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Catalytic and Surface Characteristics of Newly Imported, Exhausted, and Regenerated V_2O_5 Catalysts Used in H_2SO_4 Manufacturing

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A new method of regeneration of already exhausted V_2O_5 catalyst in H_2SO_4 manufacturing is suggested. Chemical analysis of regenerated catalyst showed that the fundamental components of the fresh catalyst were completely retained. Surface studies of fresh, exhausted, and regenerated catalysts by means of nitrogen adsorption could explain the main differences between the surface characteristics of these catalysts. The appearance of a group of narrow pores in the regenerated catalyst could be interpreted in view of the removal of amorphous envelope, produced as a result of exhaustion of the catalyst. The results of electron microscopy and X-ray analysis gave fairly close agreement with those of chemical analysis and pore structure analysis.

The study of catalytic activity as a function of reaction temperature, SO_2/air ratio, and exhaustion period could lead to a much more complete picture of the optimum conditions of use of both newly imported and regenerated V_2O_5 catalysts. The V_2O_5 catalyst, regenerated by the given method, showed higher activity values over the whole range of conditions studied.

INTRODUCTION

In many developing countries, most of the catalysts used in chemical industries are patented and are sold as finished products. However, most of these catalysts have a short efficient life and are nonrecoverable which would, ultimately, increase their cost (represented in their continual consumption).

One of these catalysts is V_2O_5 which is used in sulfuric acid manufacturing. The information available from the literature shows a marked deficiency in the direction of the regeneration techniques of the V_2O_5 catalyst. However, the few examples of the known catalyst-regeneration processes were based either on changing the form or shape of produced granules (*1*) or on preparing a porous structure by treatment of SiO_2 carrier with an H_2SO_4 solution of V_2O_5 and $KHSO_4$ followed by sintering at elevated temperatures up to 900°C (*2*). Sometimes promoters such as SnO_2 and TiO_2 were used (*3*). Regeneration by HCl treatment followed by extraction of vanadyl ions was also used in several investigations (*4–7*).

In all these studies, severe conditions were required for regeneration to be applied in industry. On the other hand, most of these studies neither account for the activity and texture of the regenerated catalyst nor give any information about whether the activity was completely retained after regeneration.

It therefore became necessary, academically, economically, and practically, to investigate simple means of recovery of already used catalysts. This of course required various types of academic studies before certain recommendations could be drawn in this direction. Therefore, besides

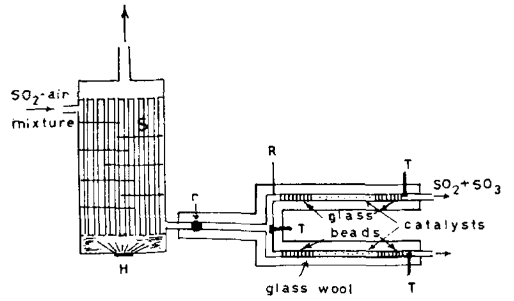

FIG. 1. Schematic representation of the catalytic activity apparatus. H, heating chamber; R, catalytic reactor; T, thermocouples; S, shields; r, regulating valve for adjusting rate of flow.

testing the activity of newly imported, already exhausted, and regenerated V_2O_5 catalyst by the suggested method, a study was made on structure and texture with an extended investigation into the effect of degeneration with time of use.

EXPERIMENTAL

1. Catalyst materials. The materials used in the present investigation were all V_2O_5 catalyst imported from West Germany and manufactured by BASF and are designated as samples I, II, and III for the fresh, exhausted, and regenerated catalysts, respectively. The exhausted catalyst (sample II) was that obtained by using the fresh sample (I) in the H_2SO_4 industry for a period of 10 years. The regenerated catalyst (sample III) was produced from the exhausted V_2O_5 (sample II) using a new method which is discussed in this investigation.

2. X-ray analysis. The degree of crystallinity and the ratios of different components were determined in all samples by using the X-ray diffraction technique. The X-ray diffractometer used in this study was of the Philips type.

3. Electron microscopy. The morphology and microstructure of the various catalysts were studied using an electron microscope, type JEM-6 C, manufactured in Japan, using a magnification of 20,000×.

