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Loss of Activity of Commercial Vanadia SO_2 Oxidation Catalysts during Run-in Period

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A pronounced loss of activity of a Cyanamid "Aero" vanadia catalyst is observed if the catalyst is brought to operating conditions existing at the entrance of a multibed SO_2 oxidation reactor in a stream of diluent. A second industrial catalyst manufactured in Japan exhibits just a small loss in activity under the same conditions. Some of the decrease may be attributed to specific surface area. However, the activity decrease is only about half the loss in surface area. A second process which activates the catalyst seems to occur. This might be reduction of V^{5+} in the catalyst to V^{4+} or an increase in potassium pyrosulfate in the catalyst phase which reduces the catalyst melting point, thereby raising the mobility of molecular species. The activity increase is substantial. If the catalyst is brought to temperature in the presence of air, the catalyst activity actually increases.

INTRODUCTION

Vanadia catalysts now used in sulfuric acid production exhibit remarkably long lifetimes. Some installations have operated on the same catalyst load for a decade. Catalyst activity changes little over periods of years and it appears that it is mechanical deterioration of the catalyst that eventually leads to its replacement. Yet, in laboratory experiments a precipitous loss in activity occurs when the catalyst is placed on-stream (*1*). This early activity loss has not been mentioned in descriptions of the operation of commercial SO_2 oxidation reactions although such an oversight is not surprising since the activity change would occur in the start up period and might therefore remain undetected.

The purpose of our study was to identify the source of this initial activity loss in the hope that an understanding of the causes could lead to means of attaining higher catalyst activity throughout the catalyst life. It was *not* the intent of the study to explore the mechanism of the activity loss, so the experiments undertaken were not designed to this end.

EXPERIMENTAL WORK

Most of the studies were made with an Aero SA potassium oxide-promoted vanadia catalyst marketed by Cyanamid of Canada (*2*). The catalyst is furnished as 9.1% by weight V_2O_5 on a diatomaceous silica support. Potassium as the oxide accounts for 10.1% by weight while the iron is 0.45 wt%. Additional work was undertaken with a catalyst produced by the Japan Catalytic Chemical Industry (Nippon Shokubai Kagaku Kogyo Co., Ltd. or NSKK). This catalyst is reported to be 7.5% by weight V_2O_5, 10.8 wt% SO_3 and 11.1 wt% K_2O. The alumina content is 3.0% (*3*). Again, the support is diatomaceous earth.

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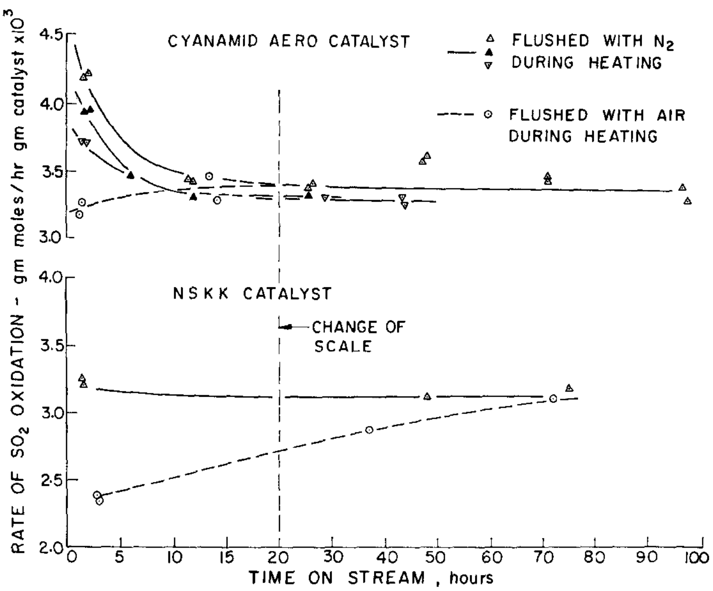

FIG. 1. Change of commercial vanadia catalyst activity vs time.

