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# On the Effects of Crystalline Planes and Purities on Working States of Vanadium Oxide Catalysts in CO-oxidation

Yoshiya KERA
*Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560*

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It was confirmed that the kinetics of CO-oxidation over powdered $V_2O_5$ under the condition of $(P_{CO}/P_{O_2})$ more than 2 differed clearly from that under the $(P_{CO}/P_{O_2})$ less than 2 at 450 °C. The activation energies were 5.6 kcal/mol at 250—410 °C and 13 kcal/mol at 410—490 °C under a reductive condition of $(P_{CO}/P_{O_2})=4.4$, and on the other hand 5.9 kcal/mol at 250—490 °C under an oxidative condition of $(P_{CO}/P_{O_2})=0.43$. On a thin crystalline sample, in which the (010) plane was exposed extensively to the surface, a very rapid process appeared at the initial stage but was soon followed by a steady process. The rapid process was explained well by the Elovich law. On the thin crystalline, cautiously purified, the Elovich process did not appear, but the initial rapid process was kept steadily for 10—20 min and then followed by the other steady process. Accompanied by the change in the kinetics during the reaction, the activation energy changed from 2.3 kcal/mol at 271—410 °C and 17 kcal/mol at 410—480 °C to 29 kcal/mol at 271—480 °C under the $(P_{CO}/P_{O_2})=2.1$. Based on these results, the effects of the crystalline planes and the purities on the working states of $V_2O_5$ crystal in CO-oxidation are discussed.

Many investigators have devoted themselves to the discussions on the working states of vanadium oxide catalysts-especially as to whether oxygen in the catalyst takes part directly in the catalysis or only adsorbed oxygen and which phases of vanadium oxide play an important role in the working state.[1–13] A unified understanding of the problem, however, has not yet been established fully for the differences from author to author in the biography of the catalysts (purity, carrier *etc.*), in the reaction systems, and in the reaction conditions. By the same reason, divergence is seen in the proposed kinetics even in such a simple reaction as CO-oxidation on vanadium oxide catalysts.[14–18]

Previously, CO-oxidation on crystalline powder of $V_2O_5$ has been studied by using $^{18}O$-tracer[19] and the rates of isotopic exchange between the surface oxygen and $^{18}O$-carbon dioxide on the crystalline powder and on the thin plate crystalline, in which the (010) plane was highly exposed to the surface, were compared with each other.[20] These results suggested clearly an important role and a high activity of the (010) plane to CO-oxidation.

In this paper, in order to obtain further information on the effects of the crystalline planes and also the purities of $V_2O_5$ on the catalytic activity and the working states, the rates of CO-oxidation over various kinds of $V_2O_5$ crystalline- powdered and thin plate, and unpurified and purified- were investigated under various reaction conditions: temperature, pressure and the ratio of CO to $O_2$. From the results it was deduced that the catalytic properties of the surface, especially the (010) plane, changed remarkably only by the elimination of a very little amount of impurities.

## Experimetnal

*Materials.* $V_2O_5$ obtained by thermal decomposition of $NH_4VO_3$ (special grade, Wako Pure Chem. Co.) at 600 °C in air stream for 3 h was used as the powdered catalyst. Thin plate crystallines were prepared by a soft touched pulverization of single crystals of $V_2O_5$ with an agate mortar and then sieving. The single crystals, unpurified and purified, were made from the unpurified $V_2O_5$ and cautiously purified $V_2O_5$ powder, respectively, by a zone-melting method.[24] The purification was done chemically according to the methods of McCarely *et al.*[21] and Haemers.[22] The BET surface areas of the $V_2O_5$ catalysts are summarized in Table 1. In the unpurified single crystal, $S_s$-u, ESR signals ascribed to $V^{4+}$ ions and $Fe^{3+}$ ions[23] were found. According to a chemical analysis, the content of Fe was 0.005%(Fe/V). On the other hand, in the purified single crystal, $S_s$-p, no ESR signal was detected.[24]

TABLE 1. $V_2O_5$ CATALYSTS AND BET SURFACE AREA

| $V_2O_5$ catalyst | | | Surface area ($m^2$/g) |
|---|---|---|---|
| Powdered $V_2O_5$ (commercial, special grade) | | $S_p$-c | 2.5 |
| Powdered $V_2O_5$ (dec. of $NH_4VO_3$, special grade) | | $S_p$-d | 8.0 |
| Thin plate crystallines (unpurified $V_2O_5$) | 20—42 mesh | $S_s$-u-1 | 0.09 |
| | 80—100 mesh | $S_s$-u-2 | 0.3 |
| | 170—200 mesh | $S_s$-u-3 | 1.2 |
| Thin plate crystallines (purified $V_2O_5$) | 20—42 mesh | $S_s$-p | 0.09 |

The preparations and purifications of CO and $O_2$ gases were done by usual methods. In the reactants no impurity was detected mass-spectrometrically.

