity at operating temperatures below 430°C (2). Since temperatures below 380°C are necessary to achieve greater than 99.5% thermodynamic equilibrium conversions, sulfuric acid plants must absorb SO₃ from the gas before reacting in another catalyst bed to achieve more than 99.5% conversion. This additional absorption of SO₃ is a costly step. As a result, there is great interest in understanding why the vanadium becomes inactive below 420°C.

To explain how the vanadium catalyst oxidizes SO₂, Glueck and Kenney (3) studied unstirred K/V molten salts and proposed a three-step reaction mechanism which included two different V⁴⁺ species. This type of mechanism can show why unsupported melts have a much higher V⁴⁺/

V⁵⁺ ratio than well dispersed melts on supports. By carrying out kinetic studies on the same silica supports with various liquid loadings, the vanadium activity was found to decrease at higher loadings (2). This result was explained in terms of liquid phase diffusion restriction which apart from diminishing the utilization of vanadium may lead to a bulk change in the liquid composition. A thermodynamic theory for formation of clusters in porous bodies imbibed with a fluid was also developed (2). On silica controlled pore glass (CPG) supports, clusters were found to form spontaneously as soon as a certain critical loading was reached. Based on various data in the literature and their own experimental results, Villadsen and Livbjerg (2) indicated that the rate-limiting step appeared to be reoxidation of V⁴⁺ due to very low O₂ uptake by the melt. Formation of clusters adds a further transport restriction to the reoxidation step and must be avoided for the efficient use of the vanadium.

Boreskov *et al.* (4-6) varied the film thickness on various supports for K/V catalysts and found that the effective film thickness of the molten salt decreased with decreasing temperature and increased with increasing conversion. As temperature de-

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creased, Boreskov *et al.* (4) stated that oxygen diffusion into the melt decreased because of an increase in the melt's viscosity and precipitation of V^{4+} compounds from the melt. EPR data (5) confirmed the V^{4+} precipitation and showed that thicker melt films produced V^{4+} precipitation at higher temperatures. Polyakova *et al.* (6) did some calculations for the oxygen diffusion coefficient, and they showed using their rate data that the reaction is limited by the diffusion of dissolved oxygen into the melt. Holroyd and Kenney (7) also suggested from studies on stirred K/V molten salts that the reoxidation reaction for V^{4+} is diffusion controlled.

Several studies (8, 9) have shown that the V^{4+} content of the catalyst is a function of temperature, film thickness and the equilibrium reaction $V^{5+} + SO_2 \rightarrow SO_3 \cdot V^{4+}$. In fact, Boreskov *et al.* (8) claimed with EPR data that the oxidation of V^{4+} is independent of the oxygen content of the gas, but they only studied a catalyst with a thin film in 95% preconverted gas. Grydgaard *et al.* (9) indicated that for a constant temperature and a certain film thickness only SO_2 partial pressure affects the V^{4+} content due to the equilibrium reaction mentioned above. The steady state reaction rate can still be a function of oxygen diffusion into the melt. Boreskov *et al.* (10, 11) showed that an associative reaction mechanism which did not change the valence state of vanadium was possible, and oxidation of $V_2O_5 \cdot SO_2$ was the rate-determining step.

Jensen-Holm (12) used experimental data and a general model of diffusion with reaction in a liquid catalytic film to show that diffusion of oxygen in the melt becomes an important transport restriction below 450°C. The degree of vanadium reduction increased significantly with increasing film thickness when the diffusion model was used. Jensen-Holm (12) compared activities for K/V = 3.5 and Cs/V = 3.5 catalysts and found that above 400°C the cesium catalyst was 30–40% more active. Below 400°C the activation energy increased

abruptly for both low and high liquid loading K/V catalysts. This was not observed for two corresponding Cs/V catalysts. The sharp break on the Arrhenius curve at 400°C for K/V catalysts was blamed on precipitation of a V^{4+} compound (5). The Cs/V catalysts did not appear to precipitate a V^{4+} species at 400°C.

Since the original proposal by Mars and Maessen (13) of a two-step reaction mechanism and their observance of a sharp increase in activation energy at low temperatures, many workers have shown for K/V catalysts that oxygen diffusion affects the rate-limiting step for SO_2 oxidation. In the present study, intrinsic kinetics of SO_2 oxidation were measured on K/V and Cs/V catalysts to determine the differences for the two catalysts. The effects of Cs/V ratios, temperatures and SO_2 and O_2 concentrations upon the kinetics were compared. A simple kinetic model was used to predict the experimental results. A reaction mechanism is proposed for deriving a kinetic model, and the model is used to fit the kinetic data for a Cs/V catalyst.

EXPERIMENTAL METHODS

A recirculation reactor was built to obtain intrinsic kinetic data at conversions greater than 90% in the 350 to 450°C range of interest. A system was designed with a high rate of recirculation to ensure isothermal operation with negligible gradients in the bulk gas phase. Based on 3 to 4 liters/min recirculation, calculations verified that the reactor was truly differential when less than 5 g of catalyst were tested.

