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A Study of the Behavior of Surface Oxygen of V_2O_5 Catalysts by the Use of the ^{18}O-Tracer

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By the use of highly concentrated ^{18}O-carbon dioxide, both the rate of the isotopic exchange of CO_2 and the surface oxygen of a powderd V_2O_5 catalyst and that of the isotopic equilibration of CO_2 on the surface were determined simultaneously in the temperature range from 330 to 450 °C. The rate of the isotopic exchange on the thin-plate crystallines, in which the (010) plane of V_2O_5 crystal was mainly exposed, was also determined. The equilibration rate was 30—40 times faster than the exchange rate. The exchange process on the thin-plate crystallines was found to be extremely rapid, although such a phenomenon has never been found on the powdered catalyst. Based on these results, the relationship of the reaction steps of the isotopic exchange and the isotopic equilibration with those on the triangular scheme of CO-oxidation, previously proposed, was discussed in detail. A small cycle of alternate reduction-oxidation on the top of the surface, especially on the (010) plane, was conclusively confirmed.

The bonding energy of the surface oxygen of metal oxides and its energy distribution have been determined by many authors[1—12] as important parameters for catalytic activities. Information on the dynamical aspects of oxygen species on the surface of metal oxides has also been obtained successfully by the applications of ^{18}O-tracer techniques.[13—16]

In our previous paper[17] the behavior of the surface oxygens of powdered V_2O_5 during the course of CO-oxidation were examined by the use of ^{18}O-tracer techniques, and a mechanism, that is, a "triangular" reaction scheme, was proposed. The very high activity of the surface V=O group, asserted by Tarama *et al.*,[18] was confirmed practically by the simultaneous applications of the IR and ^{18}O-tracer techniques.[19] Evidence of the alternate reduction-oxidation of the oxygen of the V=O group has also been given by the measurements of the reflectance spectra of IR by Fahrenfort *et al.*[20] However, the relationship between the exchangeable oxygen and the most reactive oxygen in CO-oxidation has not been established well enough, as has been pointed out by Sachtler[20] and Emmett.[21]

In this work, first the rates of two processes, the isotopic exchange between CO_2 and the surface oxygen of powdered V_2O_5, Eq. 1, and the isotopic equilibration of oxygen in CO_2 on the surface, Eq. 2, were simultaneously determined and compared with each other:

$$C^{18}O_2 + {}^{16}O(s) = C^{18}O^{16}O + {}^{18}O(s), \tag{1}$$

$$C^{18}O_2 + C^{16}O_2 = 2C^{18}O^{16}O. \tag{2}$$

Secondly, the rate of the exchange process on the powdered V_2O_5 was compared with that on the thin-plate crystallines, in which the (010) plane of V_2O_5 crystal was mainly exposed. On the basis of the results, the relationship of the reaction steps of the isotopic exchange and the isotopic equilibration with those of CO-oxidation was successfully discussed and the triangular scheme, previously proposed, was confirmed further.

Experimental

Materials. A commercial V_2O_5 (special grade, Mitsuwa Chem. Ind. Co.) was used as the powdered catalyst without further treatment. Thin-plate crystallines of V_2O_5, with the (010) plane mainly exposed, were obtained by the pulverization of a single crystal and by sieving with an 80-mesh sieve. Crystal I (smaller size—above 80-mesh) and Crystal II (larger size—below 80-mesh) were used as the catalysts of the thin-plate crystallines. The BET surface area of powdered V_2O_5 and Crystal I were determined to be 2.5 and 0.55 m^2/g respectively.

Gaseous CO_2 containing ^{18}O was prepared by the oxidation of carbon with heavy gaseous oxygen (^{18}O), which had been highly concentrated by the thermal diffusion method.[22] After purification by the usual procedures, no impurities were detected mass-spectrometrically.

Procedure and Experimental Conditions. Reaction systems and procedures similar to those of previous papers[17,19] were adopted. The reaction conditions are summarized in Table 1. The reaction temperatures were controlled within ±1 °C, and the accuracies in the determination of the ^{18}O-concentration were ±0.02—0.05 atom%.