*Apparatus and Procedures.* The reaction was done statically with a cylindrical glass vessel (diameter=8 cm, length=6 cm). In the reaction apparatus, the dead volume of the trap and the manometer, $V_D(\approx 25\ cm^3)$, was kept as small as possible compared with the reaction volume, $V_R$ ($\approx 310\ cm^3$). The catalysts were dispersed widely on the side wall. The changes in the pressures during the reaction were determined by reading the level of the Hg-manometer with a cathetometer. Reaction temperature were controlled within ±1 °C.

For the measurement of a very rapid rate at the initial stage on $S_s$-u and $S_s$-p, a small trap, inserted between the manometer and the reaction vessel, was cooled with liq.$N_2$. For the measurements of a steady rate it was not cooled. The catalysts were previously heated in air and then *in vacuo* at 490 °C for 1 h. Activities of the catalysts were almost recovered by such a pretreatment. Thus, for a series of determinations of the temperature- and pressure-dependences of the rates, the same catalyst was used repeatedly.

## Results

*Effects of the Sizes, the Shapes, and the Purities of $V_2O_5$ Catalysts on the Rate of the Catalytic Oxidation of CO-a Survey of the Kinetics. CO-oxidation on the Unpurified $V_2O_5$- the Powdered ($S_p$-d) and the Thin Plate Crystalline($S_s$-u)*: In the catalytic oxidation of carbon monoxide over the unpurified $V_2O_5$ catalyst, $S_p$-d and $S_s$-u, a very rapid process appeared at the initial stage but was soon followed by a slow steady process. The period of the appearance of the initial process was prolonged on a small amount of the catalysts and at a low temperature, as illustrated in Fig. 1. The rapid process, which is almost invisible at 450 °C on $S_p$-d of 0.122 g (Fig. 1-a), appears clearly at 450 °C on that of 0.03 g (Fig. 1-b) and at 256 °C on that of 0.116 g (Fig. 1-c).

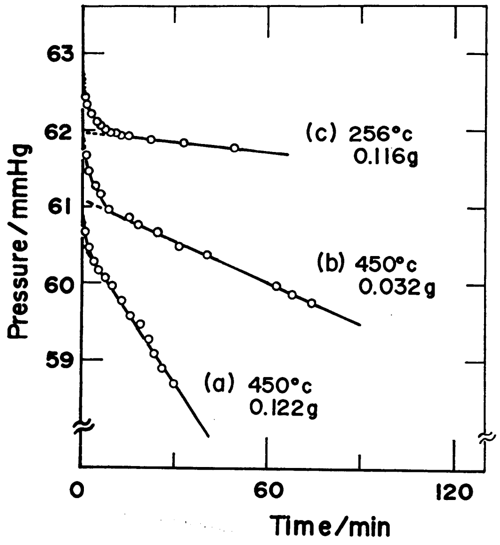

Fig. 1. Appearence of an initial fast process in CO-oxidation at a decreased temperature by use of a reduced amount of $V_2O_5$ catalyst.

The rapid process was recovered easily by the evacuation at $10^{-5}$ mmHg above 450 °C for 1 h. When the temperature of the trap, inserted between the reaction vessel and the manometer, was suddenly changed from 195 to 77 K in the steady state, the rapid process seems to be recovered again for a while. The results obtained at 434 °C on $S_s$-u-3 of 0.027 g are illustrated in Fig. 2. Under the condition that the produced $CO_2$ was always removed from the gaseous phase by the liq. $N_2$ trap, the period of the appearance of the process was further prolonged. The result obtained on $S_s$-u-1 of 0.121 g at 410 °C under the total pressure of 42 mmHg and the ratio ($P_{CO}/P_{O_2}$) of 2.1 is given in Fig. 3-a as an example. The analysis of the process by the "Elovich equation,"[25] $(P_0-P)/(P_0-P_\infty)=\log(t_0+t)$, is shown in Fig. 3-b, where $P$ is the total pressure and $t_0$ is a parameter assumed as 5 min. The initial rapid process seems to be described well by the Elovich law. This feature of the kinetics suggests that the surface is gradually deactivated, accompanied by adsorption of the produced $CO_2$. However, no further discussion on the kinetics is done. Only the mean rates for 5 min at the start of the rapid process, measured repeatedly on $S_s$-u-1 of 0.121 g at various temperatures from 210 to 490 °C under the total pressure of 20 mmHg and the $(P_{CO}/P_{O_2})=2.1$, are evaluated. The results are discussed below.

