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The Exchange Reaction of Oxygen Atoms between Oxygen and Carbon Dioxide on Metal Oxides of the Fourth Period of the Periodic System*

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The exchange reactions of oxygen atoms between oxygen and carbon dioxide on metal oxides were studied by the static batch method in the temperature range from 150 to 600°C. The order of the catalytic activity of the oxides in the reaction was found to be; (higher activity) $Co_3O_4>MnO_2>NiO>Fe_2O_3>Cr_2O_3>V_2O_5>TiO_2$. A very close similarity of the change in the reactivity of these oxides was found in the exchange between oxygen and oxides. There is an approximately linear relationship between the catalyst activity of the metal oxides and the heat of the formation of these oxides. At any temperature examined, carbon dioxide exchanged their oxygen atoms with those of oxide rapidly. The rate of isotopic exchange decreased in the following order on any oxide examined: CO_2-Oxide$>O_2$-Oxide$>O_2$-CO_2 on oxide. The exchange between oxygen and carbon dioxide was observed only when the exchange between oxygen and oxide took place. According to these results, it was concluded that the exchange between oxygen and carbon dioxide takes place through the exchange between these gases and oxygen atoms of oxide, and that the rate-determining step is the exchange with oxygen.

About twenty-five years ago Titani and his collaborators[1-3] investigated the isotopic oxygen exchange reaction between oxygen and water vapor on various kinds of metal oxides. They found that there is a regular relationship between the catalyst activity of the metal oxide and the position where the metal element is placed in the periodic system. From group to group, there is a progressive shift of the catalyst activity. For instance, in the case of the fourth-period elements, titanium oxide (the fourth group) has the lowest activity, and manganese oxide (the seventh group) has the highest activity, with the catalyst activity of the other fourth-period elements arranged in good order between these two elements. Recently Boreskov et al.[4,5] studied the homomolecular oxygen exchange reaction on metal oxides of the fourth-period elements, and discussed the relations between the catalyst activity and the physical and chemical properties of the oxides. However, to the author's knowledge, no systematic investigation has been made into the exchange reaction between oxygen and carbon dioxide on metal oxides. The present author has, therefore, investigated the exchange reaction between oxygen and carbon dioxide on metal oxides of the fourth period of the periodic system, hoping thereby to give an order of the catalyst activity of the oxides and a general picture of the reaction. In the isotopic exchange reaction $\Delta H \fallingdotseq 0$, so the influence of the heat of reaction can be ignored in the comparison of the catalyst activity. It is of interest to study the possible relations between the exchange reaction and the other oxidation reactions on an oxide catalyst. In the exchange reaction between oxygen and carbon dioxide on metal oxides, it may be expected that the catalyst activity of the metal oxides will show the same regular relations as that reported by Titani and his collaborators[1-3] and by Boreskov et al.[4,5] However, such a conclusion could hardly be regarded as certain before experiments have been performed to test this point. The results of the present experiment show that, in the exchange between oxygen and carbon dioxide, there is a regular relation in the catalyst activity of the metal oxides. In the investigation of the oxygen exchange reaction on an oxide catalyst, the measurement of the oxygen exchange between a reactant and an oxide catalyst provides a strong clue to the mechanism of the reaction; therefore, the exchange between oxygen and oxides, and that between carbon dioxide and oxides were studied in the initial step.

Experimental

Gases.—Heavy oxygen, $O^{18}O$, was prepared in our laboratory by the thermal diffusion method;[6] its concentration was 1.81 atom%. Carbon dioxide labeled with ^{18}O (1.79 atom%) was prepared by equilibrating samples of water enriched with ^{18}O

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[1] N. Morita, H. Nakata and T. Titani, This Bulletin, **14**, 9 (1939).

[2] N. Morita, ibid., **15**, 47 (1940).

[3] N. Morita, ibid., **15**, 71 (1940).

[4] A. P. Dzisjak, G. K. Boreskov and L. A. Kasatkina, *Kinetika i Kataliz,* **3**, 81 (1962).