Results

1) Simultaneous Determinations of the Rates of the Isotopic Exchange and the Isotopic Equilibration. Simultaneous determinations of the rates of both the isotopic exchange, Eq. 1, and isotopic equilibration, Eq. 2, over powdered V_2O_5 were attempted. In a preliminary experiment, the determination of the rate of the isotopic equilibration was quite difficult, for the isotopic compositions in carbon dioxide ($C^{16}O_2$, $C^{18}O_2$, and $C^{16}O^{18}O$) were greatly disturbed by the exchange process, which occurred simultaneously. In this experiment, therefore, small amounts of V_2O_5 (0.03 g) were used, and the changes in the isotopic compositions were measured only at the initial stage in order to avoid the trouble as much as possible. The results under the conditions shown in Table 1 are given in Table 2. In the Table, x, y, and K denote ^{18}O atom% in CO_2, $C^{16}O^{18}O$ molecular percent in CO_2, and the value of $\{C^{16}O^{18}O\}^2/\{C^{16}O_2\}\{C^{18}O_2\}$ at a certain reaction time respectively. The increases in y and K indicate the progress of the equilibration reaction and the decrease in x the progress in the exchange reaction. When the changes in x become large, the values of y and K will be affected directly and the rate of the equilibration can not be determined accurately. The changes in x and y with the time are illustrated again by Fig. 1. It can clearly be seen at 450 °C that y is practically disturbed by

Table 1. Reaction conditions

Experiment	V_2O_5 Catalyst	Temperature °C	CO_2 Pressure mmHg	Volume cm^3	Catalyst weight g
Exchange and equilibration reactions	Powdered	330—450	12	130	0.03
Exchange reaction	Crystal I (below 80 mesh)	410	23	300	0.3
	Crystal II (above 80 mesh)	410	21	300	0.3
		490	21	300	0.3
	Powdered	410	12	130	0.3

Table 2. Changes in the isotopic compositions of CO_2 on the powdered V_2O_5 at 450 °C (x: ^{18}O atomic%, y: $C^{16}O^{18}O$ molecular%, K: $(C^{16}O^{18}O)^2/(C^{16}O)(C^{18}O)$)

		Reaction time/h						
		0	0.25	0.5	1.0	1.5	2.0	3.0
450 °C	x	17.70	17.87	17.37	17.12	16.90	—	—
	y	21.40	24.07	25.34	26.35	27.03	—	—
	K	0.8_8	1.4_3	1.9_4	2.5_3	3.0_3	—	—
410 °C	x	17.57	—	17.45	17.37	17.23	—	—
	y	21.61	—	24.90	26.50	27.34	—	—
	K	0.9_9	—	1.7_5	2.4_8	2.9_2	—	—
370 °C	x	17.66	—	17.60	17.53	17.50	17.44	—
	y	22.16	—	23.75	24.81	25.70	26.37	—
	K	0.9_9	—	1.3_9	1.7_4	2.0_3	2.3_4	—
330 °C	x	17.69	—	17.66	17.66	17.57	17.58	17.50
	y	21.83	—	23.08	24.01	24.68	25.39	26.14
	K	0.9_8	—	1.2_6	1.4_5	1.6_8	1.9_0	2.2_3

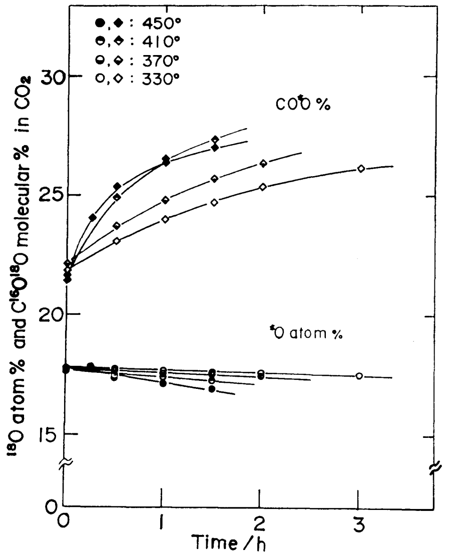

Fig. 1. Changes in ^{18}O atom% and $C^{16}O^{18}O$ molecular % in CO_2 with time over powdered V_2O_5 in the temperature range from 330 to 450 °C.