4. Specific surface area and pore analysis. Low temperature adsorption of nitrogen was measured by standard volumetric methods. Complete adsorption–desorption isotherms were determined at $-195°C$, from which the pore structure of the catalysts was fully studied. The specific surface area could be evaluated from the obtained isotherms by applying the BET equation.

5. Determination of catalytic activity. The catalytic activity in all cases was determined in the reaction of oxidation of SO_2 gas with atmospheric oxygen, using the apparatus shown in Fig. 1. The apparatus consisted mainly of (a) a heating chamber and (b) a catalytic reactor.

In one of the branches of the catalytic reactor a 150-g sample of fresh catalyst of pellet size 0.6 × 1.5 cm was placed in the central part, while in the other branch the regenerated catalyst of the same weight and pellet size was used.

After attaining a constant temperature in the range of 400–500°C from the heater, a stream of the gas mixture was allowed to pass from the heating chamber to the catalytic reactor with a flow rate of 70 liters/hr.

The SO_2 content of the gas mixture entering originally and of the gas finally produced after passing over the catalyst

TABLE 1

Chemical Analysis of Fresh, Exhausted, and Regenerated Catalysts (8)

Constituent	Fresh catalyst	Exhausted catalyst	Regenerated catalyst
SiO_2	66.10[a]	66.75	66.35
R_2O_3 (Fe and Al)	3.23	5.45	4.10
MgO	0.12	0.11	0.07
Cl	0.53	0.62	0.44
SO_3	10.16	16.16	11.58
V_2O_5	7.73	6.43	7.53
K_2O	7.65	3.60	7.10
Other (including Na_2O)	4.48	0.88	2.83

[a] Percentage of constituent.