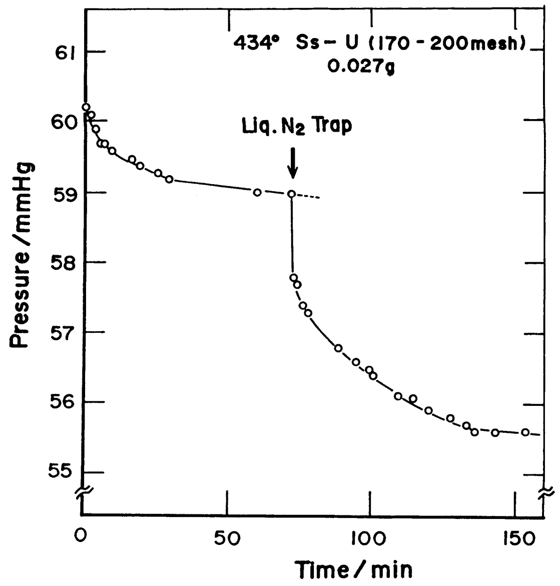

Fig. 2. Effect of elimination of produced $CO_2$ from gaseous phase and surface after a steady state was reached on the initial fast process.

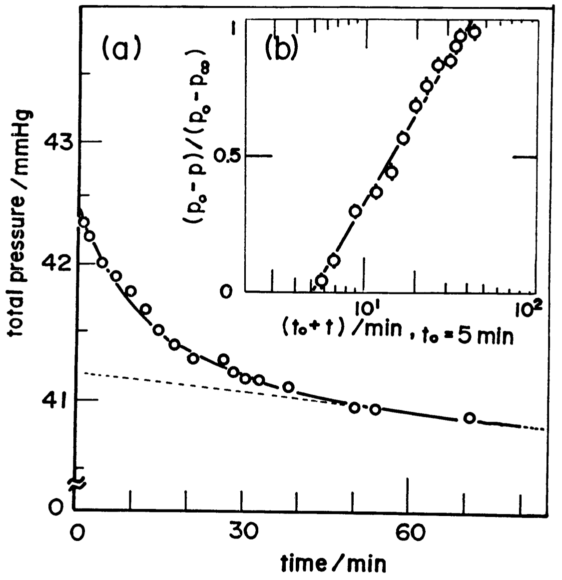

Fig. 3. A kinetical treatment of the initial fast process. (a) reaction curve of CO-oxidation on thin crystallines of $V_2O_5$ at initial. (b) analysis of the initial process according to Elovich low; $(P_0-P)/(P-P_\infty)=\log(t_0+t)$, where $P$ is total pressure, $P_0$ and $P_\infty$ are given by the cross point between the vertical axis and the reaction curve and the points on the dotted line at each time, respectively, $t$ is reaction time, and $t_0$ is a parameter, assumed as 5 min.

The rates of the steady process were evaluated from the slope at the steady state of the reaction curves on the catalysts of $S_p$-c, $S_p$-d, and $S_s$-u. The rates are summarized in Fig. 4 for comparison. In spite of the rather large differences in the particle sizes, the shapes, and the surface areas, the rates per unit surface area were very similar, especially at the lower pressures. The difference in the rates between the fresh and the repeated runs is seen in Fig. 4. The steady rate on $S_p$-d at 450 °C changed linearly with the increase in the amount of the catalyst from 0.03 to 0.3 g, as is shown in Fig. 5. The contribution of the diffusion process to the rate may, therefore, be ignored for the steady process.