[5] G. K. Boreskov, A. P. Dzisjak and L. A. Kasatkina, ibid., **4**, 388 (1963).

[6] Y. Horibe, *Isotopes and Radiation,* **2**, 25 (1959).

TABLE I. OXIDE CATALYSTS

Oxide	Method of preparation	Specific surface area, m²/g.	Amount of oxide used, mg.
TiO_2	Hydrolysis of $TiCl_4$	14	215
V_2O_5	Thermal decomposition of NH_4VO_3	2.5	300
Cr_2O_3	Thermal decomposition of hydroxide	15	200
MnO_2	Thermal decomposition of nitrate	18	170
Fe_2O_3	Thermal decomposition of hydroxide	10	300
Co_3O_4	Thermal decomposition of nitrate	16	200
NiO	Thermal decomposition of carbonate	31	100

with tank carbon dioxide of a natural isotopic composition prepurified by pumping off the vapors not condensable at the temperature of liquid nitrogen. All the gases used were dried through a train of traps immersed in solid carbon dioxide. A search for impurities in the gases after purification was made by a mass spectrometer up to mass 100; it was found that they were mass-spectrometrically pure, except for traces of other inert gases.

Oxide Catalysts.—The methods of preparation and the specific surface area of the oxides are shown in Table I, together with the amount of the oxides used for the reaction.

For the purpose of comparing the catalyst activity of these oxides, the following precaution was taken, The amount of oxide used for the reaction was adjusted in order to give a fixed total surface area for the different oxides; therefore, the total surface area of a single portion of each oxide used for the reaction was about 3 m² except in the case of vanadium pentoxide.

Procedure.—The reaction was carried out by the static batch method. The reaction vessel was made of pyrex or of fused silica glass. In order to maintain a constant pressure of the gas at each reaction temperature (14 cmHg for CO_2–Oxide, and O_2–Oxide; 27 cmHg for O_2–CO_2 on oxide), reaction vessels of different volumes were chosen for the different reaction temperatures. A single portion of each oxide used for the reaction is listed in the last column of Table I. For the exchange between carbon dioxide and oxides or that between oxygen and oxides, a weighed amount of oxide was placed in the reaction vessel and then outgassed at 550°C for 3 hr., using a mercury diffusion pump, through a liquid nitrogen trap. (Manganese dioxide was, however, outgassed at 200°C for 1 hr.) Then the temperature of the reaction vessel was adjusted to the desired temperature, and 1.8 ml. (NTP) of the enriched carbon dioxide or heavy oxygen was introduced. At desired time intervals, the entire amount of gas was collected and the ^{18}O content of the gas was analyzed by the use of a mass spectrometer. For the exchange between oxygen and carbon dioxide on oxides, a 3.4-ml. portion (NTP) of the gas mixture of heavy oxygen and normal carbon dioxide in a ratio of 1 to 1 was used. The weight of oxides used, the outgassing and the other procedures were the same as those used in investigation of the exchange between gases and oxides.

Results and Discussion

The Isotopic Oxygen Exchange between Gases and the Reaction Vessel, and the Catalytic Action of the Reaction Vessel.—Within the limits of experimental error, the surface of the reaction vessel did not participate in the exchange reaction.

The Exchange between Carbon Dioxide and Metal Oxides in the Absence of Oxygen, and between Oxygen and Metal Oxides in the Absence of Carbon Dioxide.—The exchange reaction between carbon dioxide and oxides proceeded rapidly, and the quantitative measurement of the reaction rate was difficult in the ordinary static method. In any of the oxides examined, carbon dioxide actively exchanged its oxygen atoms with those of oxide, even below the temperature at which no exchange between oxygen and oxides was observed. As an example of the experimental results, the exchange between carbon dioxide and chromic oxide, and that between oxygen and chromic oxide are graphically shown in Fig. 1. From the shapes of the curves shown in Fig. 1, the temperature dependence of the rate of the exchange with carbon dioxide may be seen to be not very appreciable; therefore, the apparent energy of activation can be estimated within a few kcal./mol. Within ten minutes after introduction of the enriched carbon dioxide into the reaction vessel, the ^{18}O content of the carbon dioxide reached a definite value. This value was characteristic of the reaction temperature. At this stage of the reaction, an isotopic equilibrium was established