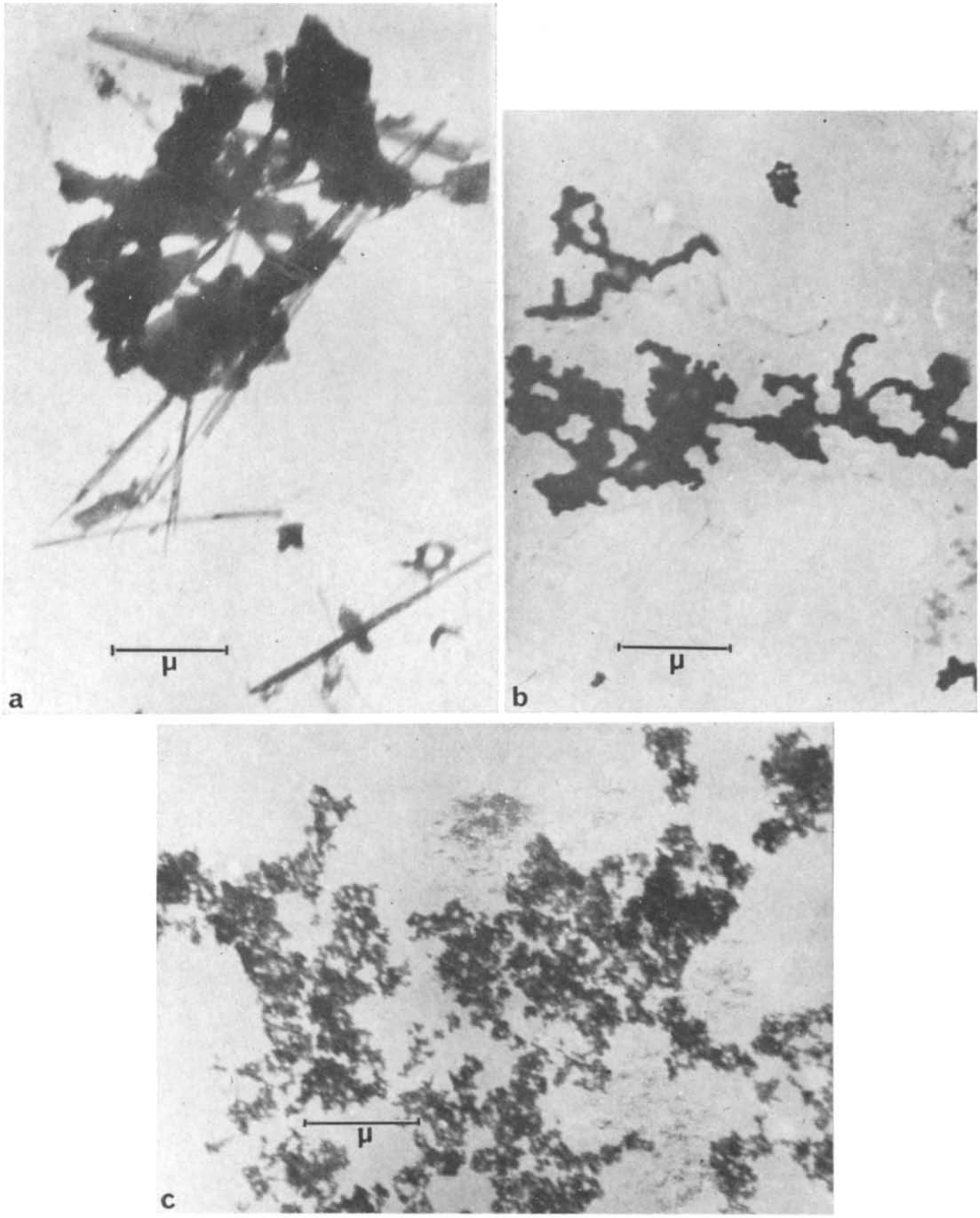

FIG. 2. (a), The microstructure of fresh catalyst. (b), The microstructure of exhausted catalyst. (c), The microstructure of regenerated catalyst.

surface for 1 hr was determined by the Reich method (*8*).

The catalytic activity could be expressed as percentage of conversion by using the following equation: % conversion = [(volume of entering SO_2 − volume of unreacted SO_2)/(volume of entering SO_2)] × 100.

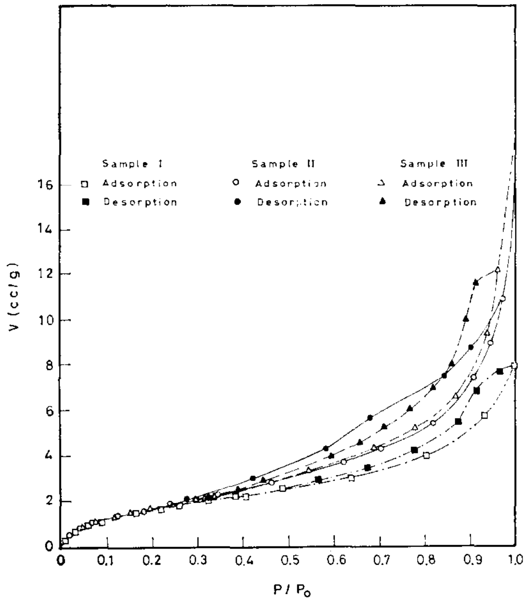

FIG. 3. Adsorption–desorption isotherms of N_2 for fresh, exhausted, and regenerated V_2O_5 catalysts outgassed at room temperature.

RESULTS AND DISCUSSION

1. A New Method for Regeneration of the Already Exhausted V_2O_5 Catalyst

The basic principle of this method is to provide complete removal of various impurities in the exhausted catalyst which affect its characteristic properties. This must be done in such a way that the main constituents remain unchanged after the regeneration process.

The method is as follows: The fine particles and most of the impurities were first removed from the catalyst surface by shaking through a No. 10 mesh. The large particles were then heated gradually in an electric oven up to 500°C. During this treatment, the catalyst was stirred to remove the volatile gases and vapors which were determined to be mainly SO_2, SO_3, H_2O, and As_2O_3. The catalyst was ground into a fine powder and was then well mixed with 5% fine sulfur. A solution of 10% ammonium sulfate was added in the ratio of 35–40% of the weight of the mixture and mixed well to produce a workable paste. From this paste, compressed specimens with a cylindrical shape having 0.5–0.7-cm diameter and 1.5–2-cm length were made. The specimens were dried at 200°C for 2 hr, then heated gradually at higher temperatures, viz., up to 750–800°C, while the air was thoroughly renewed.