The flow diagram of the reactor system is in Fig. 1. The external displacement-type pump had one Teflon-coated Viton diaphragm, Teflon valves, and a 316 stainless-steel body operating at 1725 rpm with a maximum flow rate of 22 standard liters/min. The pump was manufactured by Air Control Inc., Model 08-410-77. The recirculation flow rate was varied by passing a portion of the flow around the reactor while the

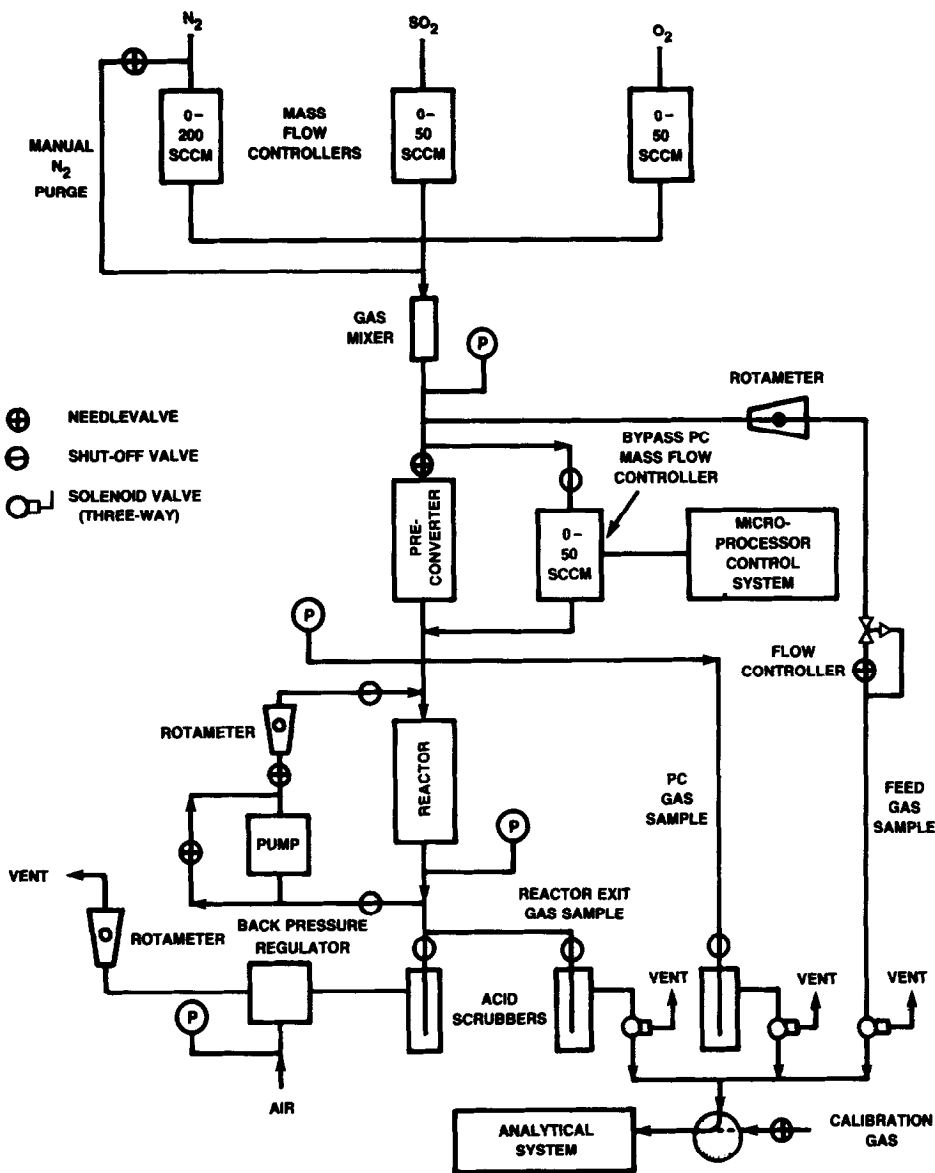


FIG. 1. Recirculation reactor flow diagram.

pump speed remained constant. The portion of the flow that goes through the reactor was measured with a heated rotameter (Matheson No. 604 tube). One problem with the pump was that after 6 weeks of operation, the Teflon cracked from wear and the SO_3 would attack the Viton diaphragm. The pump would begin to leak and the run had to be stopped. As a result, the

pump diaphragm was routinely replaced after every 800 h of operation.

The feed gas system consisted of two dual-channel mass flow controllers made by Brooks (Model 5841). The N_2 stream had a flow range of 0–200 scc/min (standard cubic centimeters at 1 atm and $0^\circ C$) while the O_2 and SO_2 streams had a range of 0–50 scc/min. The SO_2 gas came from a liquid

SO₂ cylinder. A 0–50 scc/min mass flow controller was used for bypassing flow around the preconverter. A gas stream was withdrawn from the feed gas before reaching the preconverter for sample analysis. The feed gas sample flow was kept at 30 scc/min by a Moore flow controller operating by constant downstream pressure.