Measurement of Catalyst Activity

Catalyst activity was measured with a crushed sample, collected between 20 and 30 US mesh screens. The sample was dried in air at 110°C for 10 hr. A differential reactor fabricated from 0.25-in. o.d., 316 steel tubing was used (*4*). It was charged with about 2.5 g of catalyst, held in the middle of a fluidizing sand bath (Cole-Parmer Inc., Chicago) having a uniform temperature (±0.5°C).

The catalyst sample was brought to run temperature, usually 404°C, in either a water-free nitrogen or an air purge. After about 0.5 hr, 12 mole% SO_2 in air replaced the nitrogen or air stream. These oxidation conditions are comparable to those encountered at the entrance to the first bed of a commercial reactor. Run length was usually 100 hr; some runs of 30–50 hr were used and one run with the NSKK sample lasted 300 hr. Conversion to sulfur trioxide ranged between 7.5 and 9.7% based on SO_2. Contact times were about 0.2 sec, at pressures of about 1.5 atm, and at feed-rates of about 0.91 g moles/hr.

The analysis method for SO_2 and SO_3 in the product was similar to that developed by Yeramian *et al.* (*1*) and is detailed elsewhere (*4*).

About a 20% loss of the initial activity was observed over a 100 hr run when the catalyst was brought to the operating temperature in a nitrogen atmosphere. As Fig. 1 shows, replicate runs carried out over shorter periods of time confirm the loss of activity. If, however, air is passed through the reactor as it is brought to operating temperature, the Aero catalyst data suggest either a slight (ca. 5%) increase or no change in activity. After about 10 hr, Fig. 1 indicates that the catalyst activity becomes the same regardless of the atmosphere in which the catalyst is heated. Initially, the activity is lower if air is used in place of nitrogen as the purge when the catalyst sample is heated to 400°C.

Fewer runs were made with the NSKK catalyst; nonetheless, the trends observed with the Cyanamid Aero catalyst are evident. An increase in catalyst activity is observed if an air purge is used during heating; a small but still perceivable activity decrease takes place if N_2 is used. Eventually, the catalyst activity reaches the same level regardless of the purge used. Measurements of rate changes with the NSKK catalyst at 500 and 600°C, temperatures akin to those usually found in the upper sections of the first beds of commercial SO_2 oxidation reactors, showed no significant change with time on-stream when the catalyst was brought to temperature in an air atmosphere (*4*). These runs are not shown in Fig. 1.

Although the NSKK catalyst did not exhibit the sharp loss of activity seen with the Cyanamid catalyst, its run-in activity is up to 10% less than that of the Aero catalyst at 400°C. The catalyst composition, surface area, support of the two catalysts are sufficiently alike that the difference in behâvior seems attributable to manufacturing procedures.

Wells, commenting on a paper by Mars and Maessen (*5*), mentions and activity increases in commercial vanadia catalysts during the first 8 hr on-stream.

DEGREE OF VANADIUM OXIDATION

To test the possibility that the change in catalyst activity might be attributable to the valence of vanadium in the catalyst, color of the catalyst was observed by making separate runs with small amounts of catalyst to simulate portions of the run-in period. It has been known for some time (*6*) that oxides corresponding to different vanadium valences have quite different colors.

The Aero catalyst is obtained from Cyanamid as greenish yellow cylindrical pellets. On crushing, the greenish yellow color is retained. The color also persists when the catalyst is brought to a temperature of about 400°C in a stream of pure nitrogen. However, when the SO_2–air mixture is introduced at 400°C the color lightens to a yellowish green. The color change occurs within minutes and no further change in color is observed in the first 10-hr on-stream. It was noticed that when the catalyst was cooled to ambient temperature in a stream of nitrogen the color became a greyish green.