The sulfur added to the paste was, thus, oxidized to SO_2 which penetrates into the paste leading to an increase in the porosity. The same effect could be achieved by the decomposition of ammonium sulfate. The remaining impurities such as As, Se, Cl_2, and F_2 were evaporated or became, by themselves, volatile in the temperature range of 400–800°C. The main constituents of the fresh sample (I), were retained by using the above-mentioned treatment, as shown in Table 1. Therefore, as a result of exhaustion, the amount of sulfate (calculated as SO_3) increased markedly from 10 to 16% and, consequently, the other

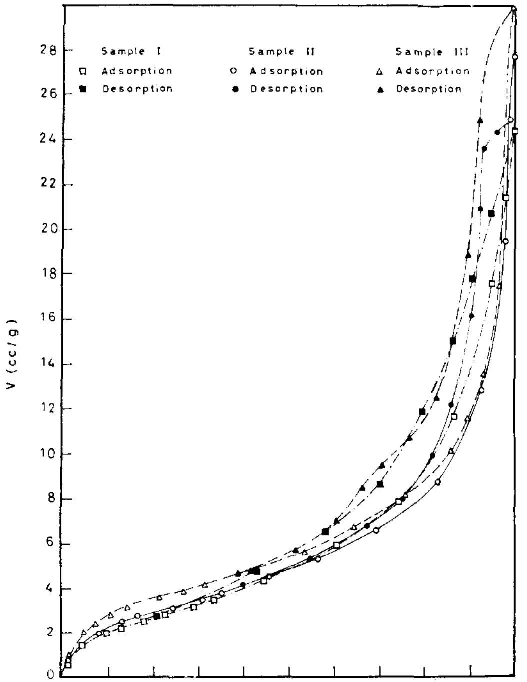

FIG. 4. Adsorption–desorption isotherms of N_2 for fresh exhausted, and regenerated V_2O_5 catalysts treated *in vacuo* at 470°C.

constituents, e.g., V_2O_5, potassium, sodium, etc., (calculated as oxide) showed a relative decrease. After the regeneration process, the ratio of sulfate was retained, showing only a very slight increase (about 1.4%) over the original catalyst, and relatively the other constituents regained their loss.

2. X-ray Analysis of the Fresh, Exhausted, and Regenerated Catalysts

The X-ray diffraction diagram of fresh catalyst showed all the lines characteristic for V_5O_9, K_2SO_4, and V_2O_5 as indicated from ASTM cards.

In addition to these crystalline phases, some amorphous components were present which were mainly composed of amorphous silica and the α-phase of K_2SO_4 rising as very weak peaks.

The X-ray diffraction diagram of exhausted catalyst indicated all the lines characteristic for the components mentioned above for the fresh sample with one main difference; namely, the appearance of an extremely intense peak, characteristic of the α-phase of K_2SO_4, interfered with the peak of V_5O_9.

After regenerating the exhausted catalyst, the X-ray diffraction diagram reflected the same components shown in the fresh sample with their characteristic lines. The only difference was a slight increase in the relative amount of V_5O_9 content in the regenerated sample.

3. Electron Microscopy

The microstructure of the fresh catalyst was found to consist mainly of interlocking large particles together with some rod-like crystals as shown in Fig. 2a. After exhaustion for a long period, the catalyst showed a marked change in its microstructure. The long rods and large particles seemed to be disintegrated leading to an extended structure of small grains coated with amorphous components as shown in Fig. 2b. This structure disappeared on regeneration due to the removal of the amorphous coat. The microstructure appeared, therefore, as clean, fine and interlocking crystals as indicated from Fig. 2c.

TABLE 2

The Monolayer Capacities, BET Constants, Surface Areas, and Total Pore Volumes for the Fresh (I), Exhausted (II), and Regenerated (III) Catalysts Obtained from Nitrogen Adsorption

Sample No.	V_m (cm³/g)	BET-C constant	S_{BET} (m²/g)	V_p (ml/g)
Catalysts outgassed at room temperature				
I	1.52	20.5	5.40	0.0124
II	1.84	16.0	6.51	0.0286
III	1.70	18.4	6.03	0.0225
Catalysts outgassed at 470°C				
I	2.56	30.2	11.2	0.0387
II	2.65	21.6	12.1	0.0542
III	3.35	28.6	14.6	0.0618

4. Surface Area and Pore Structure of Fresh, Exhausted, and Regenerated Catalysts

4.1. Adsorption–desorption isotherms and BET surface areas. Adsorption–desorption isotherms of nitrogen were measured volumetrically at −195°C, for fresh, exhausted, and regenerated catalysts. Two different methods were adopted as standard pretreatment, namely, evacuation of the samples for 3 hr at room temperature and evacuation for 3 hr at 470°C at a pressure less than 10^{-5} mm.