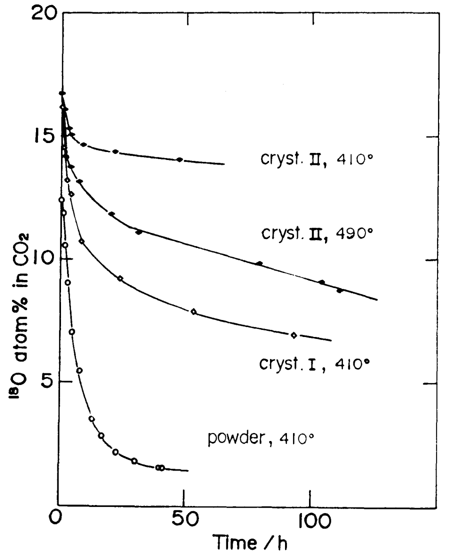

Fig. 2. Changes in ^{18}O atom% in CO_2 with time over powdered V_2O_5 and thin plate crystallines of V_2O_5.

relatively large changes in x.

2) Comparison of the Rates of the Isotopic Exchange on the Powdered V_2O_5 with That on the Thin-plate Crystallines. In order to make clear the effects of the particle size and shapes of V_2O_5 on the catalytic activities and to ascertain the differences in the activities among the crystalline planes, the rate of the isotopic exchange was measured over three types of V_2O_5 samples, shown in Table 1, and compared. The changes in the ^{18}O-concentration-(atom%) in CO_2 with the time are given in Fig. 2. The equilibration reaction took place too fast to determine the rate — the equilibration has already arrived at the first point in the figure. From Fig. 2 it is clear at 410 °C that the rate on the powdered V_2O_5 is faster than that on the Crystal I, while that on the Crystal I faster than that on the Crystal II. These differences must be caused by the differences in the surface areas. In the figure it can also be seen in the initial stage that the rates on the Crystal II are less even at 490 °C

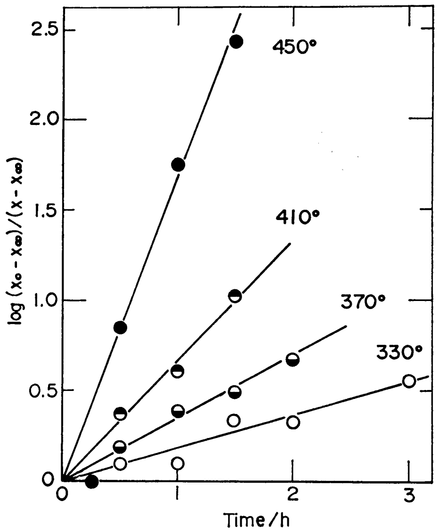

Fig. 3. Kinetical treatment of the data on the isotopic exchange in Table 2 with Eq. 4.

than those on the Crystal I at 410 °C. The slope of the curve of the ^{18}O-concentration *vs.* the time was kept constant; however, after 30 h on the former sample, it became considerably larger than that on the latter. This feature may correspond to the indication[14,16)] that oxygen diffusion in the inner bulk of V_2O_5 crystal is extremely stimulated above 500 °C.

Discussion

Comparison of the Rate of the Isotopic Exchange with That of the Isotopic Equilibration on the Powdered V_2O_5. The rate of the isotopic exchange can be generally described by Eq. 3 if the oxygen atoms in the oxide (O_1) are alike in exchangeability and if the kinetical isotope effects are neglected:

$$-(\mathrm{d}x/\mathrm{d}t) = k_{\mathrm{ex}}(x - x_\infty). \tag{3}$$

The integrated form is given by Eq. 4:[13—16)]