TABLE 1

Catalyst Color Observations

Condition (°C)	45 wt% V_2O_5 55 wt% K_2O	Mixture on diatomaceous earth support	Aero/NSKK catalysts
Air, 400	Light brown, translucent	Brown	Brown
SO_2, 400	Purplish black, opaque	Greenish yellow	Greenish yellow

The NSKK catalyst is received from the manufacturer as brown tinted pellets. On exposure to the air–SO_2 reactant mixture the color changes to become similar to that observed for the Cyanamid catalyst in the same environment.

To interpret the color changes observed, the catalyst phase composition was duplicated by dissolving vanadium pentoxide in a potassium hydroxide solution, evaporating the solution to dryness and then bringing the crystals to about 400°C in the presence of air or SO_2. To explore the influence of the catalyst support on the color change, a separate batch of catalysts was prepared and impregnated onto diatomaceous earth by soaking the support in the potassium hydroxide solution of vanadia for several hours. The saturated support was then dried and brought to reactant conditions once the procedure with catalyst alone was duplicated. Finally, samples of both the Aero and NSKK catalyst were exposed to first air and then SO_2 at 400°C. Table 1 reports the colors observed.

In addition to color change, it was observed that unsupported catalyst remained granular when heated to well above 400°C in the presence of air. A mixture of K_2SO_4 and V_2O_5 fused into a single phase only at 450°C. In the presence of pure SO_2, however, the unsupported catalyst was observed to soften and fuse.

TABLE 2

Composition–Color Relationships

System	Color	Vanadium valence	Observer
V_2O_5	Reddish-yellow	+5	Weiss *et al.* (*6*)
$K_2SO_4 \cdot V_2O_5$	Brown-olive	95% +5	Bazarova *et al.* (*7*)
2.5 $K_2S_2O_7 \cdot V_2O_5$	Dark brown	+5	Tandy (*8*)
Alkali promoted vanadia catalysts	Brown	+5	Topsøe and Nielsen (*9*)
V_2O_4	Bright blue	+4	Weiss *et al.* (*6*)
K_2O–V_2O_5–SO_3 melt	Green	+4	Glueck and Kenney (*10*)
Alkali promoted vanadia catalysts on silica support	Bluish green	Between +4 and +5	Topsøe and Nielsen (*9*)
Alkali promoted vanadia catalysts on silica support in presence of SO_3	Yellow	Between +4 and +5	Topsøe and Nielsen (*9*)
V_2O_3	Black	+3	Weiss *et al.* (*6*)

The widespread use of potassium oxide-promoted vanadia catalysts has caused extensive investigation of the $(V_2O_5)_m$-$(K_2SO_4)_n(SO_3)_p$ system thought to be the composition of the active catalyst. Tables 2 and 3 summarize the color and melting point observations in the literature.

Since the catalyst was prepared for the observations given in Table 1 from vanadium pentoxide and no color change was observed when the substance was exposed to air at high temperatures, the brown color observed in both the Aero and NSKK catalysts when they are exposed to air corresponds to V^{5+}. The greenish yellow color found when the commerical catalysts are exposed to SO_2 is more difficult to interpret. The greenish yellow color appears to correspond to mixture of V^{4+} and V^{5+} compounds. The free energy change for the reduction of V_2O_5 to V_2O_4 by SO_2 is +58.4 kJ/mole of the pentoxide at 400°C. No doubt the presence of potassium and sulfate influences this increase; however, thermodynamic data to calculate the actual change are simply not available. Tandy (*8*) resorts to reduction with SO_2 at high temperatures to obtain V^{4+}; thus, eliminating the V^{5+} state with a SO_2, CO or H_2 purge at 400°C is probably not pos-

TABLE 3

Melting Point–Composition Relationships

System	Melting point (°C)	Observer
2.5 $K_2S_2O_7 \cdot V_2O_5$	ca. 400	Tandy (*8*)
$K_2SO_4 \cdot V_2O_5$ (equimolar)	478	Bazarova *et al.* (*7*)
K_2SO_4–V_2O_5	mp–composition diagram determined[a]	Bazarova *et al.* (*7*)
$K_2S_2O_7$–V_2O_5	mp–composition diagram determined[b]	Bazarova *et al.* (*7*)
Alkali promoted vanadia	ca. 450	Topsøe and Nielsen (*9*)
K_2O–V_2O_5–SO_3	440	Wells commenting on a paper by Mars and Maessen (*5*)
$K_2S_2O_7$–V_2O_5	mp–composition diagram determined[c]	Holroyd (*11*)

[a] Eutectic mp at 430°C at ca. 70% K_2SO_4; mp of K_2SO_4 is 585°C.