*CO-oxidation on the Purified $V_2O_5$-the Thin Plate Crystalline, $S_s$-p*: CO-oxidation on the thin plate crystalline, $S_s$-p, of 0.075 g was examined in the temperature range from 271 °C to 480 °C under the total pressure $((P_{CO}/P_{O_2})=2.1)$ of 23 mmHg. The results are illustrated in Fig. 6. The features of the kinetics seem to be completely different from that on the unpurified catalyst, $S_s$-u, except for the run at 271 °C. The total pressures decrease linearly and it is noted that the slopes in the reaction curves change abruptly at 10—20 min : from given values to smaller values in the runs at 330 and 370 °C and on the contrary to larger values in the runs at 410—480 °C. The temperature dependences of the rates of the first and the second processes are discussed quantitatively below.

*Pressure Dependences of the Steady Rate. The Steady Rate on $S_p$-d*: The steady rates on $S_p$-d, determined

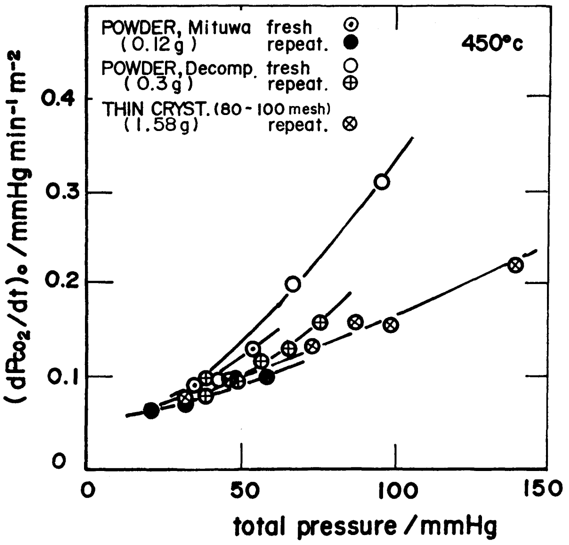

Fig. 4. Comparisons of activities of CO-oxidation among some kinds of powdered and thin crystalline $V_2O_5$ catalysts at 450 °C.

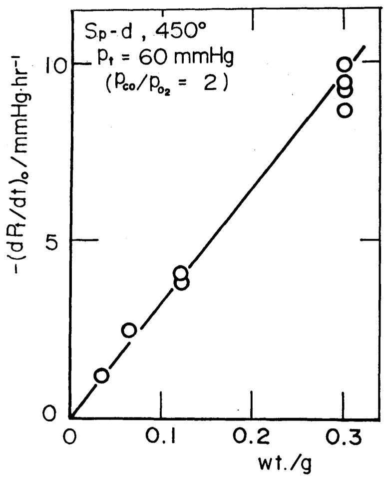

Fig. 5. Verification of linear relation of the steady rate of CO-oxidation with used amount of powdered $V_2O_5$, $S_p$-d, at 450 °C.

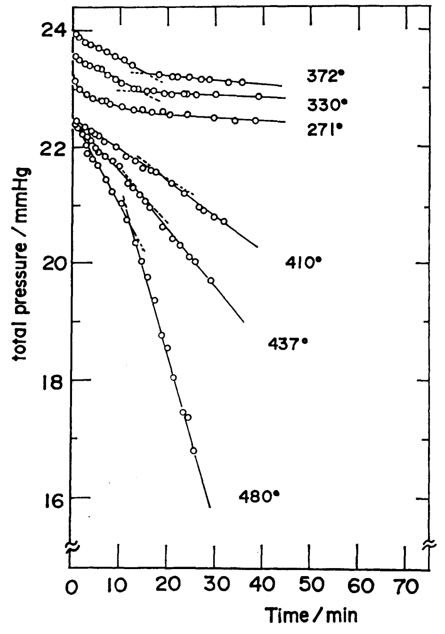

Fig. 6. Reaction curves of CO-oxidation on highly purified $V_2O_5$ crystallines, $S_s$-p. Changes in kinetical feature with reaction temperatures.

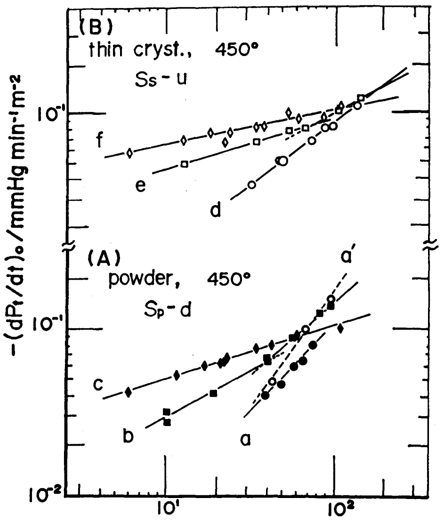

Fig. 7. Pressure dependences of the steady rate at 450 °C on unpurified powdered $V_2O_5$, $S_p$-d, (A), (a; the rate *vs*. total pressure, a'; *vs*. total pressure on fresh catalyst, b, *vs*. partial pressure of CO and c; *vs*. partial pressure of $O_2$) and on unpurified thin crystallines of $V_2O_5$, $S_s$-u, (B), (d; the rate *vs*. total pressure, e; *vs*. CO and f; *vs*. $O_2$).