$$\ln\{(x_0 - x_\infty)/(x - x_\infty)\} = k_{\mathrm{ex}}\cdot t, \tag{4}$$

where x is the ^{18}O-concentration in carbon dioxide at any time, x_0 and x_∞ denote the initial and the final values respectively, and k_{ex} is an apparent rate constant. The total reaction rate, R_{ex}, is obtained by multiplying k_{ex} by the total number of oxygen atoms in carbon dioxide, n_{g}. x_∞ in Eq. 4 can be estimated using Eq. 5:

$$x_\infty = \{n_{\mathrm{g}}/(n_{\mathrm{g}} + n_{\mathrm{ex}})\}x_0. \tag{5}$$

Since the amount of exchangeable oxygen in V_2O_5, n_{ex}, is not known in the present experiment, it is assumed preliminarily that n_{ex} is equal to the total number of oxygen atoms in V_2O_5, n_{t}. x_∞ was estimated as about 3 atom% by using the values of $n_{\mathrm{g}} = 1 \times 10^{20}$ and $n_{\mathrm{t}} = 5 \times 10^{20}$ atoms. Plots of $\log\{(x_0 - x_\infty)/(x - x_\infty)\}$ *vs.* the time are shown in Fig. 3.

The rate of the isotopic equilibration, Eq. 2, can be described by Eq. 6 if there is no disturbance of the isotopic composition in carbon dioxide by the exchange reaction:

$$(\mathrm{d}y/\mathrm{d}t) = k_{\mathrm{eq}}(y_\infty - y). \tag{6}$$

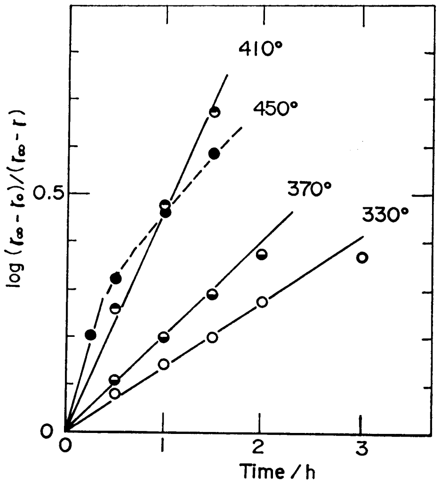

Fig. 4. Kinetical treatment of the data on the isotopic equilibration in Table 2 with Eq. 6.

The integrated form is given by Eq. 7:[13—16)]

$$\ln\{(\gamma_0 - \gamma_\infty)/(\gamma - \gamma_\infty)\} = k_{\mathrm{eq}}\cdot t, \tag{7}$$

where γ is the concentration of $C^{16}O^{18}O$ in carbon dioxide, γ_0 and γ_∞ denote the initial and the final values respectively, and k_{eq} is an apparent rate constant. The total reaction rate, R_{eq}, is obtained by multiplying k_{eq} by the total number of CO_2 molecules.

γ_∞ in Eq. 6 can be estimated as follows: when the initial contents of $C^{16}O_2$, $C^{18}O_2$, and $C^{16}O^{18}O$ are denoted by α_0, β_0, and γ_0, the values at equilibrium can be described as $(\alpha_0 - u)$, $(\beta_0 - u)$, and $(\gamma_0 + 2u)$ respectively, using an unknown value, u. The value of K is approximately equal to 4 in the present temperature range. Therefore, Eq. 8 holds:

$$K = (\gamma_0 + 2u)^2/(\alpha_0 - u)(\beta_0 - u) = 4, \tag{8}$$

and thus u can be represented by Eq. 9:

$$u = (4\alpha_0\beta_0 - \gamma_0^2)/4. \tag{9}$$

Therefore, γ_∞ is described by Eq. 10:

$$\gamma_\infty = \gamma_0 + 2u = \gamma_0 + (4\alpha_0\beta_0 - \gamma_0^2)/2. \tag{10}$$

Plots of $\log\{(\gamma_0 - \gamma_\infty)/(\gamma - \gamma_\infty)\}$ *vs.* the time are shown in Fig. 4.