[b] Eutectic mp at 230°C at ca. 55% $K_2S_2O_7$.

[c] Compounds corresponding to 1.25 $K_2S_2O_7 \cdot V_2O_5$ detected melting at 380°C and to 6 $K_2S_2O_7 \cdot V_2O_5$ melting at 330°C; $K_2S_2O_7$ melts at 415°C.

sible. Reduction of V_2O_4 to V_2O_3 by SO_2 is even less favorable; the free energy change at 400°C is positive and +125 kJ/mole. Mars and Maessen (*5*) suggest V^{3+} is not formed in the SO_2–O_2–V_2O_5 system. Topsøe and Nielsen (*9*) associate the green color in potassium-promoted vanadia catalyst with a vanadium valence between +4 and +5, but claim a yellow color appears in the presence of high SO_3 levels, that is, when the potassium pyrosulfate would be found.

We conclude from the color change observations that the Cyanamid catalyst is supplied as a sulfate compound containing both V^{4+} and V^{5+}, and potassium as a mixture of $K_2S_2O_7$ and K_2SO_4. On exposure to the reactant mixture some reduction occurs. The change of color to greyish green when the catalyst is purged with nitrogen and cooled suggests that SO_3 may be stripped from the catalyst. It probably comes from decomposition of $K_2S_2O_7$. By contrast, the NSKK catalyst would appear to be supplied with vanadium as V^{5+}.

SURFACE AREA CHANGE

Surface areas and pore volumes of fresh and used catalysts were measured by the standard volumetric (BET) procedure employing argon in place of nitrogen because of the low specific surface area of the catalysts. Argon absorption isotherms were obtained with both 1.8 and 9 g of catalyst; nitrogen was also used with the larger sample. Differences of well under 10% indicated that satisfactory measurements could be obtained with under 2 g of catalyst sample, the size subsequently used in the study. Both the classical BET procedure and the method of Dollimore–Heal (*12*) were used to determine surface area. Both methods gave areas within better than 15% of each other. Macropore volumes were determined by mercury porosimetry. Details of the measurements are described elsewhere (*4*).

The results of the pore surface and volume measurements are shown in Table 4 for the Aero catalyst and in Table 5 for the NSKK catalyst. Data for the Aero catalysts are more complete. These show a 37% loss in BET surface area after 100 hr on-stream. The loss of micropore surface area as measured by the Dollimore–Heal method is 51%. The concomitant loss in micropore volume suggests that the surface area loss arises from the disappearance of micropore volume and not simply from

TABLE 4

Decrease in Aero SA Catalyst Surface Area and Pore Volume

	Surface area (m^2/g)		Vol (ml/g)	
	BET	Micropore	Micropore[a]	Macropore[b]
Fresh catalyst	0.899	1.03	1.034	0.468
Catalyst heated to 400°C and held for 10 hr	0.699	0.772	0.738	0.428
Catalyst on-stream for 100 hr	0.440	0.376	0.405	0.489
Loss (%) during heating without reactants in N_2 stream	22	25	29	8.5
Loss (%) during time on-stream assuming loss during heating	37	51	45	−14
Loss (%) during on-stream period assuming no loss in heating	51	63	61	−4.5

[a] Volume of pores of radii less than 20 nm.

[b] Volume of pores of radii greater than 20 nm.