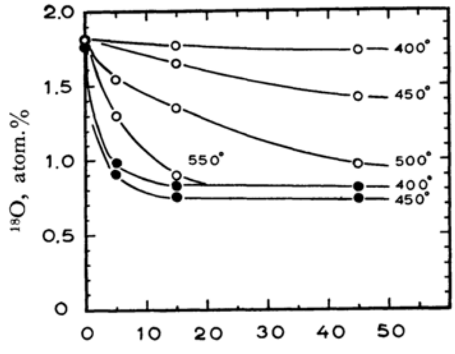

Fig. 1. Extent of the exchange reaction between $CO^{18}O$ and Cr_2O_3, $O^{18}O$ and Cr_2O_3.

Open circle, $O^{18}O$ and Cr_2O_3
Filled circle, $CO^{18}O$ and Cr_2O_3

Table II. The values of n_s at different temperatures
(The numerals in parentheses are the reaction temperatures, °C)

Oxide	n_s (g. atom/g. of oxide)				
Co_3O_4	3.0×10^{-5} (100)	5.1×10^{-5} (150)	7.8×10^{-5} (200)	9.3×10^{-5} (250)	1.5×10^{-4} (300)
MnO_2	2.5×10^{-4} (200)	3.4×10^{-4} (250)	4.1×10^{-4} (300)	4.5×10^{-4} (350)	4.9×10^{-4} (400)
NiO	1.5×10^{-4} (200)	3.2×10^{-4} (250)	4.8×10^{-4} (300)	6.0×10^{-4} (350)	7.0×10^{-4} (400)
Fe_2O_3	5.4×10^{-5} (300)	9.3×10^{-5} (350)	1.6×10^{-4} (400)	2.0×10^{-4} (450)	2.3×10^{-4} (500)
Cr_2O_3	7.4×10^{-4} (350)	9.4×10^{-4} (400)	1.1×10^{-3} (450)	1.2×10^{-3} (500)	1.3×10^{-3} (550)
V_2O_5	5.9×10^{-5} (450)	9.4×10^{-5} (500)	1.4×10^{-4} (550)	3.5×10^{-4} (600)	
TiO_2	3.5×10^{-4} (450)	4.8×10^{-4} (500)	6.1×10^{-4} (550)	6.7×10^{-4} (600)	

between the carbon dioxide in the gas phase and a certain part of the oxide. After the fast initial reaction had finished, there was a slow downward drift of the ^{18}O content of the carbon dioxide. From Fig. 1, the definite ^{18}O content may be obtained by the extrapolation of the drift line to time zero. From this quantity, and from the amount of carbon dioxide and chromic oxide used, we calculated the amount of rapidly-exchangeable oxygen of the oxide, n_s (gram atom per gram of oxide). It was assumed that the ^{18}O content of the exchangeable part of the oxide becomes equal to that of the ambient gas. The values of n_s at different temperatures are tabulated in Table II. The n_s values of these oxides are in the order of 10^{-5} g. atom/m², and there is not very remarkable difference in these values in each oxide. The density of the oxygen atoms on the surface of the oxides is in the order of 10^{-5} g. atom/m²; this agrees with the n_r values.

The surface area of these oxides was measured at the beginning and at the end of the reaction; the difference was within 15%.

As is shown in Fig. 1, the exchange with oxygen proceeded more slowly than that with carbon dioxide. The same results were obtained with the other oxides examined. We have calculated F_1, the fractional attainment of the equilibrium of the exchange reaction between oxygen and oxides, from Eq. 1, where $^{18}O_0$, $^{18}O_t$, and $^{18}O_\infty$, are the initial, at time t, and equilibrium ^{18}O contents of the oxygen gas respectively.

$$F_1 = [(^{18}O_0 - {}^{18}O_t)/(^{18}O_0 - {}^{18}O_\infty)] \times 100 \qquad (1)$$

A random distribution of ^{18}O between the oxygen gas and the exchangeable surface oxygen of the oxide being assumed, the value of $^{18}O_\infty$ was calculated through the value of n_s and through the amount of heavy oxygen and the oxide used. The value of $^{18}O_\infty$ is characteristic of the reaction temperature because the value of n_s depends on the temperature. The results obtained with chromic oxide are shown in Table III.