k_{ex} and k_{eq} can be directly estimated from the slopes of the curves in Figs. 3 and 4 respectively, although the errors are rather large. In Fig. 4 the higher the temperature and the longer the reaction time, the larger the deviation from the straight lines. This indicates that the disturbance of the isotopic compositions by the exchange reaction can not be neglected as the temperature increases and as the time becomes longer. At 450 °C especially, disturbance appeared more clearly as time passes; thus, k_{eq} was estimated by considering only the first point in the curve. k_{ex}, k_{eq}, R_{ex}, and R_{eq} are summarized in Table 3. From the comparison of R_{ex} with R_{eq}, the equilibration rate is known to be about 20—40 times faster than the exchange rate. Arrhenius plots of k_{ex} and k_{eq} are given in Fig. 5. The apparent pre-exponential factors and activation energies were evaluated as follows:

$$k_{0,\mathrm{eq}} = 1.3 \times 10^{-2}(\mathrm{cm^{-2}\,s^{-1}}), \quad E_{\mathrm{eq}} = 14(\mathrm{kcal/mol}),$$

$$k_{0,\mathrm{ex}} = 5 \times 10^{-4}(\mathrm{cm^{-2}\,s^{-1}}), \quad E_{\mathrm{ex}} = 15(\mathrm{kcal/mol}),$$

TABLE 3. THE ISOTOPIC EXCHANGE RATE AND THE ISOTOPE EQUILIBRATION RATE

Temperature °C	k_{ex} 10^{-9} cm^{-2} s^{-1}	Exchange rate 10^{11} atoms cm^{-2} s^{-1}	k_{eq} 10^{-7} cm^{-2} s^{-1}	Equilibration rate 10^{13} molecules cm^{-2} s^{-1}
450	14.4	15.8	7.0	3.8
410	5.6	6.1	4.0	2.2
370	3.0	3.3	1.7	0.9
330	1.5	1.6	1.2	0.6

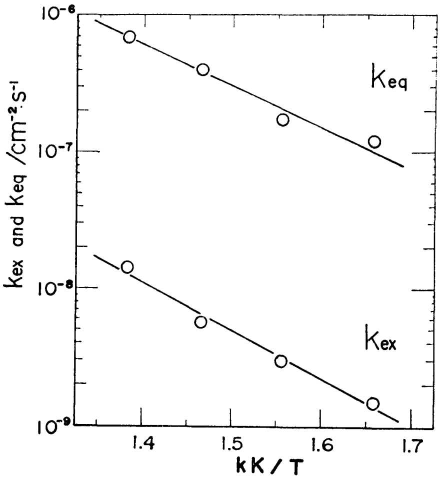

Fig. 5. Arrhenius plots of k_{ex} and k_{eq}.

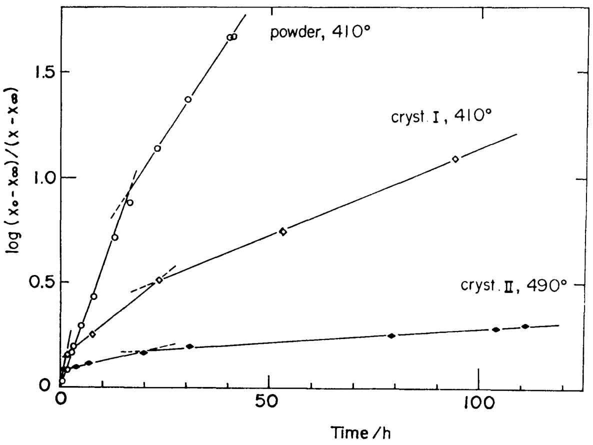

Fig. 6. Comparison of kinetics of the isotopic exchange on the powdered V_2O_5 with that on the thin plate crystallines.

Comparison of the Exchange Rate on the Powdered V_2O_5 with That on the Thin-plate Crystallines. On the application of Eq. 4 to the data of the exchange reaction on the powdered V_2O_5, if an appropriate value is assumed for x_∞, plots of $\log\{(x_0-x_\infty)/(x-x_\infty)\}$ *vs.* the time show two clear straight lines with a break point, as has been mentioned in a previous paper.[17] The appearance of the break suggests that the reactivity or mobility of oxygen in the surface layer of the powdered V_2O_5 can be differentiated from that in the inner bulk during the exchange reaction.