at 450 °C under various pressures, are summarized in Fig. 7(A). On the vertical axis, the total pressure change (mmHg) per unit time (min) and per unit surface area (m$^2$) are given in a common logarithm scale. On the abscissa, the total pressure and the partial pressures of CO and $O_2$ (mmHg) are given in a common logarithm scale, corresponding to the curves a, b, and c, respectively. In curve a, the ratio of CO to $O_2$, $(P_{CO}/P_{O_2}) \equiv r$, was fixed at 2 and the total pressure, $P_t$, was varied from 39 to 75 mmHg. The curve a′ indicates the rate on the fresh catalyst. It is known from the comparison between the curves a and a′ that the reaction order for $P_t$ is higher on the fresh catalyst than on the catalysts used repeatedly. In the curve b, $P_{O_2}$ was fixed at 20 mmHg and $P_{CO}$ was varied from 10 to 95 mmHg. It should be noted that when $P_{CO}$ exceeded 40 mmHg, that is, the ratio $(P_{CO}/P_{O_2})$ exceeded 2, the reaction order for $P_{CO}$ changed at once from a given value to a larger one. In the curve c, $P_{CO}$ was fixed at 40 mmHg and $P_{O_2}$ was varied from 6 to 109 mmHg. The reaction order for $P_{O_2}$ was kept constant over all the pressure ranges.

The reaction rates of the steady state can be described by an empirical equation:

$$V_{\text{steady}} = k(r) \cdot P_{CO}^{n} \cdot P_{O_2}^{m}. \qquad (1)$$

In the case of the stoichiometric mixture of the reactant, $r=2$, Eq. 2 is available:

$$V_{\text{steady}} = k(2) \cdot 2^{n} \cdot 3^{-(n+m)} \cdot P_t^{(n+m)}. \qquad (2)$$

The reaction orders and the apparent rate constants, evaluated by Eqs. 1 and 2, are summarized in Table 2. It is seen in the table that as soon as $r$ exceeds 2, $n$ increases from 0.57 to 1.0 and at the same time $k(r)$ decreases to one-fifth. The changes in the reaction order and $k(r)$ suggest a change in the working state of the catalyst from $V_2O_5$ to some lower oxides.

*The Steady Rate on the Thin Crystalline, $S_s$-u*: Pressure dependences of the steady rate on the thin crystallines, $S_s$-u-2 of 1.58 g, were examined at 450 °C. The results are also given in log-log plots in Fig. 7(B). In the curve d, the $(P_{CO}/P_{O_2})$ was kept constant as 2 and $P_t$ was varied from 32 to 139 mmHg. In the curve e, $P_{O_2}$ was fixed at 30 mmHg and $P_{CO}$ was varied from 12 to 143 mmHg. In the curve f, $P_{CO}$ was fixed at 60 mmHg and $P_{O_2}$ was varied from 6 to 108 mmHg. By the repetition the activity decreased more or less. The activity for the curve d at $P_t=60$ mmHg ($r=2$) was selected as a standard. The activities for the curves e and f at the same condition as $P_t=60$ mmHg ($r=2$) were compared with the standard to estimate the correction factors. The activities of the other points in the curves e and f were evaluated by the use of the correction factors. The reaction orders and the apparent rate constants are also given in Table 2. In the case of $S_s$-u the changes in $n$ and $k(r)$ are also seen at $r=2$, as shown in Fig. 7 and in Table 2.

The data on the thin plate crystallines are scattered, but the general feature of the kinetics agrees fairly well with that on the powder. The value of $k(r)$ in the former is about 10 times as large as that in the latter. On the other hand, the reaction order for $P_{CO}$, $n$, on the former was below one-half of the value on the latter, while the order for $P_{O_2}$, $m$, is nearly the same for the two cases. These differences might be caused by the difference in the extent of the (010) plane exposed to the surface between the powder and the thin plate crystalline.

