The Thermal Decomposition of Zinc Oxide in an Oxygen and a Nitrogen Stream

By Tatsuya IMOTO, Yoshio HARANO and Yasuhide NISHI

(Received December 14, 1964)

In a previous paper[1] on the thermal decomposition of zinc oxide in vacuo, it was reported that oxygen and zinc are not evolved equally with stoichiometric composition, but that more oxygen is released than zinc. If zinc oxide decomposes by such a process, the rate of the decomposition of zinc oxide will be affected by the oxygen pressure. As far as we know, very few investigations of the rate of the decomposition of zinc oxide in an oxygen or a nitrogen stream have been made except for Moore and Williams's.[2] Their report, however, shows neither the initial amount of zinc oxide nor the pressures of the flowing gases, i. e., oxygen and nitrogen. Therefore, it is very difficult to gather enough quantitative information concerning the effect of oxygen on the rate of decomposition.

Meanwhile, we[3] have studied the kinetics of the reduction of zinc oxide by hydrogen over the range of temperature, 617—762°C, with a hydrogen pressure of 10—95 mmHg, and have deduced that the reduction proceeds via the following two processes: the decomposition of zinc oxide into oxygen and zinc vapor, and the reaction of the evolved oxygen with hydrogen. When the amount of zinc oxide is smaller than that of hydrogen, the decomposition process of zinc oxide controls the overall reaction.[4] In this case, the effect of nitrogen gas on the decomposition of zinc oxide is found to be represented by the following relation:

$$\frac{\text{Reduction rate by mixed gas}}{\text{Reduction rate by hydrogen}}=1-\theta_{N_2}$$

where θ_{N_2} is expressed by a form similar to the Langmuir-type adsorption isotherm. Here, the rate of the decomposition of zinc oxide is expected to be affected by the nitrogen pressure. In this expectation the present work was carried out.

Experimental

The apparatus is the same as that used in a previous work[6] on the reduction of zinc oxide by hydrogen by a flow method at low pressures. In this work, oxygen or nitrogen was used as the flowing gas instead of hydrogen. The samples used in this work are that used in our previous papers[1,3-6] and a sintered one. The former is a commercial product supplied by the Sakai Chemicals Co., Ltd., while the latter is prepared from the former by sintering it at 900°C for several hours and then sieving it (−40+60 mesh). The decomposition time was 200 min. In this period, the amount of decomposed zinc oxide was very small compared with its initial amount, and the change of its surface area by decomposition was negligibly small. Hence, the rate of decomposition can be expressed as $\Delta w/w_0t$, where Δw is the total weight loss for the decomposition time, w_0 is the initial amount, and t is the decomposition time.

---

[1] T. Imoto, Y. Harano and Y. Nishi, This Bulletin, 37, 1181 (1964).

[2] W. J. Moore and E. L. Williams, *J. Phys. Chem.*, **63**, 1516 (1959).

[3] T. Imoto, Y. Harano and Y. Nishi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 115 (1963).

[4] T. Imoto, Y. Harano, Y. Nishi and S. Masuda, ibid., **85**, 106 (1964).

[5] T. Imoto, Y. Harano, Y. Nishi and S. Masuda, This Bulletin, 37, 441 (1964).

[6] T. Imoto, Y. Harano and Y. Nishi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **86**, 485 (1965).

Results and Discussion

Experimental results at 740°C are shown in Fig. 1. The ordinate is the rate of decomposition, and the abscissa is the pressures of oxygen or nitrogen.

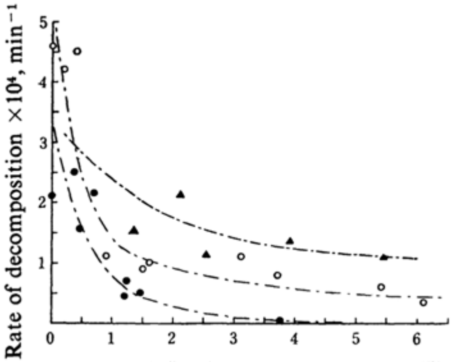

Fig. 1.

○………unsintered ZnO
● ▲…sintered ZnO
O_2 N_2

The Effect of Oxygen.—Figure 1 shows that the rate of decomposition decreases with the increase in oxygen pressure, while the effect of oxygen is much greater than that of nitrogen. No sintered zinc oxide decomposed at about 10^{-2} mmHg of oxygen pressure, a level which is nearly equal to the decomposition equilibrium pressure at 740°C. These observations clealy reveal that oxygen in the gas phase retards the evolution of oxygen from the surface of zinc oxide. This is quite reasonable, since the higher oxygen pressure means a higher oxygen concentration in the vicinity of the zinc oxide surface.

The Effect of Nitrogen.—Figure 1 shows that the rate of decomposition also decreases with the increase in nitrogen pressure. The results obtained are applied to Eq. 1. From Eq. 1, one gets:

$$\theta_{N_2}=1-\frac{r_{N_2}}{r_{N_2=0}} \tag{2}$$

were $r_{N_2=0}$ is the rate of decomposition in vacuo, and r_{N_2} is that in the nitrogen stream. Now, θ_{N_2} will be expressed by Eq. 3:⁴⁾

$$\theta_{N_2}=\frac{K_{N_2}P_{N_2}}{1+K_{N_2}P_{N_2}}=1-\frac{1}{1+K_{N_2}P_{N_2}} \tag{3}$$

The combination of Eqs. 2 and 3 gives:

$$\frac{r_{N_2}}{r_{N_2=0}}=\frac{1}{1+K_{N_2}P_{N_2}} \text{ or } \frac{r_{N_2=0}}{r_{N_2}}=1+K_{N_2}P_{N_2} \tag{4}$$

When we substitute experimental values into Ep. 4, K_{N_2} is calculated to be 533 mmHg^{-1}. This value is in fairly good areement with that of a previous paper⁴⁾ ($K_{N_2}=657$ mmHg^{-1}). In both cases the same sintered samples were used. The reactivity of zinc oxide depends very much on the nature of the surface state of the samples. It seems that the fluctuation in the experimental values and the difference between the two values for K_{N_2} may originate in the variation in the surface state of zinc oxide. These results seem to verify our previous deduction that nitrogen interacts with the surface of zinc oxide to produce a retarding substance. At present, we have very little information about the nature of this retarding substance.

Department of Applied Chemistry
Faculty of Engineering
Osaka City University
Sumiyoshi-ku, Osaka