The adsorption–desorption isotherms for the three catalysts, outgased at room temperature, are illustrated in Fig. 3. The isotherms of the catalysts, evacuated at 470°C are given in Fig. 4.

All the isotherms seem to belong to type II of Brunauer's classification (*9*), exhibiting pronounced hysteresis loops which close in the low pressure range for all catalysts.

It is clear from Fig. 3 that the differences in the amount adsorbed on the surface of the catalysts outgassed at room temperature are very small. On the other hand, for the catalysts outgassed at 470°C, the differ-

TABLE 3

Characteristics of Pore Structure of Catalysts, Outgassed at 470°C from Nitrogen Adsorption at −195.8°C

Sample No.	S_{BET} (m²/g)	S_t (m²/g)	$S_{\mathrm{cum}}{}^{pp}$ (ml/g)	$V_{\mathrm{cum}}{}^{pp}$ (ml/g)
I	11 20	11.60	11.20	0.0374
II	12.10	12.50	12.60	0.0523
III	14.60	15.90	16.80	0.0623

ences become more pronounced as shown from Fig. 4.

From the isotherms obtained, the specific surface areas could be evaluated by the application of the BET equation (*10*). The monolayer capacity V_m could also be calculated from the BET plots. The results obtained from the nitrogen adsorption are illustrated in Table 2.

The authors prefer to compare the results obtained by treating the samples at 470°C, i.e., the temperature of industrial use of these catalysts in the oxidation reaction. The following discussion is, therefore, made only for the samples treated at 470°C.

4.2. V_1-t plots and pore analysis. Several investigators have offered *t*-curves for nitrogen, e.g., Cranston and Inkley (*11*), de Boer *et al.* (*12*), and Mikhail *et al.* (*13*), on the basis of nonporous adsorbents. In the present investigation the *t*-curve published by Mikhail *et al.* (*13*) was adopted for the adsorption of nitrogen, taking into consideration the behavior of the first adsorbed layer.

The experimental adsorption curves were plotted as a function of the *t*-values; hence $V = f(t)$ instead of $V = f(P/P_0)$. In any normal case of multimolecular adsorption, the experimental points should then fall on a straight line passing through the origin. The slope of this line gives the surface area, S_t, in square meters per gram, according to the following equation $S_t = 10^4(V_e/t)$, where V_e is the volume of nitrogen adsorbed in milliliters per gram, and t is the statistical thickness in angstrom units.

Analysis of pores of various sizes was made by means of the corrected modelless method (*14*) for sample I and II where only meso-pores are present. In the case of sample III both narrow and meso-pores are present as indicated from the downward and upward deviations in the $V_1 - t$ plots. In this case the micropores were analyzed by the use of the modified micropores method (MP-method) (*13*). The combination of the corrected modelless method and the MP-method gives the total pore structure analysis of the catalyst sample III.

It was found that the parallel plate model can reasonably describe the shape of pores present, while the cylindrical-shaped model gives higher cumulative values. Characteristics of the pore structure of various catalysts outgassed at 470°C are given in Table 3. These results indicate a fairely good agreement between the values of S_{BET}, calculated from the BET plots, S_t, calculated from $V_1 - t$ plots and $S_{\mathrm{cum}}{}^{pp}$, obtained from the mesopore structure analysis of samples I and II and from the total pore structure analysis (micro and meso-) of sample III.

It is to be noted that the cumulative values of the pore volume, $V_{\mathrm{cum}}{}^{pp}$, calculated from the parallel plate model are in reasonable agreement with the measured values V_p (Table 2).