The rate of the exchange, R (g. atom/min.), is expressed by Mckay's equation:

$$R = -2.303[(a\cdot b)/(a+b)] \log (1-F_1/100)/t \qquad (2)$$

where a and b are the amount of heavy oxygen gas used and the amount of exchangeable surface oxygen of the oxide used respectively, where t

Table III. The exchange between $O^{18}O$ and Cr_2O_3

[The initial ^{18}O contents in O_2 and Cr_2O_3 are 1.81 and 0.204 atom.% respectively.]

Temp. °C	Time min.	^{18}O atom% in O_2	F_1 %
400	15	1.77	4.3
400	45	1.72	11
400	∞	0.87	100
450	15	1.65	15
450	45	1.42	41
450	∞	0.79	100
500	5	1.54	17
500	15	1.37	42
500	45	0.970	89
500	∞	0.760	100
550	5	1.30	48
550	15	0.891	86
550	∞	0.74	100

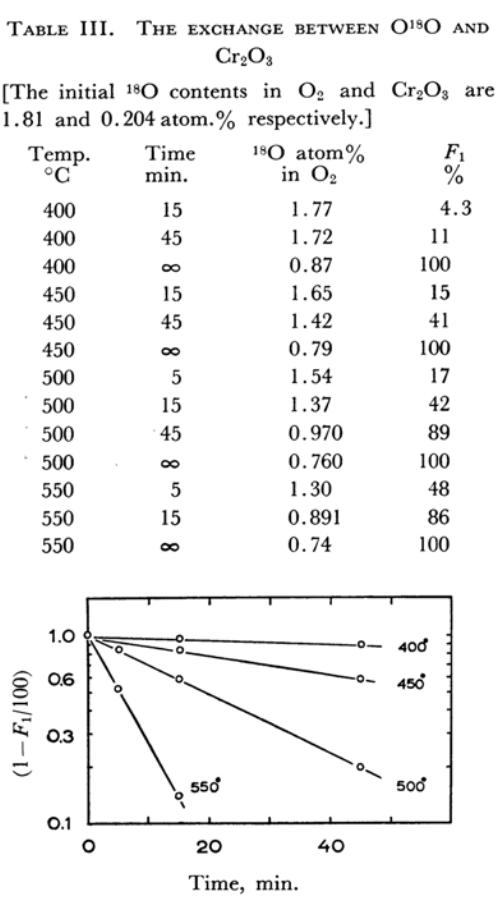

Fig. 2. Exchange between $O^{18}O$ and Cr_2O_3. Semilogarithmic plot of one minus fractional exchange versus time.

TABLE IV. THE APPARENT ENERGY OF ACTIVATION OF THE EXCHANGE REACTION BETWEEN OXYGEN AND OXIDE

Oxide	TiO_2	Cr_2O_3	MnO_2	Fe_2O_3	V_2O_5	Co_3O_4	NiO
A, kcal./mol.	39	31	16	21	41	14	15

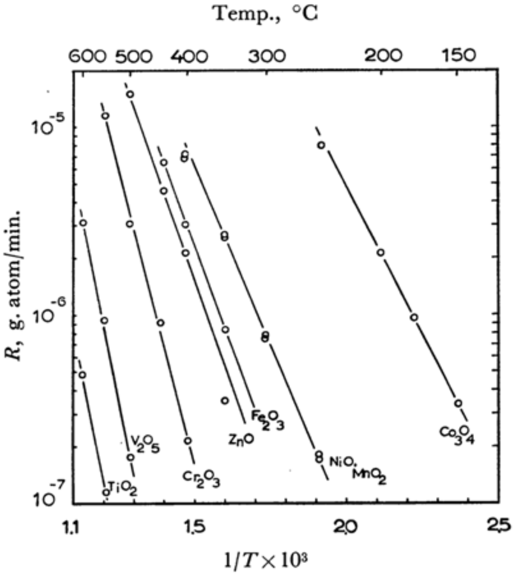

Fig. 3. Temperature dependence of rate of the exchange reaction between oxygen gas and various oxides.