*Temperature Dependences of the Rates.* *The Steady Rates on $S_p$-d*: The steady rates on $S_p$-d of 0.116 g were measured in the temperature range from 250 to 490 °C under an oxidative ($r=0.43$) and a reductive ($r=4.4$) condition; the total pressures were 70 mmHg. Arrhenius plots of the overall rates (per min and per m$^2$) are given in Fig. 8. The curve a indicates the

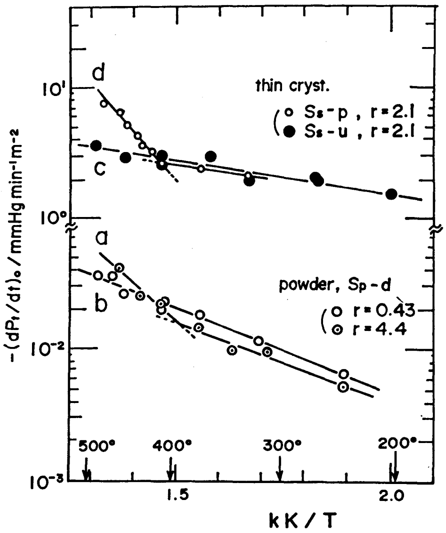

Fig. 8. Arrhenius plots of overall rates of various processes of CO-oxidation. curve-a and -b indicate the run on unpurified powdered $V_2O_5$, $S_p$-d, under $P_{CO}/P_{O_2}=4.4$ and 0.43, respectively, curve-c on unpurified thin crystallines, $S_s$-u, under $P_{CO}/P_{O_2}=2.1$, and curve-d on purified thin crystallines, $S_s$-p under $P_{CO}/P_{O_2}=2.1$.

TABLE 2. CHANGES IN THE REACTION ORDERS ON $S_p$-d AND $S_s$-u WITH MIXING RATIOS OF THE REACTANT

| Sample | Temp °C | The ratio $P_{CO}/P_{O_2}$ | $m+n$ | $m$ | $n$ | $k(r)$ molecules·cm$^{-2}$·s$^{-1}$·$P_{CO}^{-n}$·$P_{O_2}^{-m}$ |
|---|---|---|---|---|---|---|
| Powdered $V_2O_5$ | | $r>2$ | 1.30 | 0.30 | 1.00 | $0.93\times10^{-2}$ |
| $S_p$-d, 0.122 g | 450 | $r<2$ | 0.87 | 0.30 | 0.57 | $4.5\times10^{-2}$ |
| (0.98 m$^2$) | | $r=2$ | 1.10 | | | |
| | | | (1.48)$^{a)}$ | | | |
| Thin plate crystallines | | $r>2$ | 0.78 | 0.25 | 0.53 | $1.1\times10^{-1}$ |
| $S_s$-u, 1.58 g | 450 | $r<2$ | 0.54 | 0.25 | 0.29 | $3.1\times10^{-1}$ |
| (0.48 m$^2$) | | $r=2$ | 0.75 | | | |

a) The value on the fresh catalyst.

Table 3. Comparison of the activation energies among various processes and catalysts

| Total pressure/mmHg ($P_{CO}/P_{O_2}$ ratio) | Catalyst (process) | $E_{ex}$/kcal·mol$^{-1}$ | Temp ranges/°C | Reference |
|---|---|---|---|---|
| 70<br>($r$=4.4) | $S_p$-d<br>(at steady process) | 5.6<br>13 | 250—400<br>400—460 | Fig. 8 |
| 70<br>($r$=0.43) | $S_p$-d<br>(at steady process) | 5.9 | 250—490 | Fig. 8<br>curve b |
| 20<br>($r$=2.1) | $S_s$-u<br>(at the initial stage of Elovich's process) | 2.3 | 210—490 | Fig. 8<br>curve c |
| 23<br>($r$=2.1) | $S_s$-p<br>(1st process up to initial 10—20 min) | 2.3<br>17 | 330—410<br>410—480 | Fig. 8<br>curve d<br>and Fig. 9 |
| | $S_s$-p<br>(2nd process after 10—20 min) | 29 | 330—480 | Fig. 9 |

run of $r$=4.4 and the curve b the run of $r$=0.43. Although the data are rather scattered for repeated measurements, the apparent activation energy clearly increased above 400 °C in the run of $r$=4.4 but was constant over all the temperature range in the run of $r$=0.43. The activation energies are summarized in Table 3.