The data on the powdered V_2O_5 (410 °C), the Crystal I (410 °C) and the Crystal II (490 °C), given in Fig. 2, were treated with Eq. 4 assuming appropriate values of x_∞. The results are given in Fig. 6. In the cases of the thin-plate crystallines, an extremely rapid process appeared before the two processes found in the powdered run. The extremely rapid process must have appeared because of relatively high exposure of the (010) plane. This would also give experimental proof that the (010) plane has a considerably higher activity than the other planes. In the case of the powdered V_2O_5, only the process on the (010) plane seems not to be differentiated from that on the other planes; this is because of following reasons: a rapid process would occur not only on the (010) plane, but also on many kinds of surface grain boundaries, and all planes might be exposed with a nearly equal possibility on powdered V_2O_5.

It was found previously by the simultaneous applications of IR and ^{18}O-tracer techniques that the oxygen in the V=O group, projected from the (010) plane, was first exchanged, followed by the oxygen in the V–O–V layer.[19] With reference to these results, of the three straight lines in Fig. 6, the first line corresponds to the exchange of the oxygen in the V=O group, projected perpendicularly to the (010) plane; the second, to that of oxygen in the surface layer (that is, the oxygen near the surface of the other planes or the V–O–V layer), and the third, to the exchange between the surface layer and the inner bulk. Kakioka *et al.*[23] have examined in detail the rate of the isotopic exchange of oxygen in CO_2 with that in powdered V_2O_5 and Mo-doped V_2O_5. They have also demonstrated the existence of two processes — the exchange between the gaseous phase and the surface layer and the diffusion in the inner bulk. The rate and the activation energy of the present second process, R_{ex}, are nearly equal to the rate and the activation energy of the exchange process respectively, as obtained by Kakioka *et al.*

From the intersections of vertical axis with the extrapolated second and third straight lines in Fig. 6, the idealized amounts of exchangeable oxygen atoms corresponding to the top of the surface, n_{S_1}, and the surface layer, n_{S_2}, respectively, could be estimated. Besides, the amounts of the exchangeable oxygen corresponding to the inner bulk, n_b, can be easily estimated as the difference between the total exchangeable oxygen, n_{ex} and $n_{S_1}+n_{S_2}$. The amounts of exchangeable oxygen obtained by those procedures are summarized in Table 4. The overall rates at the initial stage, $R_{0,ex}$, were preliminarily estimated as the decrease in the ^{18}O-concentration for the initial hour. The results are added to Table 4 for the sake of comparison. n_{S_1} is 4—5 times less than n_g in Table 4. The initial rates, $R_{0,ex}$, may not indicate the real values because, in this situation, the exchange between the gaseous phase and the top of the surface possibly arrives at equilibrium within

TABLE 4. AMOUNTS OF EXCHANGEABLE OXYGENS OF V_2O_5 CRYSTAL AND THE INITIAL EXCHANGE RATE

Sample (Temp/°C)	n_g 10^{20} atoms	n_{s1} 10^{20} atoms	n_{s2} 10^{20} atoms	n_b 10^{20} atoms	n_t 10^{20} atoms	$R_{0,ex}$ atoms cm^{-2} s^{-1}
Powder (410)	1.03	1.36		7.4	49.4	3.8×10^{11}
Crystal I (410)	1.92	0.37	0.57	2.2	49.4	3.3×10^{12}
Crystal II (490)	1.58	0.30	0.31	35.1	49.4	(1.1×10^{13}) a)

a) The surface area was assumed to be 0.2 m^2/g in this run.