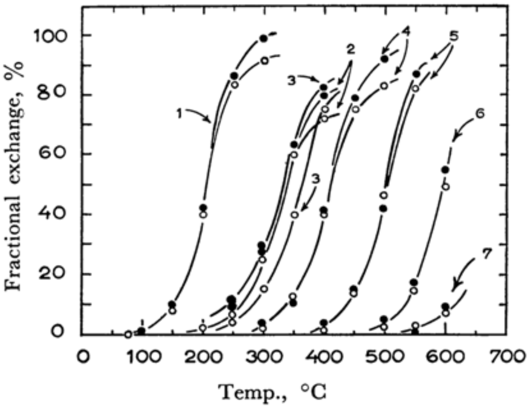

Fig. 4. Fractional attainment of the exchange reaction vs. reaction temperature.

Open circle, $O^{18}O$-CO_2
Filled circle, $O^{18}O$- Oxide
1, Co_3O_4; 2, MnO_2; 3, NiO; 4, Fe_2O_3;
5, Cr_2O_3; 6, V_2O_5; 7, TiO_2

is the reaction time, and where F_1 is the fractional attainment of the exchange reaction.

Equation 2 requires a linear relationship between $\log(1-F_1/100)$ and t, which are shown in Fig. 2. The values of R, which are calculated from the slopes of Fig. 2, are shown in Fig. 3, together with those of the other oxides examined. The apparent energies of activation, A, were obtained from the slopes of Fig. 3; they are listed in Table IV.

The values of F_1 at various temperatures, 15 min. after the beginning of the reaction are shown in Fig. 4. From Fig. 4, the reactivity of the oxides was estimated by means of the temperature threshold of the reaction. The order of reactivity of these oxides in relation to the exchange with oxygen is in the following sequence:

$$\text{(Higher activity)}\quad Co_3O_4>MnO_2=NiO>Fe_2O_3>Cr_2O_3>V_2O_5>TiO_2$$

As is shown in Fig. 4, the temperature threshold of the reaction is characteristic of each metal oxide. Above this temperature, the chemisorbed state of oxygen is probably in the form of O^-. In the case of exchange reaction between oxygen and zinc oxide,⁷⁾ the temperature threshold is about 350°C. Kwan et al.⁸⁾ studied the adsorbed state of oxygen on zinc oxide by the ESR method; they reported that at about 370°C the adsorbed state is in the form of O^-.

The Exchange between Oxygen and Carbon Dioxide on Metal Oxides.—As an example, the case of chromic oxide used as a catalyst is shown in Fig. 5 and Table V. The exchange of oxygen occurred at a measureable rate around 400°C. This result is similar to that shown in Fig. 1. The number of ^{18}O that the carbon dioxide had gained was less than that the oxygen had lost. This difference may be ascribed to the

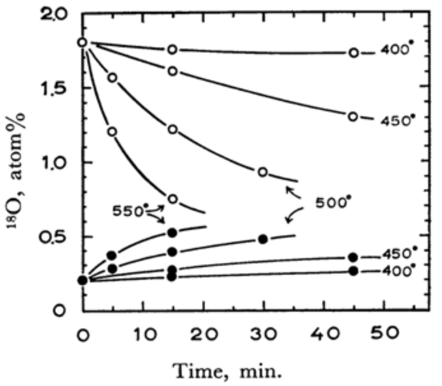

Fig. 5. Extent of the exchange reaction between $O^{18}O$ and CO_2 on Cr_2O_3.