*Mean Rates at the Start of the Elovich Process on $S_s$-u*: The mean rates for 5 min at the initial stage of the Elovich process on $S_s$-u-1 of 0.121 g (*cf.* Fig. 3), which were measured repeatedly at various temperatures from 210 to 490 °C under the pressure of 20 mmHg and the ($P_{CO}/P_{O_2}$) of 2.1, are plotted in Fig. 8(c). The values seem to correspond to the rates on the (010) plane without poisoning by the produced $CO_2$. The activation energy is as low as 2.3 kcal/mol over all the range of the temperature.

*The Rates on $S_s$-p*: The reaction rates were evaluated from the slope of the reaction curves in Fig. 6. The Arrhenius plots of the overall rates are given in Fig. 9. The circles (○) and the squares (□) denote the rates of the first and the second process, respectively. The sequence of the repetition of the measurements is indicated by the numbers given in the upper part of Fig. 9. The number 5 is missing in Fig. 9, because the run was done at 271 °C and the reaction curve did not give a linear change but seemed to correspond to the Elovich equation, as mentioned above. The number 1 indicates the run on the fresh catalyst. By comparison of the activities between the numbers 1 and 11, it is known that the activity decreases only 20—30% even after the catalyst was used eleven times insuccession. Such as extent of deactivation is inessential to the discussion given below.

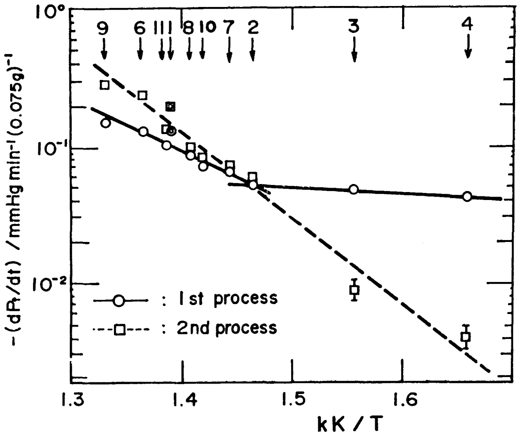

Fig. 9. Arrhenius plots of the first and second processes of CO-oxidation on highly purified thin crystallines, $S_s$-p. The numbers of the upper part of the Figure indicate sequence of repetition of the measurements.

It should be noted that the experimental points for the second process in the temperature regions above and below 410 °C can be connected with each other by the dotted line in Fig. 9. On the other hand, the Arrhenius plot of the first process consists of two lines crossing each other— the line above 410 °C shows a considerably larger slope than that below the temperature. The temperature dependence of the first process is also given in Fig. 8(d), for comparison.

## Discussion

Hughes and Hill[14] have suggested for CO-oxidation over vanadium pentoxide catalyst that a high activation energy is required in the process in the elimination of surface oxygen by carbon monoxide and on the other hand the process in the re-oxidation by oxygen occurs easily. Boreskov *et al.*[17] have indicated that the rates of the reduction of vanadium pentoxide by carbon monoxide and the re-oxidation by oxygen largely depends upon the extent of reduction and oxidation of the surface. Based on their results, the activation energy of 13 kcal/mol, obtained on the unpurified powder above 400 °C under a reductive condition ($r$=4.4) (*cf.* Fig. 8 and Table 3), would arise from the process on the surface reduced to some extent. On the other hand, at the temperatures below 400 °C, even under such a reductive condition ($r$=4.4) the surface would be kept in an oxidative state, since the activation energy is as low as 5.6 kcal/mol and is almost the same as 5.9 kcal/mol obtained for the process under an oxidative condition ($r$=0.43) (*cf.* Fig. 8 and Table 3).

The change in the kinetics, which appeared as soon as the ($P_{CO}/P_{O_2}$) became larger than 2 with the increase in the CO partial pressure (*cf.* Fig. 7), would also be understood favorably as corresponding to the changes in the surface state on working. That is, the surface of the powder and the thin plate crystalline, unpurified, is kept in the reduced state on working to some extent at 450 °C under the condition that the $(P_{CO}/P_{O_2})$ is larger than 2. The differences in the kinetic parameters, $k(r)$ and $n$, however, are not so small between the powder and the thin plate crystalline (*cf.* Table 2). These differences would arise from the difference in the extent of the (010) plane exposed to the surface. In the thin plate crystalline, the extent of the (010) plane was estimated roughly to be higher by about 38 times than the other planes. In the estimation it was assumed that each crystalline is a square plate with mean sides of 160 μm (*cf.* the sizes of sieves of 80 and 100 meshes, which correspond to 177 and 149 μm, respectively), and the values of 0.31 $m^2/g$ and 3.3 $g/cm^3$ were used as the surface area of $S_s$-u-2 and as the density, respectively.