The pore volume distribution curves for the three catalysts are illustrated in Fig. 5. These curves represent the distribution of pore volumes ($\Delta V/\Delta r$ in milliliters per angstrom unit) as a function of the mean hydraulic radius, $r_{h(pp)}$ in angstrom units, assuming a parallel plate model.

The distribution curves obtained reflect some interesting features which can be summarized as follows: (i) In both fresh and exhausted catalysts, only wider groups of pores are existing, which are characterized by a most probable hydraulic radius of ~14–16 Å. However, the fraction of these pores is reduced markedly in the exhausted sample, which seems to be due to the coating of disintegrated particles by amorphous

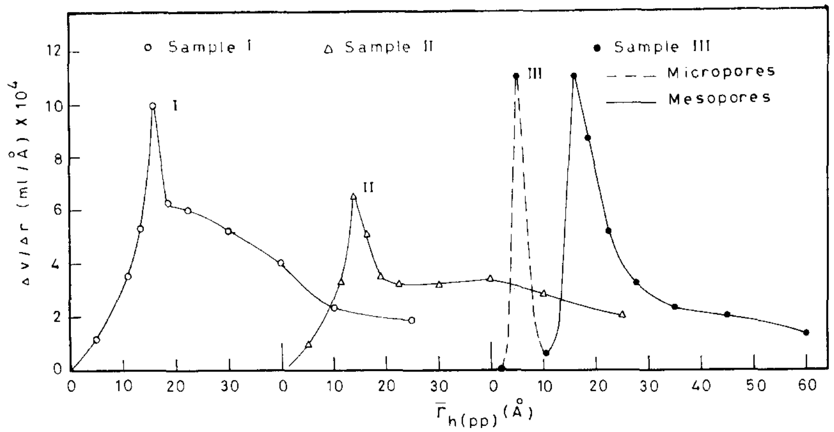

FIG. 5. Pore size distribution for the various catalysts outgassed at 470°C from nitrogen adsorption.

components inhibiting the penetration of nitrogen molecules. (ii) In the regenerated sample, a group of narrow pores, characterized by a hydraulic radius of ~5 Å appears beside a group of meso-pores of ~16 Å radius. These narrow pores might be created as a result of the removal of most of the amorphous components which were formed during the use of the catalyst.

5. Catalytic Activity of Fresh, Exhausted, and Regenerated V_2O_5 Catalysts

Samples I, II, and III were tested in the reaction of oxidation of SO_2 by atmospheric oxygen using the same apparatus described before. Owing to relatively slow adsorption and desorption of the gases on the catalysts, it was found to be essential to maintain steady conditions in the apparatus prior to taking measurements. Thus, the first tests could not be made until 2-3 hr after starting up. The Reich method was used for the determination of SO_2, content and the catalytic activity was estimated using the same equation as given before.

5.1. Catalytic activity as a function of reaction temperature. As has been investigated before, the catalytic activity is strongly affected by changing both the reaction temperature and SO_2/air ratio as well as the flow rate of the reactants.

The temperature effect was first tested at constant SO_2 content (7%) and constant flow rate (80 liters/hr). The results are illustrated in Fig. 6. The studied temperature range is from 410 to 575°C. It is clear from this figure that the exhausted catalyst, which was used for more than 10 years in H_2SO_4 manufacturing, shows markedly lower values of activity than fresh and regenerated ones. The catalytic activity remained unchanged over the temperature

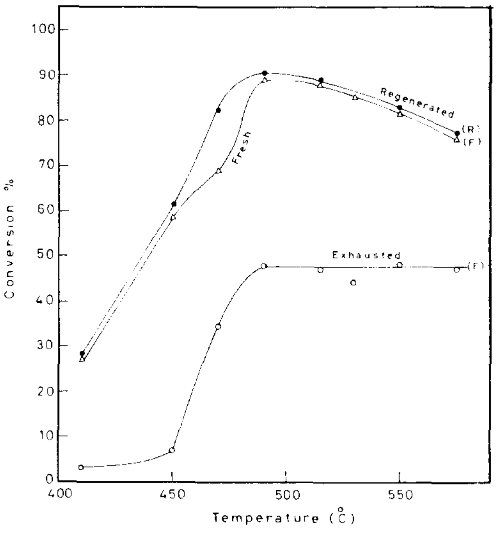

FIG. 6. Catalytic activity (percentage of conversion) of fresh, exhausted, and regenerated catalysts as a function of reaction temperature. SO_2 content = 7.0%; flow rate = 80 liters/hr.

