An Isotopic Exchange Reaction between Oxygen and Carbon Dioxide on Zinc Oxide

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Zinc oxide has been extensively studied by many investigators in terms of semiconductivity, and there are several works on the isotopic exchange between oxygen and zinc oxide.[1-6] However, only a little information is available on the isotopic exchange between oxygen and carbon dioxide on zinc oxide, or on that between carbon dioxide and zinc oxide. We have recently investigated the exchange reaction over the temperature range from 350 to 550°C in a rather qualitative way in order to provide preliminary data for further tracer studies. It appears worthwhile, therefore, to publish our results at this time. In this paper we shall discuss the general features of the isotopic exchange between carbon dioxide and zinc oxide, and that between oxygen and carbon dioxide on zinc oxide.

Experimental

Zinc oxide was prepared by the thermal decomposition of zinc oxalate at 500°C for 15 hr. in the presence of air; the B. E. T. area of the zinc oxide was 5.8 m^2/g. Zinc oxalate was obtained by the addition of an aqueous solution of ammonium oxalate to a solution of zinc chloride. The precipitate was washed so that it was free from chloride ions and then dried in the

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1) N. Morita, This Bulletin, **15**, 47 (1940).

2) E. R. S. Winter, *J. Chem. Soc.*, **1950**, 1170.

3) J. A. Barnard, E. R. S. Winter and H. V. A. Briscoe, ibid., **1954**, 1517.

4) T. J. Barry and F. S. Stone, *Proc. Roy. Soc.*, **A225**, 124 (1960).

5) G. K. Boreskov et. al., *Kinetika i Kataliz*, **4**, 388 (1963).

6) K. Hirota and M. Chono, *J. Catalysis*, **3**, 196 (1964).

air 110°C for 8 hr. prior to its thermal decomposition. Heavy oxygen, $O^{18}O$, was prepared in our laboratory by the thermal diffusion method;[7] its concentration was 1.81 atom.%. Carbon dioxide enriched in ^{18}O, $CO^{18}O$ (3.01 atom.%) was obtained by equilibrating ordinary carbon dioxide with ^{18}O enriched water, $H_2{}^{18}O$. As the source of ordinary oxygen and carbon dioxide, commercial gases were used with some purification. All the gases used were dried through a train of traps at -78°C. The search for an impurity in the gases used was made by using a mass spectrometer up to mass 100. They contained about 0.3 to 0.5% of one impurity, giving rise to mass 28 (nitrogen); none other was found in any detectable amount.

The exchange reaction was studied by the static batch method. The reaction vessel was made of borosilicate glass. For the exchange between carbon dioxide and zinc oxide, an accurately-weighed 400 mg. portion of zinc oxide was placed in the reaction vessel and was then outgassed at 500°C for 3 hr., using a mercury diffusion pump, through a liquid nitrogen trap. Then the temperature of the reaction vessel was adjusted to the desired temperature, and 1.5 ml. (N. T. P.) of ^{18}O-enriched carbon dioxide was introduced. The temperature range studied was from 350 to 550°C, with 50°C intervals. At desired time intervals, all the carbon dioxide was collected by a Toepler pump and the ^{18}O content of the carbon dioxide was analyzed by the use of a mass spectrometer. For the exchange between oxygen and carbon dioxide on zinc oxide, 2.7 ml. (N. T. P.) of the gas mixture of enriched oxygen and normal carbon dioxide or of normal oxygen and enriched carbon dioxide in a ratio of 1 to 1 was used. The amount of zinc oxide and the out-gassing and other procedures were the same as those in the exchange between carbon dioxide and zinc oxide. In order to maintain a constant pressure of the gas at each reaction temperature (14 cmHg for the CO_2-ZnO system and 25 cmHg for the O_2-CO_2-ZnO system), a reaction vessels of different volumes were chosen for the different temperatures; 19.0 ml. for 350°C, 20.0 for 400°C, 21.5 for 450°C, 23.0 for 500°C, and 25.0 for 550°C. The pressure change due to adsorption was ignored, since the accompanying pressure changes were less than 10% of the total pressure. In all the experiments, the pressure of the carbon dioxide was kept lower than the decomposition pressure of zinc carbonate (76 cmHg at 300°C).[8]

Results and Discussion

First, the isotopic oxygen exchanges between carbon dioxide and the surface of the reaction vessel, and between oxygen and the surface, and also the catalytic action of the surface were examined. It was found that, within the limits of experimental error, the reaction vessel surface did not participate in the exchange reaction.