In this work, if the measurements of the oxidation rate of CO over $V_2O_5$ had been carried out without special attention, only the steady process could be found. On the reduced amount of the catalyst at a low temperature, a very rapid process appeared at the initial stage, as was shown in Fig. 1. On the thin plate crystalline, in which the (010) plane was highly exposed to the surface compared to the other planes, the rapid process was completely differentiated from the steady process and was analyzed well with an Elovich equation, as was shown in Fig. 3. The rapid process could occur mainly on the (010) plane, because in the thin plate crystalline the (010) is exposed to the surface much more than the other planes. Furthermore, from the fact that the rapid process is recovered easily by the evacuation at 450 °C and is prolonged on the elimination of the produced $CO_2$ from the gaseous phase by the insertion of the liq. $N_2$ trap, the initial rapid process may be attributed to a process accompanied by the poisoning of the surface by the produced $CO_2$. Such a process is really consistent with the physical content of the Elovich law.

On the thin plate crystalline, purified carefully, such Elovich kinetics have never been found, and inversely the rapid rate was kept for a while at the beginning but was soon followed by the second rapid process with a very high activation energy (29 kcal/mol), as is shown in Figs. 6, and 9 and Table 3. The initial mean rate for 5 min on the unpurified thin crystalline was almost the same as the rate of the first process on the purified thin crystalline and its temperature dependence was also the same as that on the latter at the temperatures lower than 410 °C (*cf.* Fig. 8). Those consistencies suggest that the active site for CO-oxidation is the same for the thin plate crystallines, unpurified and purified, at least at the start. The sites for the subsequent process, however, differ largely among the crystallines, unpurified and purified, depending upon whether there are very small amounts of impurities. That is, the site on the unpurified seems to be inhibited by the produced $CO_2$ mentioned above; on the other hand, the sites on the purified seem to vary easily into other sites during the oxidation, as is suggested by Figs. 6 and 9. Such a low activation energy as 2.3 kcal/mol was reported by Kazanskii *et al.*,[18] who obtained the value of 1.6 kcal/mol for a radical process on a vanadium oxide catalyst, $CO + O^-_{ads} \rightarrow CO_2$, below room temperature. From comparison of the activation energies, the very initial process on the thin plate crystallines, unpurified and purified, could be ascribed to a small cycle of reduction and oxidation on the (010) plane. Such a large activation energy as 29 kcal/mol may arise from the process on a considerably reduced surface, according to the indication by Hughes *et al.*[14] and Boreskov *et al.*[17] Thus, the large changes in the activation energies from 2.3 kcal/mol below 410 °C and 17 kcal/mol above 410 °C in the first process to 29 kcal/mol in the second process during the oxidation (*cf.* Fig. 9 and Table 3) suggest clearly the changes in the surface state on working in the purified thin plate crystalline.

In TGA of $V_2O_5$ in an $SO_2$ stream, clear-cut and stepwise weight losses were found by Kawashima *et al.*[26] Each step corresponds to a phase change from a given oxide to a different lower one. The clear-cut transitions were explained favorably on the basis of the fact that each vanadium oxide phase has a shear structure and belongs to the Magnéli phase.[27] On the other hand, the recent studies on vanadium bronzes[28] would suggest that such clear-cut transitions between the vanadium oxides are inhibited by the existence of metal impurities, even if the amount is very little. Based on these references, the clear-cut changes in the activation energies, seen only on the highly purified crystalline, could be related to a phase transition of the surface from $V_2O_5$ to a given lower oxide. However, the question still remains as to which states or phases of the surface are realized on working, depending upon the reaction condition.

The high activity of the (010) plane to CO-oxidation, obtained in this work, is fairly consistent with the results of the previous paper on the isotopic exchange[20] and gives support to the suggestion by Hirota[29] that the pure vanadium oxides themselves without carrier and impurity would play an important role in catalysis. The steady rate on the unpurified powder or thin plate crystalline was slower by one or two orders than the rate on the purified thin crystalline, but the former seemed to be more stable than the latter. Those features of vanadium(V) oxide should also be discussed in view of the stabilities and activities of vanadium bronzes.[28]

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