TABLE 5

Decrease in NSKK Catalyst Surface Area and Pore Volume

	Surface area (m^2/g)		Vol (ml/g)	
	BET	Micropore	Micropore	Macropore
Fresh catalyst	1.07	1.21	1.17	0.550
Catalyst on-stream for 100 hr	0.672	1.03	0.884	0.505
Loss (%) during time on-stream	37	15	25	8.2

surface realignment. The macropore volume change is small and may not be significant.

Table 4 also shows a smaller loss of surface area and micropore volume if the catalyst is just brought to 400°C without exposure to the reactants. For these measurements, fresh catalyst samples were held at 400°C for about 10 hr in the presence of nitrogen.

Interpretation of Table 4 draws on Table 3 which indicates the existence of potassium vanadium sulfates and pyrosulfates melting between 230 and 500°C. Probably the catalyst phase softens when the catalyst is brought to 400°C permitting flow to occur, smoothing the surface and perhaps closing off micropores. Sulfur is removed during heating, probably as SO_3, causing a shift in the phase towards the oxides which have higher melting points than sulfates. We reason then that the melting point of the catalyst rises during heating, hardening the catalyst phase and limiting, thereby, the potential decrease in micropores. When the catalyst is exposed to the reactant mixture, the flow of the catalyst phase sets in again because the SO_3 produced reacts with the catalyst phase shifting the composition toward the lower melting sulfates. Holroyd's data (*11*) suggest that a pyrosulfate $(S_2O_7)^{2-}$ may be formed. The compound $K_2V(S_2O_7)_3$ has a melting point of 230°C. Consequently, further reduction of micropore volume and surface is observed.

However, in the activity measurements, the time required to bring the catalyst to temperature is only about 0.5 hr in contrast to the 10 hr period taken for the measurement of surface area loss on heating. Thus, probably little surface loss occurs initially. We believe, therefore, that the loss of BET surface area over the initial 10 hr on-stream will be closer to 50% than the 37% shown in Table 4.

The NSKK catalyst is furnished with vanadium as V^{5+} and only partially sulfated. The melting points of V^{5+} compounds appear to be higher than those observed for V^{4+} compounds. We conclude that there is negligible loss of surface area in the short heating period before reactants are introduced. The loss of surface area over the first 100 hr, then, is that shown in Table 5 or about half that observed for the Aero catalyst.

The loss of catalyst surface area established in Table 4 undoubtedly contributes to the reduction in catalyst activity shown in Fig. 1. Catalyst activity and specific surface are both measured per unit mass of catalyst. However, the loss of activity is less than half the estimated loss of surface area. Application of the criteria proposed by Hudgins (*13*) to the measured rates indicates that the rates were free of film and intraparticle mass transfer interferences. Measurements by Yeramian *et al.* (*1*) on the Aero catalyst at higher temperatures confirm that SO_2 oxidation is kinetically controlled. In a similar way, with criteria proposed by Mears (*14*) and Weisz and Hicks (*15*), it was demonstrated that the catalyst particle was isothermal.

The temperature difference between the reactants and catalyst was found to be negligible and furthermore the reactor was shown to be isothermal (*4*). The point of these calculations is to establish that the measurements were made under kinetic, not transport, control. Consequently, the rate of reaction should have been proportional to the surface area. If only loss of surface area occurred, the activity loss expected should have been more than twice that actually observed.

SEM EXAMINATION

Scanning electron micrographs were made of the crushed fresh catalyst, catalyst support and catalysts removed after a 100 hr on-stream, using a Cambridge Mark IIA stereo scanner electron microscope operating at 20 kV. It was hoped by this means to determine any surface changes resulting from placing the catalyst on-stream.

SEM micrographs at 6000 X magnification for the used and fresh catalyst show that the NSKK and Aero catalysts are similar in appearance. The changes between new and used catalysts are quite subtle making it impossible to tell by examination of a photomicrograph whether it was taken with fresh or used catalysts. Nonetheless, observation of a large number of photomicrographs show smoothing and suggests that the catalyst phase is at least softening when the catalyst is brought on-stream, and perhaps some flow is occurring. It is surprising in view of the fairly large changes in surface area that so little change was observed in the photographs.