Open circle, Decrease of ^{18}O in O_2
Closed circle, Increase of ^{18}O in CO_2

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7) T. Titani, T. Kiyoura and A. Adachi, This Bulletin, **38**, 2075 (1965).
8) M. Sedaka and T. Kwan, ibid., **38**, 1414 (1965).

TABLE V. THE EXCHANGE BETWEEN $O^{18}O$ AND CO_2 ON Cr_2O_3

(The initial $O^{18}O$ contents in O_2 and CO_2 are 1.81 and 0.204 atom% respectively.)

Temp. °C	Time min.	^{18}O atom% in CO_2	F_2 %
400	15	0.221	3.5
400	45	0.261	12.0
400	∞	0.685	100
450	15	0.264	14.0
450	45	0.366	38.9
450	∞	0.620	100
500	5	0.280	19.5
500	15	0.393	47.1
500	30	0.492	72.0
500	∞	0.607	100
550	5	0.383	44.0
550	15	0.527	83.2
550	∞	0.594	100

exchange with oxide. We have calculated F_2, the fractional attainment of the equilibrium of the reaction, from Eq. 3, where $CO^{18}O_t$ is the ^{18}O content of the carbon dioxide at time t, where $CO^{18}O_\infty$ is the ^{18}O content of the carbon dioxide when the reaction attains equilibrium, and where the numerical constant, 0.204, is the natural abundance of ^{18}O.

$$F_2=[(CO^{18}O_t-0.204)/(CO^{18}O_\infty-0.204)]\times 100 \quad (3)$$

A random distribution of ^{18}O among the oxygen, the carbon dioxide, and the exchangeable surface oxygen of the metal oxide being assumed, the value of $CO^{18}O_\infty$ was calculated using the amounts of the gases and the oxide used. The values of F_2 at different temperatures, 15 min. after the beginning of the reaction are shown in Fig. 4, together with those of the other oxides examined.

Using the results shown in Fig. 4, $\log[-\log(1-F_2/100)]$ was plotted against $1/T$. As is shown in Fig. 6, the plots give straight lines. The apparent energies of activation, obtained from the slopes of Fig. 6, are listed in Table VI. These values are very similar to those shown in Table IV.

For a measure of the catalytic activity of the oxides, the temperature threshold for the reaction was chosen. From Fig. 4, the temperatures at which the F_1 and F_2 reached 10% for the respective oxide, $t(10\%)$°C, may be obtained; these temperatures are summarized in Table VII. From Fig. 4 and Table VII, the order of the catalytic activity of these oxides in the reaction is found to be:

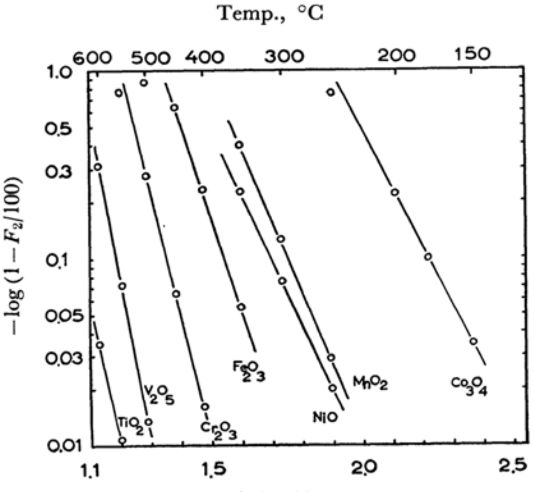

Fig. 6. Temperature dependence of $\log[-\log(1-F_2/100)]$.

$$\text{(Higher activity)}\quad Co_3O_4>MnO_2>NiO>Fe_2O_3>Cr_2O_3>V_2O_5>TiO_2$$

This is very close to the experimental results of the exchange between oxygen and oxide.

The following questions have been raised concerning the reaction mechanism:

(a) Does the reaction proceed through the interaction of the chemisorbed oxygen and the chemisorbed carbon dioxide?

(b) Does the reaction proceed through the exchange between these gases and the oxygen atoms of metal oxide ?

(c) Does the reaction proceed through both mechanisms a and b ?