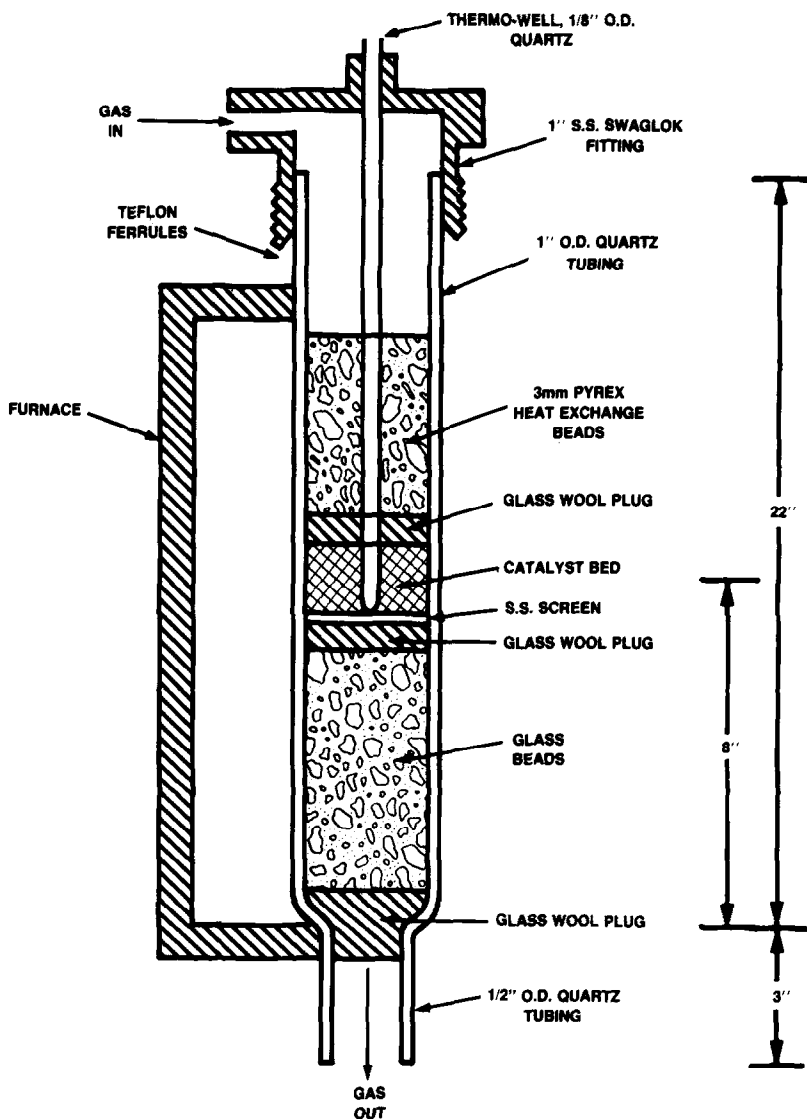
The preconverter was made of Pyrex tubing with a stainless-steel inlet–outlet fitting on top. The inlet gas was preheated by flowing downward through a 3.6-cm-i.d. outer shell. The gas then traveled upward through 60 g of 8–20 mesh commercial catalyst which was contained in a 1.7-cm-i.d. center tube. A 0.3-cm-o.d. Pyrex thermowell containing a type K thermocouple was placed in the center of the preconverter at the bottom of the 1.7-cm-i.d. center tube. The preconverter temperature, printed out by a Digitec Datalogger, was set at 450°C to give 98% conversion of 200 scc/min feed gas. The furnace was a radiant, low-mass type with Johns-Manville marinite construction, fiber frax insulation, and Nichrome wire for heating. The furnace temperature was controlled by a proportional controller.

After the preconverter bypass gas was mixed with the preconverter exit gas, 35–40 scc/min of the gas was sent through an SO₃ scrubber before being analyzed for the amount of preconversion. A volume of 100 to 200 scc/min of the preconverted gas was then mixed with the recirculation gas and fed to a quartz downflow reactor. The reactor furnace and thermocouple were the same as those used in the preconverter. The reactor drawing is shown on Fig. 2. Pyrex heat exchanger beads (0.3 cm) were placed above and below the catalyst bed so that the reaction gas was at a constant temperature in the bed. Three to five grams of 80–120 mesh catalyst was set on 50 and 150 mesh stainless-steel screens which rested on a Pyrex glass wool plug. These screens were necessary to ensure that no catalyst particles passed into the pump where they would damage the diaphragm. The tip of

the quartz thermowell was at the bottom of the bed while the thermocouple was in the center of the 2-cm-deep bed. The thermocouple was calibrated with ice, boiling water, boiling naphthalene (217°C), and boiling anthracene (341°C).

The reactor exit gas then divided and flowed to two SO₃ scrubbers. One scrubber contained about 50 cc of 93% H₂SO₄ which removed the SO₃ from 40 scc/min of gas before flowing to the gas chromatograph (GC). Before entering the GC sample loop, the gas flowed through a 90- μ m mist filter and a 0.16-cm-o.d. by 1-m-long flow capillary. A differential pressure gauge (Orange Research Model 1506 DG-1-4.5, 0–75 cm water range) across the capillary tube gave calibrated flow measurements. A Skinner three-way solenoid valve (Model V55 DA2100, 120 V, ac) either sent the gas to the GC sample loop when actuated or vented it. The preconverter gas had the same flow arrangement. The remainder of the reactor exit gas went through a larger SO₃ scrubber with 250 cc of 93% H₂SO₄, a Moore back-pressure regulator, a Brooks R-2-15-D rotameter and, finally, to a hood exhaust. The regulator was set at 1.0 psig (psi = 6894.8 N/m²) so that a constant flow existed through the flow capillaries for the preconverter and exit analysis gases. All three acid scrubbers had fritted tubes for good dispersion of the gas through the sulfuric acid. A pressure of 1.75 psig was required at the reactor exit to get the gas through the acid scrubber and the flow capillary. At least 1.12 atm (1 atm = 101,325 N/m²) was the minimum pressure in the reactor for kinetic runs. For the small catalyst particles and a 3.5 liter/min recirculation rate, the reactor pressure drop was 2.0 psi.

The gas chromatograph sampled feed gas, preconverter gas, and reactor exit gas with a Hunt Model 6 pneumatic sampling valve. The GC was a Carle Instruments Inc. Model 8700 thermal conductivity cell with two 0.32-cm-o.d. by 2.4-m-long stainless-steel columns packed with Porapak Q-S, a porous polymer bead (80–100 mesh)



1" = 2.54 cm

FIG. 2. Reactor diagram.

made by Waters Associates. The peak areas were integrated by a Columbia Scientific Model CSI-38 digital integrator. Another six-port Hunt valve was installed so that a 20–50 mesh 5A molecular sieve could be bypassed when SO₂ came off the Porapak column. The molecular sieve gave good separation of the O₂ and N₂, and the response factor for O₂ was found to be 0.99.

The reference gas for the response factor was N₂. The SO₂ response factor was 0.61 for 10% SO₂ gas and 0.64 for less than 1% SO₂ gas. The Porapak columns and TC cell were controlled at 80°C.