TABLE 6

Sulfur Content of Catalysts[a]

	Aero SA	NSKK
Fresh catalyst	12.7	7.5
Catalyst heated to 400°C in N_2 and held for 10 hr	11.9	
Catalyst on-stream for 100 hr	14.0	9.4
Change (%) in SO_3 content during time on-stream	+18	+25
Change in SO_3 content on heating	−6	

[a] g SO_3/100 g-catalyst.

CHANGE IN CATALYST COMPOSITION

Total sulfur in fresh, heated and used catalyst was measured by a gravimetric technique. No attempt was made to distinguish between adsorbed sulfur (as either SO_2 or SO_3) or between the dioxide and the trioxide because of the difficulty of interpreting measurements. It is conjectured (*5*) that an equilibria between SO_2–SO_3 and the catalyst phase exists.

Catalyst samples ranging from 0.7 to 2 g were contacted with a stoichiometric excess of 5 wt% hydrogen peroxide solution. The solution was left to stand with mild mixing for a period of 3 days whereupon it was mixed with concentrated hydrochloric acid. The sulfate content of the solution was then measured by precipitation with barium chloride, employing the procedure given by Kolthoff and Sandell (*16*). Measurements were quite reproducible and are summarized in Table 6.

Vanadium content was measured spectrophotometrically. The catalyst samples were contacted with a concentrated mixture of Hcl, HNO_3, and H_2SO_4. The suspension obtained was then diluted, heated and let stand for 1 day with gentle mixing. The heating and mixing procedure was repeated for another day and the resulting suspension was filtered. The vanadium content in the filtrate was measured in a Perkin–Elmer Model 803 atomic absorption spectrophotometer using a 3184 Å lamp. Details of the procedure are given elsewhere (*4*).

The vanadium content for the Aero catalyst was 9.1 wt% (dry) agreeing exactly with the content given by the manufacturer. No change in the vanadium content was detected for samples which had been held at 400°C for 10 hr or which had been on-stream for 100 hr. These results are what would be expected from the low volatilities of the vanadium oxides and sulfates.

The vanadium content of the NSKK catalyst at 9.4 wt% differed significantly from that given by the manufacturer. Essentially no change in the vanadium content occurred after 100 hr on-stream.

Using these data, the fresh Aero catalyst has the nominal composition $2K_2O \cdot V_2O_5 \cdot 3SO_3$. In view of its color, its actual composition is $K_2SO_4 \cdot K_2S_2O_7 \cdot V_2O_4$, assuming vanadium is primarily present as V^{4+}. A sulfovanadia compound $VOSO_4$ is a possible form according to some investigators (*8, 10, 17*). Heating the catalyst at 400°C for 10 hr appears to decompose some of the pyrosulfate $K_2S_2O_7$ to K_2SO_4. Bazarova *et al.* (*7*) noted that the pyrosulfate is unstable in air above 420°C; Boreskov *et al.* (*18*) and Holroyd (*11*) also reported $K_2S_2O_7$ decomposition in the absence of SO_3 at temperatures above 300°C.

Increase in the sulfur content when the catalyst is contacted with the reactants comes from the formation of $K_2S_2O_7$ and possibly $VOSO_4$ by reaction of the SO_3 product with the catalyst. The results correspond approximately to $0.67\ K_2SO_4 \cdot 1.33K_2S_2O_7 \cdot V_2O_4$. It is unlikely that the increase in total sulfur arises from adsorption of SO_2 and SO_3. According to Szekely *et al.* (*19*), adsorbed SO_3 and SO_2 on vanadia catalysts between 400 and 500°C are rapidly desorbed in a nitrogen purge. A nitrogen purge was used over a period of hours in this study during cooling of the catalyst before it was removed for testing.