As is shown in Table VII, the $t(10\%)$°C value was similar in both reactions, and the exchange between oxygen and carbon dioxide was observed only when the exchange between oxygen and oxide took place. The rate of the isotopic exchange

TABLE VI. THE APPARENT ENERGY OF ACTIVATION OF THE EXCHANGE BETWEEN $O^{18}O$ AND CO_2 ON VARIOUS OXIDES

Oxide catalyst	TiO_2	Cr_2O_3	Fe_2O_3	V_2O_5	Co_3O_4	NiO	MnO_2
A, kcal./mol.	41	30	24	41	15	15	17

TABLE VII. THE $t(10\%)$°C VALUES OF VARIOUS OXIDES

Oxide	TiO_2	V_2O_5	Cr_2O_3	Fe_2O_3	MnO_2	NiO	Co_3O_4
$t(10\%)$°C of F_1	605	530	440	345	260	260	150
$t(10\%)$°C of F_2	610	535	440	350	265	280	155

decreased in the following order on all the oxides examined:

$$CO_2\text{-Oxide} > O_2\text{-Oxide} \gtrsim O_2\text{-}CO_2$$

Moreover, the apparent energies of activation, shown in Tables IV and VI, are similar in the two reactions. According to these results, it is natural to think, that the reaction proceeds through the b mechanism; that is, the reaction consists of two consecutive and simultaneous reactions, 4 and 5, with Reaction 5 being far more rapid than Reaction 4, where MO represents metal oxide.

$$O^{18}O + MO = O_2 + M^{18}O \qquad (4)$$

$$CO_2 + M^{18}O = CO^{18}O + MO \qquad (5)$$

The c mechanism was excluded, because $\log[-\log(1-F_2/100)]$ against $1/T$ gives straight lines over an appreciable wide range of reaction temperature (Fig. 6).

The catalytic activity of the oxides with respect to the exchange between oxygen and water vapor$^{1-3)}$ is in the following sequence:

(Higher activity) $MnO_2 > Fe_2O_3 > Cr_2O_3 > NiO > V_2O_5 > TiO_2$

This is similar to the exchange between oxygen and carbon dioxide, with the exception of nickel oxide. A similar change in the catalyst activity of the oxides with respect to the homomolecular oxygen exchange,$^{4,5)}$ the oxidation of hydrogen,$^{9)}$ the oxidation of carbon monoxide,$^{10,11)}$ and the oxidation of hydrocarbon$^{12)}$ has been reported. The concept that the catalyst activity of the oxide is related to the heat of formation of the corresponding oxide was recently advanced by Tamaru$^{13)}$ and by Kwan and his collaborators$^{14)}$. We also attempted to plot the $t(10\%)$°C (the measure of the catalyst activity) against the heat of formation of these oxides. The plots thus obtained are shown in Fig. 7. As this figure shows, there is an approximately linear relationship between the catalyst activity of the oxides and the heat of formation of these oxides. In other words, the weaker the oxygen bond of the metal oxide, the faster the rate of oxygen exchange reaction.

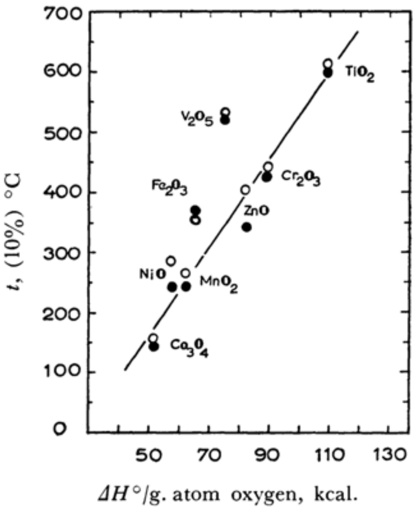

Fig. 7. The relation between the catalytic activity of metal oxides and the heat of formation of metal oxides.

Open circle, $O^{18}O$-CO_2 on oxide
Filled circle, $O^{18}O$-Oxide

The author wishes to express his deep thanks to Professor Toshizo Titani for his suggestions and guidance.

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