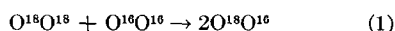


## LETTER TO THE EDITOR

## Intermolecular Exchange Reaction of Gaseous Oxygen on Zinc Oxide at Low Temperatures\*

Though a number of reports have been published about the adsorption of oxygen on zinc oxide, the nature of the chemisorbed species is not clearly determined yet (1). Some authors assume that the chemisorbed species at lower temperatures would be  $O_2^-$  ion, but Barry and Stone suggested in their report (2) a dissociative species,  $O^-$  ion, on the oxide at  $-193^\circ\text{C}$ , because the intermolecular exchange reaction of gaseous oxygen was measured, as expressed by the equation:



Since their suggestion of O-O bond scission at such a low temperature is very interesting, we repeated their experiment by use not only of the same oxide but also of the ones doped with a cation of different valency. The experiment has confirmed the result of Barry and Stone, but the possibility of the bond scission has not been derived as a necessary conclusion, as will be described.

Concentration of  $O^{18}$  in the oxygen used was 15.5 atom %<sup>†</sup>, containing a larger amount of nitrogen (67%), because the oxygen of higher  $O^{18}$  concentration had been diluted with air. Therefore, its  $O^{18}O^{18}$  mole % was larger than the value calculated under the assumption of the equilibrium between the isotopic oxygen molecules. The value  $K'$  of the gas defined by  $(O^{16}O^{18})^2 / (O^{18}O^{18})(O^{16}O^{16})$  was 0.56,

which was much smaller than the corresponding equilibrium value  $K_e$  (about 4 at  $0^\circ\text{C}$ ).

Zinc oxide was prepared by calcining pure zinc carbonate for 12 hr at  $500^\circ\text{C}$ . Doped oxides were prepared by addition of the solution (6 cc) of aluminum or lithium nitrate to the zinc oxide (3 g) prepared by calcination for 8 hr, followed by dehydration; they were kept *in vacuo* at  $500^\circ\text{C}$  for 4 hr. The doped amount of both nitrates was 3.0 mole % as alumina and lithia to the zinc oxide. The surface areas determined by the BET method were 40.9 for ZnO, 58.7 for ZnO- $Al_2O_3$ , and 33.1 for ZnO- $Li_2O$ , respectively, in  $\text{m}^2/\text{g}$ .

The mass spectrometer for the isotopic measurement was an apparatus of the Hitachi RMU-5 type, installed at the Institute for Protein Research of our University.

The degree of exchange of the products after 30 min reaction is expressed by the  $K'$  values and is shown in Table 1,

TABLE 1  
DEGREE OF EXCHANGE,  $K'$ ; AFTER 30 MINUTES

Temp. ( $^\circ\text{C}$ )	ZnO	ZnO- $Al_2O_3$	ZnO- $Li_2O$
-193	0.9 <sub>5</sub>	1.6 <sub>3</sub>	0.5 <sub>9</sub>
- 80	1.3 <sub>5</sub>	3.5 <sub>6</sub>	0.6 <sub>6</sub>
0	4.2 <sub>6</sub>	4.0 <sub>3</sub>	0.4 <sub>3</sub> <sup>a</sup>

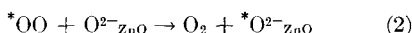
<sup>a</sup> Atom % of  $O^{18}$  decreased to 10.5 in the case of ZnO- $Li_2O$  from the initial value (15.5%).

\* A part of the paper presented at the Catalyst Symposium (Japan) at Sapporo, Sept. 1963.

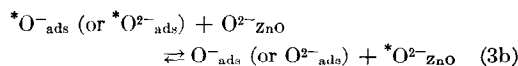
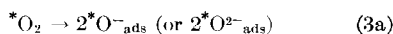
<sup>†</sup> The heavy oxygen was enriched by the thermal diffusion method in our laboratory (3).

where the numerals are the mean of two or three runs, admitting 3.0 cc (STP) of the gas to 3.0 g of the oxide.

Table 1 shows that the intermolecular exchange proceeds below 0°C, in agreement with the report of Barry and Stone, so far as ZnO and ZnO–Al<sub>2</sub>O<sub>3</sub> are concerned, i.e.,  $K'$  values increased in the cases of ZnO and, more markedly, of ZnO–Al<sub>2</sub>O<sub>3</sub> from the initial value of 0.56 to the value coinciding with  $K_e$  at 0°C in both cases. However, since O<sup>18</sup> atom % of all the runs did not change below 0°C, the intermolecular exchange observed must be due to the scheme shown by Eq. (1) and makes implausible the isotopic exchange with the oxygen ion in the oxide, as expressed by

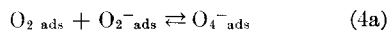


On the other hand, in the case of ZnO–Li<sub>2</sub>O the  $K'$  value remained practically the same below 0°C, and rather decreased at 0°C. Besides, the concentration of O<sup>18</sup> decreased to 10.5 atom % at 0°C, indicating the occurrence of reaction (2). Such a doping effect of lithia suggests that the chemisorbed state of oxygen on the lithia-doped oxide differs from the states on the non-doped and alumina-doped ones. Considering the easy exchangeability on ZnO–Li<sub>2</sub>O with the oxide oxygen ion, the chemisorbed species on this doped oxide may be an atomic ion, which reacts with the oxide as follows, making the first stage the rate-determining step:

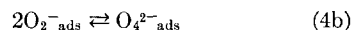


However the doping effect of alumina teaches us that some of the states of oxygen

adsorbed on zinc oxide may also be charged below 0°C, besides neutral O<sub>2</sub>, and the chemisorbed charged species would be O<sub>2</sub><sup>−</sup> ion. Therefore an associative intermediate can be assumed for the exchange to proceed at −193°C on ZnO and ZnO–Al<sub>2</sub>O<sub>3</sub>, e.g.,



or



Formation of these dimeric intermediates of oxygen may not be so curious, because the neutral O<sub>4</sub> molecule was reported by Lewis (4) to be stable at such low temperatures.

Chemisorbed states of oxygen at temperatures higher than 0°C will be reported elsewhere in the near future, so as to discuss Eq. (3) in more detail.

#### REFERENCES

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