Measurements on the NSKK catalyst and its color suggests its composition is $2.2K_2SO_4 \cdot V_2O_5$. On contact with reactants the increase in sulfur and reduction would lead to an approximate composition: $0.8K_2SO_4 \cdot 1.4K_2S_2O_7 \cdot V_2O_4$.

DISCUSSION

Our study has demonstrated that either an activity loss or an increase may be observed depending on run-in conditions. When activity decreases it is attributable to the loss of surface area when the catalyst is brought on-stream. For both catalysts studied, however, the surface area loss was substantially larger than the decrease in catalyst activity Consequently, a second process must be occurring resulting in a higher intrinsic activity for the catalyst. We can only speculate on its source.

Reduction of the vanadium seems to occur when the air–SO_2 mixture passes over the catalyst at 400°C. Indeed, the reduction is pronounced for the NSKK catalyst as evidenced by its color change. We suggest that the catalyst may be more active as V^{4+} than as V^{5+}. There is some evidence (*5, 17, 20, 21*) that the overall rate of oxidation of SO_2 may be controlled by a step either involving the adsorption of oxygen on a V^{4+} site or a complex group of surface steps resulting in the oxidation of the +4 site. The reduced form of the catalyst then might provide simply a greater number of reduced sites and therefore a higher intrinsic activity.

Alternatively, the increase of intrinsic activity may be associated with the increase in sulfur in the catalyst. It seems that the increase raises the $K_2S_2O_7$ content in the catalyst phase. The pyrosulfate serves as a flux lowering the melting point or at least causes a vitreous rather than a crystalline catalyst phase. If, as Topsøe and Nielsen (*9*) and Holroyd (*11*) suggest, the rate of reaction is associated with the viscosity of the catalyst phase then increasing $K_2S_2O_7$ should raise the rate by reducing the catalyst phase viscosity. It has been suggested (*22*) that a transport step in the catalyst phase is rate controlling in SO_2 oxidation over vanadia. Lower viscosity could increase this rate by raising mobility of species in the phase.

This work does not permit a selection between these hypotheses. Perhaps both phenomena occur. The NSKK catalyst which shows a significant rate increase when it is brought on-stream exhibits both an important increase in its sulfur content and a reduction in vanadium valence.

The loss of surface area appears to occur in two steps. Some of the loss occurs when the catalyst is brought to temperature in either an inert or oxidizing atmosphere. The largest part of the loss occurs, however, during the initial period on-stream. The formation of SO_3 shifts the potassium sulfate in the catalyst towards the pyrosulfate $(S_2O_7)^{2-}$. There is evidence that the mixed vanadium potassium salts of the pyrosulfate have melting points well below those of the sulfates. Increasing SO_3 content therefore lowers the melting point of the catalyst phase permitting surface rearrangement and flow to smooth the surface and reduced micropore volume.

The loss of surface area in the heating phase is believed to be due to a similar process. However, in the heating phase, the pyrosulfate content of the catalyst is lower, the melting point is higher so that the surface rearrangement will not be complete.

The answer to the question of whether the running-in of the catalyst could be changed to provide a higher permanent catalyst activity must be negative. However, the ability of the catalyst to change its activity depending upon its exposure to different reactant (SO_2, O_2) concentrations as discussed in this paper suggests a potentially valuable means of exploitation of this catalyst through cycling of feed concentrations (*22*).

Note added in review. Putanov *et al.* [Putanov, P., Jovanović, N., Smiljanić, D., and Milisavljević, B., *Hemijska Industrija* **10**, 1785 (1971)] investigating textural changes in Girdler 101 and Imperial Smelting Corp. vanadia catalysts during heating in air found 20-fold increases in mean macropore diameters, but a 23-fold decrease in specific surface at a temperature of 700°C. Initial catalyst activity followed surface area changes. Although the temperatures were different from that used in this work, their results confirm the pore changes we observed.

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