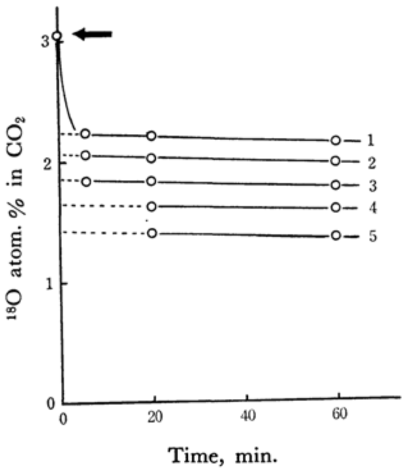

Fig. 1. Extent of the exchange reaction between $CO^{18}O$ and ZnO.
The arrow indicates the initial content of ^{18}O in CO_2.
1, 350°C 2, 400°C 3, 450°C 4, 500°C 5, 550°C

Exchange between Carbon Dioxide and Zinc Oxide.—The extent of the exchange reaction is shown in Fig. 1. The rate of the exchange was rapid, and within a few minutes after the 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 between the carbon dioxide in the gas phase and a certain part of the zinc oxide. After the initial fast reaction had finished, there was a slow downward drift of the ^{18}O content of the carbon dioxide. From Fig. 1, we obtained the definite ^{18}O content by the extrapolation of the drift line to time zero. From these quantities, we obtained the amount of the rapidly-exchangeable oxygen of the zinc oxide, n_s (gram atom per gram of zinc oxide). The calculation of n_s was carried out using Eq. 1,[2] where $^{18}O_0$ and $^{18}O_\infty$ were the initial and the definite ^{18}O content of the carbon dioxide respectively; the numerical constant, 0.204, was the ^{18}O natural abundance; n_g was the number of oxygen atoms in the amount of carbon dioxide used, and w was the weight of the zinc oxide used.

$$n_s w(^{18}O_\infty - 0.204) = n_g(^{18}O_0 - {}^{18}O_\infty) \qquad (1)$$

The values of n_s at various temperatures are listed in Table I. A random exposure of the crystalline face being assumed, the number of rapidly-exchangeable surface layers of the zinc oxide at various temperatures was obtained through the value of n_s, the surface area of zinc oxide, and the lattice constant of zinc oxide; they are also listed in Table I.

The pretreatment of the zinc oxide was changed from the normal evacuation at 500°C for 3 hr. to that at 600°C for 5 hr. However, no difference in the value of n_s was observed after this change.

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[7] Y. Horibe, *Isotopes and Radiation*, **2**, 25 (1959).
[8] K. Friedlich, *Stahl und Eisen*, **31**, 1901 (1911).

TABLE I. THE VALUE OF n_s AND THE NUMBER OF RAPIDLY-EXCHANGEABLE SURFACE LAYERS OF THE ZINC OXIDE

Temp., °C	350	400	450	500	550
n_s (g. atom./g.)·10^5	12.8	18.0	24.1	28.2	44.3
Number of exchangeable layers	0.7	0.9	1.2	1.5	2.3

Therefore, the rapidly-exchangeable oxygen of the zinc oxide was probably not a residual water nor a residual oxalate.

Below 400°C a part of the monolayer or the surface oxygen, between 400 to 450°C a monolayer, and above 450°C more than a monolayer participate in the fast initial exchange reaction.

The Exchange between Oxygen and Zinc Oxide.—The results are shown in Fig. 2. The experimental conditions were the same as those used with carbon dioxide.

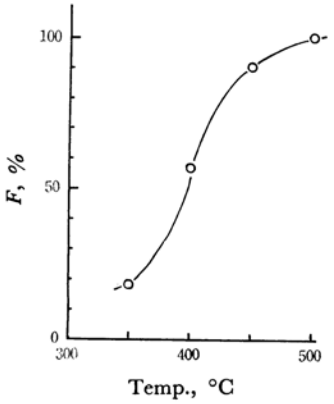

Fig. 2. Fractional attainment of the exchange between $O^{18}O$ and ZnO. Reaction time, 15 min.

$$F=100({}^{18}O_0-{}^{18}O_t)/({}^{18}O_0-{}^{18}O_\infty)$$

${}^{18}O_0$ and ${}^{18}O_t$ are the initial and the after 15 min. ${}^{18}O$ content in O_2. ${}^{18}O_\infty$ is the equilibrium content of ${}^{18}O$ in O_2, calculated from the amounts of O_2 gas used and value of n_s.