A Kim I microcomputer manufactured by MOS Technology Inc. was used to automate the six analytical functions and the selection of the six preconverter bypass

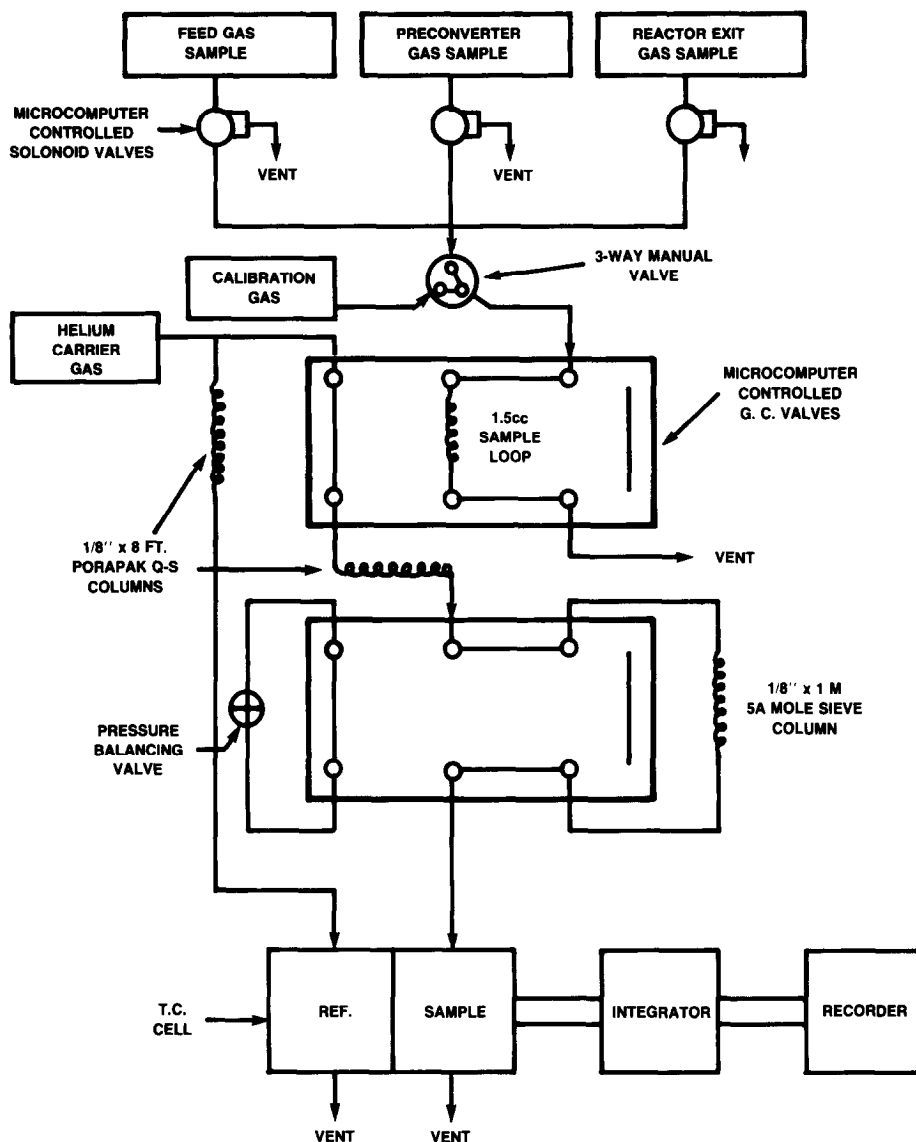


FIG. 3. Recirculation reactor analytical system.

flow rates. Using the binary computer language, the microcomputer was programmed to step through the six different preconversions, remaining at each for 4 h. A block diagram of the control system is shown in Fig. 3. For each gas analysis, the gas sampling valve was actuated for 5 s so that a gas sample could be injected into the helium carrier stream. The gas sampling valve was then shut and the next SO₂ gas

stream purged through the sample loop. The O₂ and the N₂ peaks were integrated during the first 2 min and 45 s. The molecular sieve bypass valve was actuated for 4 min 10 s while the SO₂ was integrated. Then for 3 min both columns were purged with helium. The total analysis time was 10 min for each gas. The peak retention times were 46 s for O₂, 64 s for N₂, and 225–255 s for SO₂. All three gases were analyzed every

half hour, and every 4 h the preconverter bypass setting was automatically changed to a predetermined value.

Six to ten cubic centimeters of catalyst were normally tested in the recirculation reactor. Based on 7 cc of catalyst at a recirculation flow rate of 3.5 liters/min (standard conditions = 1 atm and 0°C), the space velocity was 30000/h. A typical recycle ratio (the fraction of reactor gas recycled by the pump) was 0.95. The catalysts were prepared by impregnation with an excess solution of VOSO_4 and KHSO_4 or Cs_2SO_4 , suction filtering through a medium pore, fritted-glass disk and oven drying overnight at 85°C. The CPG silica support from Electro-Nucleonics had the following properties: 1.06 cc/g pore volume, 8.9 m²/g surface area, 2869-Å mean pore diameter, and 80–120 mesh particle size.

After the catalyst was placed in the reactor, it was activated at 475°C for 4 h in 95% preconverted 10% SO_2 , 11% O_2 feed gas. Then the catalyst was cooled to 325°C for 4 h before heating to 350°C for kinetic measurements. The catalyst was kept at each temperature for 24 h. The temperatures were normally run in the following order: 350, 375, 400, 425, and 450°C. After each 24-h period, the reactor temperature was changed manually, and the sulfuric acid was replaced in the SO_3 scrubbers for the preconverter and reactor exit gases. The vent SO_3 scrubber was changed once a week. At each temperature, the preconverter bypass mass flow controller was automatically reset every four hours to give a lower preconversion. The first setting would give a reactor conversion very close to equilibrium and the last setting would be close to 90% conversion. Reversing the order of conversion at each temperature gave the same kinetic data.