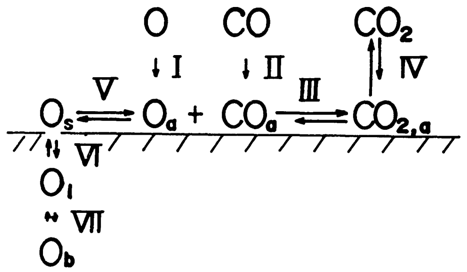

Fig. 7. Relations of reaction paths among the isotopic exchange, the isotopic equilibration, and CO-oxidation. The first, the second, and the third processes of the isotopic exchange are controlled by step V, VI, and VII, respectively and the isotopic equilibration by step V and CO-oxidation by step I and II.
$\{r(+\mathrm{I})=r(+\mathrm{II})=r(+\mathrm{III})-r(-\mathrm{III})$
$=r(+\mathrm{IV})-r(-\mathrm{IV})=r(\pm\mathrm{VI}),\ r(\pm\mathrm{V})\approx30r(\pm\mathrm{VI})\}$

1 h. Practically, larger values could be expected. The exchange rate on the thin-plate crystallines is known, from Table 4, to be more than 10 times faster than that on the powdered V_2O_5. This seems to mean that the exchange rate on the top of the surface of the (010) plane is comparable to the equilibration rate. This could be confirmed, however, only under the experimental condition of $n_g \ll n_{s1}$.

Relationship of the Reaction Steps on the Isotopic Exchange and the Isotopic Equilibration with Those on the Triangular Scheme of CO-oxidation. The previous reaction scheme[17)] of CO-oxidation was further generalized, as is shown in Fig. 7, by adding some steps of oxygen transfer in V_2O_5 crystallines on the basis of the above discussion. In the isotopic exchange on the powdered V_2O_5 Step V could not be observed, only Step VI. In the simultaneous determination of the exchange and the equilibration rates, R_{eq}, which should be related to the rate of Step V, was about 20—40 times faster than R_{ex}, correspondng to the rate of Step VI. On the other hand, on the thin-plate crystallines the rate of Step V was more than 10 times faster than that of Step VI; moreover, R_{ex} on the top of the surface of the (010) plane was suggested to be comparable to the R_{eq}, observed on the powdered V_2O_5. At the steady state of the exchange reaction, therefore, the length of the arrow of Step VI is 20—40 times shorter than the length of the forward and backward arrows in Steps III, IV, and V.

On the powdered V_2O_5, the overall rate of CO-oxidation, R_{oxid}, was nearly equal to R_{ex}, as was shown in a previous paper.[17)] It was suggested, furthermore, that the R_{oxid} was controlled by the length of the arrow of Step I or of Step II in Fig. 7. At the steady state the length should be equal to the differences between the forward and backward arrows of Steps III and IV. At the steady state of CO-oxidation, therefore, the length of the arrow of Step VI would be nearly equal to the difference between the forward and the backward arrows in Steps III and IV. With respect to the absolute length of the arrows, Steps III and IV are both also about 20—40 times longer than Step VI. On the basis of the reaction scheme it can easily be understood that the catalytic oxidation proceeds according to a small cycle of alternate reduction-oxidation on the top of the surface, especially on the (010) plane.

In the present experiment the extremely high activity of oxygen on the (010) plane was shown only under the atmosphere of CO_2. The surface composition of vanadium and oxygen seems to be nearly stoichiometric in the working states. An acceleration of the exchange rate has been previously found on the addition of CO.[17)] In this case the surface of V_2O_5 is probably kept in reduced states. Therefore, the question of whether or not the small cycle of reduction-oxidation can hold on the strongly reduced surface of V_2O_5 remains for future study.

Recently Boreskov *et al.*[24)] and Kazanskii *et al.*[25)] examined in detail the reaction of CO-oxidation over vanadium oxide, supported or not supported, and gave valuable suggestions as to the reaction mechanism. However, it is difficult to compare the mechanisms presented by Boreskov, Kazanskii, and the present authors, because the reaction conditions and surface states of the catalysts seem to be very different. In a forthcomming paper the effects on the rate of CO-oxidation will be investigated in detail in connection with the particle sizes and shapes, the degrees of oxidation and reduction of the surface, and the purities of the V_2O_5 catalyst.

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