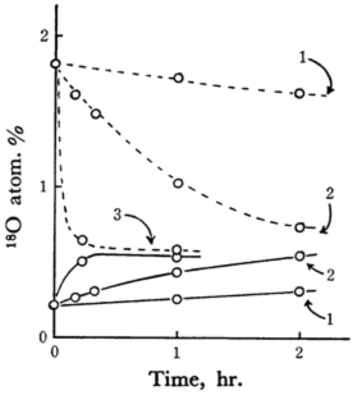

Fig. 3. Extent of the exchange reaction between $O^{18}O$ and CO_2.
Full line, increase of ${}^{18}O$ in CO_2
Broken line, decrease of ${}^{18}O$ in O_2
1, 450°C 2, 500°C 3, 550°C

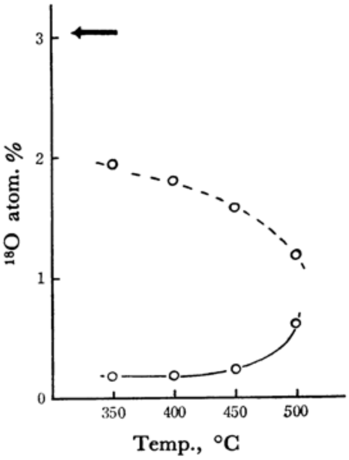

Fig. 4. ${}^{18}O$ in CO_2 and O_2. Reaction time, 1 hr.
Full line, $O^{18}O$. Broken line, $CO^{18}O$.
The arrow indicates the initial content of ${}^{18}O$ in CO_2.

The Exchange between Oxygen and Carbon Dioxide on Zinc Oxide.—The exchange of oxygen occurred at a measurable rate around 450°C. The decrease in the ${}^{18}O$ content in oxygen and the increase in carbon dioxide are shown in Fig. 3. The number of ${}^{18}O$'s that the carbon dioxide had gained was less than that which the oxygen had lost. This difference may be ascribed to the exchange with zinc oxide. In the above-mentioned experiments, ${}^{18}O$-enriched oxygen and normal carbon dioxide were used as the starting materials. The results of the exchange experiments, in which the ${}^{18}O$-enriched carbon dioxide and normal oxygen were used as the starting materials, are shown in Fig. 4. A considerable decrease in the ${}^{18}O$ content in the carbon dioxide was observed at 350°C, but no increase in the ${}^{18}O$ content of the oxygen was observed up to 400 to 450°C. This finding indicates that the ${}^{18}O$ which were transferred from carbon dioxide to zinc oxide were not transferred to oxygen up to 400 to 450°C. On the other hand, the exchange between oxygen and zinc oxide took place, even at 350°C, in the absence of carbon dioxide (see Fig. 2).

Schwab,[9] and Matsuura et al.[10] have reported that carbon dioxide inhibits the oxidation of carbon monoxide on zinc oxide. In our experiments also, carbon dioxide acts as an inhibitor of the exchange between oxygen and zinc oxide. For that reason, no exchange is observed up to 400 to 450°C in the presence of carbon dioxide. Figures. 1, 2, and

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[9] G. M. Schwab, *Z. Physik. Chem.* (*Neue Folge*), 1, 42 (1954).

[10] I. Matsuura, Y. Kubokawa and O. Toyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 81, 997 (1960).

3 indicate that the rate of the isotopic exchange decreases in the following order;

$$CO_2\text{-}ZnO > O_2\text{-}ZnO > O_2\text{-}CO_2$$

According to these results, it was concluded that the isotopic exchange between oxygen and carbon dioxide takes place through the exchange between these gases and the oxygen atoms of zinc oxide, and that the limiting step is the exchange with oxygen.

Summary

Isotopic oxygen exchange reactions between carbon dioxide and zinc oxide, and between oxygen and carbon dioxide on zinc oxide, have been studied by the static method in the temperature range from 350 to 550°C. At any temperature carbon dioxide exchanges its oxygen atoms with those of zinc oxide rapidly. Within a few minutes after the initiation of the reaction, an isotopic equilibrium is established between the carbon dioxide in the gas phase and a certain part of the zinc oxide. It has been found that the isotopic exchange between oxygen and carbon dioxide on zinc oxide takes place through the exchange between these gases and the oxygen atoms of the zinc oxide, that the limiting step is the exchange with oxygen, and that the carbon dioxide acts as an inhibitor of the exchange between oxygen and zinc oxide.

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