CALCULATION METHODS

The purpose of the recirculation reactor was to obtain reaction rate constants as a function of temperature so that Arrhenius plots could be obtained. Based on the same

kinetic model, different catalysts could then be compared directly by using reaction rate constants. Actual reaction rates were calculated by the following equation:

$$R_g = \frac{F \text{SO}_2 \Delta x}{W_c 60G}. \quad (1)$$

The feed gas flow was calculated by summing the N_2 , SO_2 , and O_2 gas flows and subtracting the feed gas and preconverted gas flows going to the GC for analyses. The feed gas flows were determined by the mass flow controllers. The preconverted gas going to the GC was measured by the pressure differential gauge on the calibrated flow capillary tube. This flow had to be corrected for the loss of SO_3 and O_2 due to the reaction in the preconverter.

The kinetic equation used for this study was developed by Jensen-Holm (12) for conversions above 90% and constant feed gas composition:

$$\text{Rate} = k p\text{SO}_2 \text{in} (1-x)(1 - (B/K_p)^{1/s}) \quad (2)$$

If it is assumed that the rate-determining step takes place just once per mole of SO_2 converted in the overall reaction, $s = 1$. This could occur if the rate-determining step is the reaction of an SO_2 molecule with a vanadium complex, redistribution of charges in a complex, or desorption of SO_3 from a vanadium complex. If absorption of O_2 or attachment of O_2 to a complex is rate determining, the stoichiometric number $s = 0.5$. Thus, two models arise.

Model 1 is based on a stoichiometric number of 1. Since the oxygen content is essentially unchanged for conversions between 90 and 99%, Eq. (2) reduces to the following for Model 1:

$$\text{Rate} = k p\text{SO}_2 \text{in} (x_{\text{eq}} - x)/x_{\text{eq}}. \quad (3)$$

Model 2 is based on a stoichiometric number of 0.5. The equation for Model 2 is

$$\text{Rate} = k p\text{SO}_2 \text{in} (1-x)(1 - (B/K_p)^2). \quad (4)$$

When it is assumed that the oxygen content

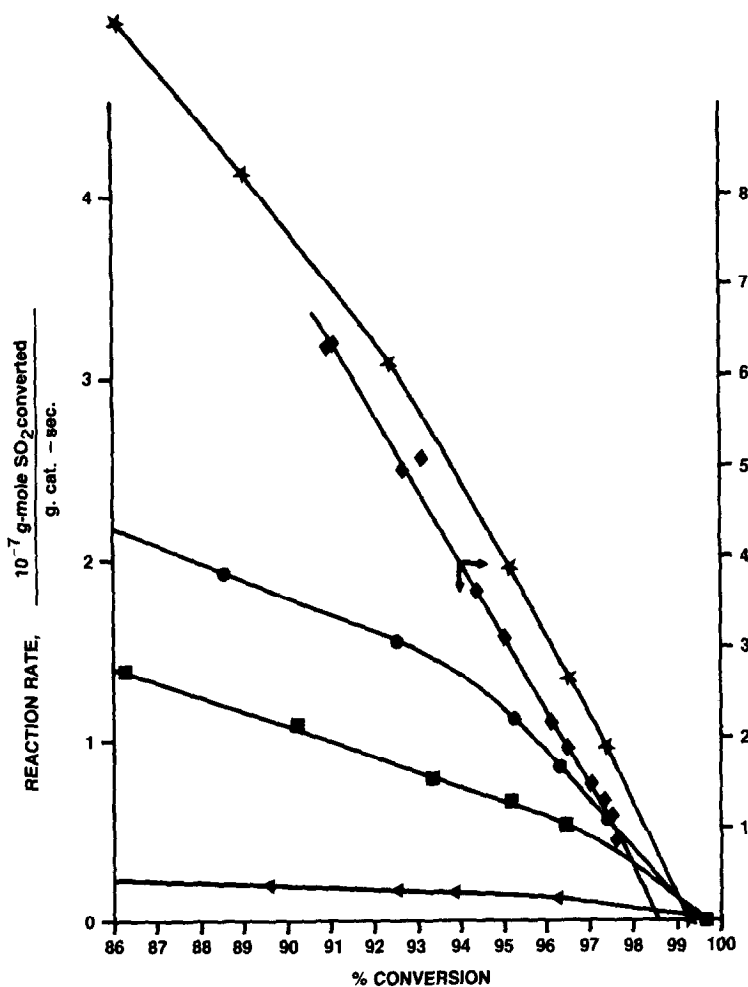


FIG. 4. Cs/V = 3 catalyst kinetics. Feed gas 10% SO₂, 11% O₂, and 79% N₂. Catalyst loading is 0.084 g V/g support, 1383 g catalyst/g-mole V. (◆) *T* = 425°C, (★) *T* = 400°C, (●) *T* = 390°C, (■) *T* = 375°C, (◄) *T* = 350°C. Note: Right-handed ordinate has the same caption as the left-hand ordinate.

remains constant for Model 2, the reaction rate constant can be expressed by

$$k = \frac{\text{Rate}}{p\text{SO}_2 \ln(1-x)(1 - [x(1-x_{\text{eq}})/x_{\text{eq}}(1-x)]^2)} \quad (5)$$

Both models assume that the reaction rate constant contains a term for $p\text{O}_2$ which was kept constant for most of our experiments. If $p\text{O}_2$ in the feed changes drastically, this oxygen dependence in the reaction rate constant must be taken into account.