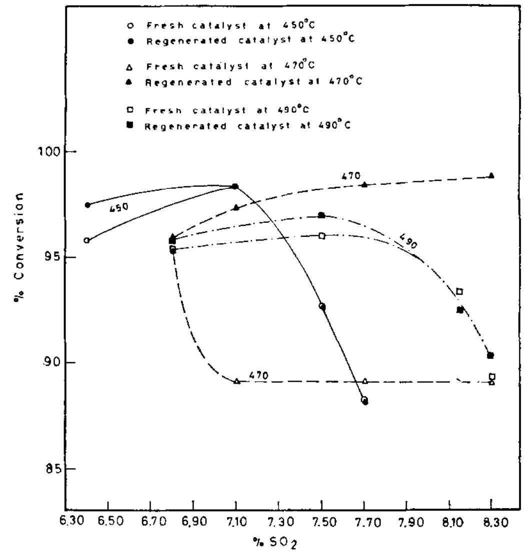

FIG. 7. Activity of various catalysts as a function of SO_2/air ratio at different temperatures; flow rate = 70 liters/hr.

range 490–575°C. The regenerated catalyst, on the other hand, shows higher activity values than the fresh catalyst. The difference becomes more pronounced at 470°C. However, a maximum activity was achieved at 490°C in both fresh and regenerated samples.

The decrease of activity with temperatures higher than 490°C, in the case of fresh and regenerated catalysts, can be explained in view of the fact that both forward oxidation and backward decomposition of already formed SO_3 are strongly catalyzed. In addition, high temperatures assist the decomposition reaction leading to a small degree of conversion. On the other hand, the constancy of activity of exhausted catalyst can be attributed to the fact that the decomposition reaction, in this case, seems to be more catalyzed leading to the establishment of equilibrium more readily.

5.2. Catalytic activity as a function of SO_2 content. From the previous study of the temperature effect, it became essential to investigate in detail the role of different ratios of SO_2 and their effect on the catalytic activity. Both fresh and regenerated catalysts were subjected to this investigation. The study of exhausted catalyst seems to be valueless, since the activity of this catalyst is relatively small, especially at the temperatures studied, namely, 450, 470, and 490°C. Figure 7 shows that, by changing the SO_2 content from 6.4 to 8.3% and using a constant flow rate (70 liters/hr), the maximum activity of both catalysts is achieved by using 7.1% SO_2 at 450°C and 7.5% at 490°C. Moreover, at 470°C, the regenerated sample shows a slight increase in activity over a wide range of SO_2 content, up to 8.3%, compared with the fresh catalyst which decreases sharply, achieving some constant value.

5.3. Catalytic activity as a function of life period (exhaustion period). Using the fresh catalyst of activity 68.9% conversion (SO_2 = 7%, flow rate = 80 liters/hr, t = 470°C) for 5 months in the manufacture of surfuric acid, the activity was tested monthly. During this period the activity decreased from 68.9 to 67.7%. The catalyst was then regenerated in the same manner as described before and its activity achieved 82.5% conversion. The regenerated catalyst in turn was allowed to be exhausted for 5 months. The activity was found to decrease in nearly the same way as the fresh one, i.e., it lost about 1.37% of its initial activity, but at the end of this period the activity was still higher than the corresponding value of the fresh catalyst. The cycle was checked at 490°C and gave similar results.

6. *Conclusion*

From the foregoing discussion, it can be concluded that the presented method provides a simple means for recovery of the already exhausted V_2O_5 catalyst. However, the method is characterized by its suitability for application in industry, compared with other known regeneration processes. As has been investigated, the texture, in particular the pore structure, has been improved by using the described regeneration method. The activity of the regenerated catalyst showed higher values than the fresh catalyst over a wide range of conditions of temperature, SO_2 content, and exhaustion period; these data had not been obtained before by applying other methods of regeneration.

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