RESULTS

Comparing *K/V* to *Cs/V*

To compare potassium to cesium at high loadings, two catalysts were prepared and run on the recirculation reactor. The reaction rate data is shown in Fig. 4 for the Cs/V = 3 catalyst. Reproducible data were obtained at 425°C after running at the other temperatures. From 400 to 350°C in Fig. 4, the reaction rate is no longer a linear function of conversion as conversion is decreased. An Arrhenius plot of the data from Fig. 4 based on the Model 1 rate constant is

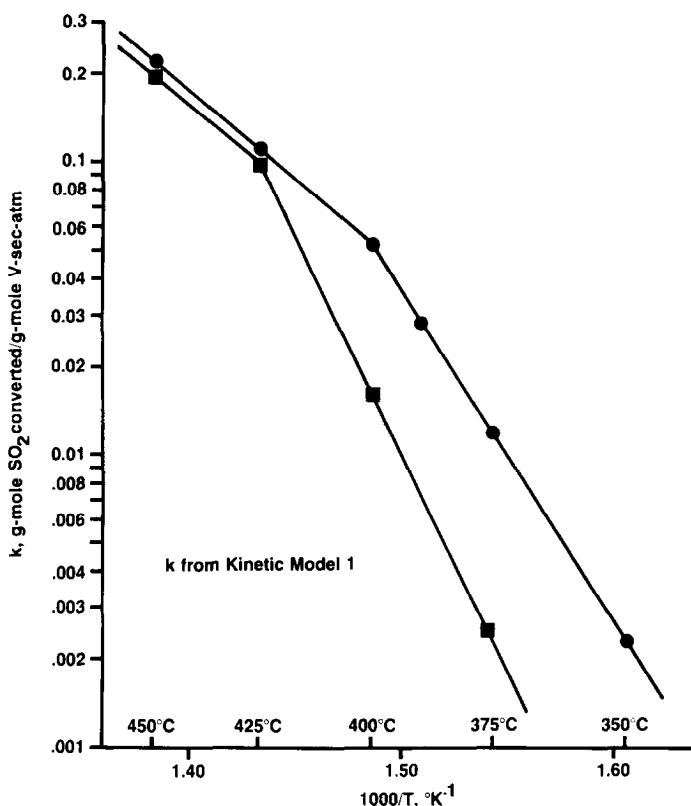


FIG. 5. Cs/V = 3 vs K/V = 3 catalyst kinetics. Feed gas 10% SO₂, 11% O₂, and 79% N₂. (●) Cs/V = 3, 0.084 g V/g support; (■) K/V = 3, 0.078 g V/g support.

shown in Fig. 5 along with the K/V catalyst data. The results show that the Cs/V = 3 catalyst was much more active than the K/V = 3 catalyst at lower temperatures. However, a sharp break in the curve is seen at 400°C for the Cs/V = 3 catalyst which does not agree with the results of Jensen-Holm (12).

Comparing Cs/V Ratios and Loadings

To see what effect the Cs/V ratio would have upon the Arrhenius plots, three catalysts were made with Cs/V ratios of 2.5, 3, and 3.5. Our CPG support had properties very similar to Jensen-Holm's support (12) except that our particle size was 80–120 mesh versus his 20–30 mesh. The kinetic results are given in Fig. 6. The reaction rate constants were calculated by using Model 1 (Eq. (3)). The important finding in

Fig. 6 is that all of the Cs/V catalysts gave breaks in the Arrhenius curves. This is contrary to what was found by Jensen-Holm (12) who reported only a small break in his Arrhenius curves for the Cs/V catalysts.

To determine why our results were different, the Cs/V = 3.5 catalyst with 0.016 g V/g support was activated at 475°C with the pump on. The catalyst was then operated from 450 to 350°C in 10% SO₂, 11% O₂ feed gas at conversions greater than 90%. At 450 and 350°C, a 7 liter/min recycle rate was run the first day and a 3.5 liter/min recycle rate was run the second day. After purging in N₂ for several weeks at 250°C, the catalyst was reactivated at 450°C for 5 h in 95% preconverted gas and then run at 375°C with no recycle rate on the first day, 3.5 liters/min on the second day, and 7 liters/

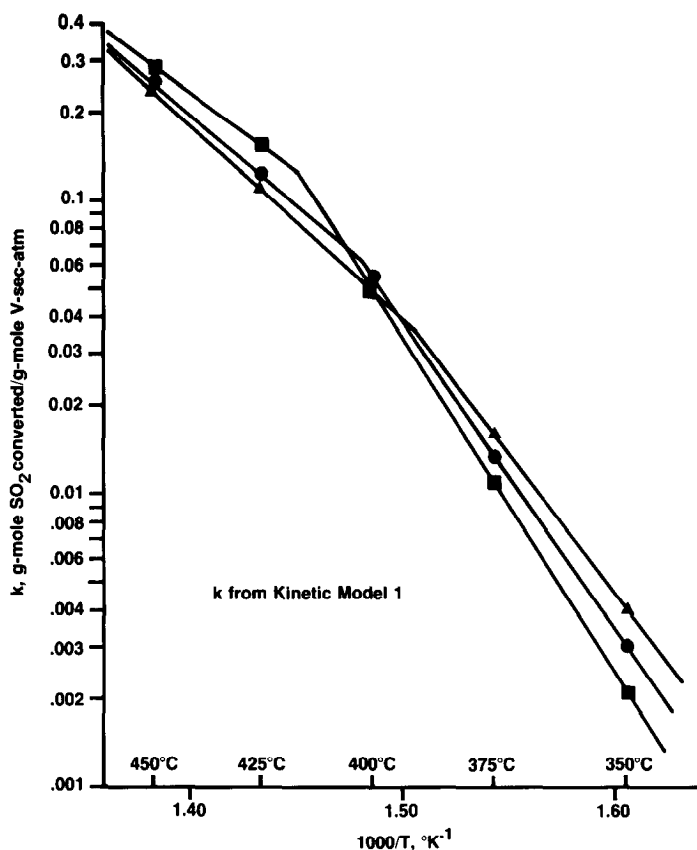


FIG. 6. Comparison of Cs/V ratios. Feed gas 10% SO₂, 11% O₂, and 79% N₂. (▲) Cs/V = 3.5, 0.017 g V/g support; (●) Cs/V = 3, 0.037 g V/g support; (■) Cs/V = 2.5, 0.028 g V/g support.

min on the third day. The Arrhenius plot for this catalyst is in Fig. 7. If only the data for the first day at each temperature (recycle rate = 7 liters/min) is used, the curve is essentially a straight line down to 350°C. However, if the data for the second day at 375 and 350°C are used, a sharp break in the Arrhenius plot at 400°C is evident. At 350°C the reaction rate constant for the second day is one-half that of the first day. The recycle rate has little effect upon the measured reaction rates as shown by the final results at 375°C. There was no change in the reaction rate constant on the second and third days even though the recycle rate had been increased from 3.5 to 7 liters/min. Apparently, an inactive V⁴⁺ or V⁵⁺ species is forming very slowly below 425°C, and it

is evident that much patience is needed to obtain accurate steady state results. Scanning electron microscope photographs showed for this low loading catalyst that clusters of molten salt were present within the support pores. Thus, the results shown in Fig. 7 can be explained by a badly dispersed molten salt in which inactive vanadium species form very slowly. Since Jensen-Holm (12) used an 8% SO₂, 12% O₂ feed gas for his experiments and did not obtain breaks in his Arrhenius plots, our 10% SO₂, 11% O₂ feed gas also may have contributed to our sharp break in the Arrhenius curves.

The effect of the Cs/V ratio upon the oxidation kinetics is shown in Fig. 6 and Table 1. The results show:

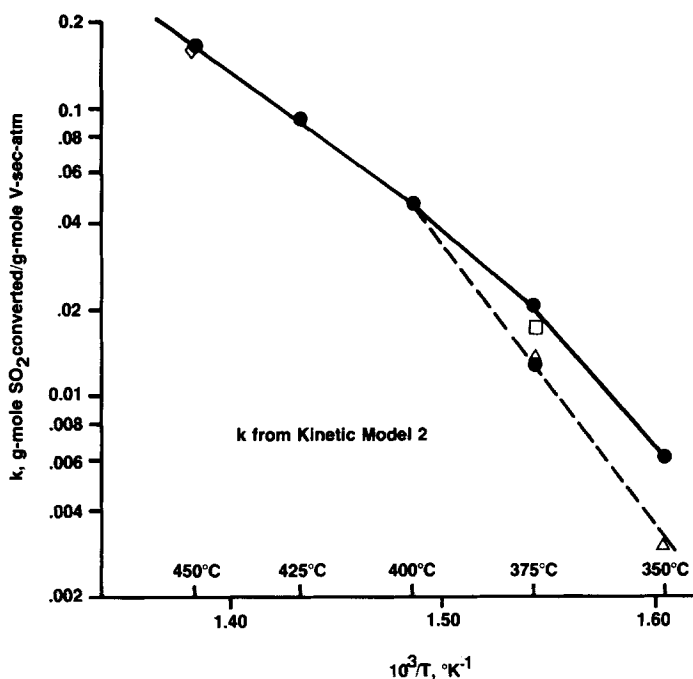


FIG. 7. Kinetics for Cs/V = 3.5 catalyst with varied recycle rates, 0.016 g V/g support. Recycle rate: (●) 7 liters/min, (△) 3.5 liters/min, (□) 0 liters/min.

1. Decreasing the Cs/V ratio from 3.5 to 2.5 increases the activation energies at the lower temperatures.

2. The break in the Arrhenius curves occur at higher temperatures for lower Cs/V ratios.

3. For the Cs/V = 3 catalyst, a higher vanadium loading does decrease specific activity 10% above 400°C and does increase the activation energy 10% below 400°C.

The low temperature activation energy for the K/V = 3 catalyst is 68 kcal/mole (1 cal = 4.184 J), and it is 52 kcal/mole for the Cs/V = 3 catalyst. The results from a future paper will show that the break in the Arrhenius curve occurs because an inactive V^{4+} species begins to form in the solution, and a higher Cs/V ratio decreases the formation of this species in the molten salt.

Kinetic Modeling

A Cs/CPG catalyst similar to the Cs/V = 3 catalyst in Fig. 6 was made to obtain ki-

netics in various feed gas compositions: 7% SO_2 , 8% O_2 ; 7% SO_2 , 15% O_2 ; 10% SO_2 , 11% O_2 ; 13% SO_2 , 8% O_2 ; 13% SO_2 , 15% O_2 . Four or five temperatures between 350 and 450°C were run for each feed gas composition. Five or six conversions above 90% were measured at each temperature.

TABLE 1

Activation Energies for the Cs/V Catalysts

Catalyst	$E1^a$	T_{break}	$E2^b$
Cs/V = 2.5 0.028 g V/g support	25	415°C	52
Cs/V = 3 0.037 g V/g support	28	403	48
Cs/V = 3 0.084 g V/g support	28	400	52
Cs/V = 3.5 0.017 g V/g support	30	390	44

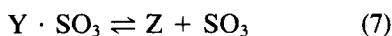
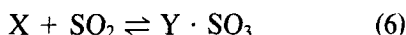
^a Activation energy above T_{break} , kcal/mole.

^b Activation energy below T_{break} , kcal/mole.

TABLE 2
Results of Regression Analyses

Temperature (°C)	A_0	E (cal/mole)	A	C	R^2 (%)
>400	4.4×10^6	24,500	10	11	95.3
350-400	5.1×10^{14}	49,600	3	50	97.6

A three-step reaction mechanism similar to that of Villadsen and Livbjerg (2) is proposed:



X is a V^{5+} compound and Y and Z are V^{4+} compounds. If we assume that Reaction (8) is the rate-limiting step and the reaction is half-order in O_2 , the reaction rate will be

$$\text{Rate} = k_3(Z)(\text{O}_2)^{1/2} - (X)/K_3 \quad (9)$$

where K_3 = equilibrium constant for Reaction (8) and (Z) = catalyst concentration of a V^{4+} compound. If Reactions (6) and (7) are in equilibrium and the vanadium species are substituted with

$$V_t = (X) + (Y \cdot \text{SO}_3) + (Z) \quad (10)$$

the following rate equation can be derived:

Rate =

$$\frac{k p \text{O}_2^{1/2} p \text{SO}_2 (1 - B/K_p)}{p \text{SO}_3 + A p \text{SO}_2 + C p \text{SO}_2 p \text{SO}_3} \quad (11)$$

where $k = A_0 \exp(-E/RT)$. The terms $C = K_1$, $A = K_1 K_2$, and $k = k_3 K_1 K_2$. A nonlinear regression analysis was performed on the kinetic data by using Eq. (11) with four parameters: A_0 , E , A , and C . All of the data were split up into two regions. The high temperature region contained 53 data points above 400°C. The low temperature region covered 64 data points at 350 to 400°C. A nonlinear regression analysis computer program was used to estimate the regression coefficients by a Gauss-Newton iterative process. A correlation coefficient

(R) was squared to show how much the regression model explained the variation about the mean. A correlation coefficient of 100% was perfect. The results of the regression analyses are shown in Table 2. Note that the activation energy above 400°C is one-half that at low temperatures. The correlation coefficients are above 95% indicating Eq. (11) fits the data very well.

DISCUSSION

Numerous experimenters (2, 4, 5, 8, 9, 12) have indicated that the break in the Arrhenius plots for K/V catalysts at the lower operating temperatures is due to precipitation of a V^{4+} complex. As the temperature goes lower, the solubility of this complex decreases and the specific activity of the vanadium drops quickly. A sudden increase in activation energies below 425°C for K/V catalysts can be explained by the V^{4+} precipitation phenomena. Our results could be explained by the fact that the cesium pyrosulfate molten salt decreases the formation of the inactive V^{4+} complex when compared to the potassium salt. Thus, the break on the Arrhenius plot occurs at a lower temperature and the activation energy is lower as shown in Fig. 5. A higher ratio of Cs/V also decreases the inactive V^{4+} formation as shown in Fig. 6. However, we found that the Cs/V catalysts still have breaks in the Arrhenius plots.

An evaluation of the kinetics for a Cs/V catalyst indicates that formation of the V^{4+} complex is very dependent upon SO_2 content of the gas and somewhat dependent upon O_2 content. Allowing the catalysts enough time to attain steady state conditions also is very critical at temperatures under 425°C since formation of the V^{4+} complex is a slow process.

The rate Eq. (11) based on the reaction mechanism [(6)-(8)] does explain our results fairly well. Reaction (6) is the "attack" of SO_2 upon the active V^{5+} compound X and the result is a sulfated V^{4+} compound $Y \cdot \text{SO}_3$. Increasing SO_2 concentration in the gas will increase the

amount of the sulfated V^{4+} by driving Reaction (6) to the right. We believe $Y \cdot SO_3$ is building up in the molten salt solution at the lower temperatures. Reaction (7) must occur to release SO_3 from $Y \cdot SO_3$ to form the active V^{4+} species Z which can be oxidized in Reaction (8) to form X . Increasing SO_3 content in the gas will reverse Reaction (7) to form more $Y \cdot SO_3$. Reducing O_2 content will slow Reaction (8) which will also result in more $Y \cdot SO_3$.

The cesium pyrosulfate molten salt helps the reaction kinetics by keeping Reaction (7) moving toward the right. As catalyst loading is increased in the support, the oxidation of Z in Reaction (8) slows down (due to oxygen diffusion restrictions in thicker metals), and Reaction (7) moves toward the left. More $Y \cdot SO_3$ is formed and the overall reaction rate slows. As a result, higher catalyst loadings will give slightly higher activation energies at low temperatures as seen in Table 1.

The reaction mechanism proposed by Boreskov *et al.* (10) could also explain our Cs/V results. Future papers will discuss how. Since our model predicted the kinetic data for the Cs/V catalyst so well, we believe that the formation of $Y \cdot SO_3$ is very important. The surprising result is that we could take a three-step reaction mechanism, develop a four-parameter kinetic model with this mechanism assuming oxidation of V^{4+} as the rate-limiting step, and fit the kinetic data for the Cs/V catalyst very well. However, this result does not imply that the proposed reaction mechanism is correct. It only indicates that the three-step mechanism develops a kinetic model which predicts our kinetic data well.

CONCLUSIONS

1. The cesium molten salt decreases the formation of the sulfated V^{4+} compound. As a result, the break in the Arrhenius curves will occur at lower temperatures as the Cs/V ratio is increased.

2. As SO_2 concentration is increased, the

effective vanadium catalyst activity drops. This result indicates that vanadium is being reduced according to Reaction (6).

3. A kinetic model based on the proposed reaction mechanism with V^{4+} oxidation as the rate-limiting step fits the Cs/V data very well at conversions above 90%.

4. A large period of time is necessary to form the inactive V^{4+} species at temperatures below 425°C.

APPENDIX: NOMENCLATURE

A_0	preexponential constant for k of Eq. (11)
A, C	parameters of Eq. (11)
B	kinetic parameter = $\rho SO_3 / (\rho SO_2 \rho O_2^{1/2})$
Δx	reactor exit conversion - preconversion
E	activation energy, cal/mole
F	unconverted feed gas flow, scc/min
G	22,413 scc/mole
k	rate constant, mole SO_2 conv./mole V-sec-atm
K_p	equilibrium constant = $10^{(5005/T - 4.743)}$, atm ^{-1/2}
$\rho SO_2, pSO_2,$ etc.	gas phase partial pressures, atm
ρSO_2 in	SO_2 partial pressure in unconv. feed gas, atm
R	gas constant, 1.986 cal/mole-°K
Rate	reaction rate, mole SO_2 conv./mole V-s
R_g	reaction rate, mole SO_2 conv./g cat.-s
s	stoichiometric number for Eq. (2)
SO_2	SO_2 content in unconv. feed gas, mole fraction
T	reaction temperature, °K
V_t	total vanadium content, g V/g support
W_c	weight of catalyst in reactor, g
x	conversion in reactor
x_{eq}	equilibrium conversion

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