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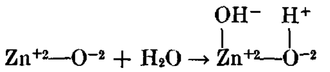
NOTES

Zinc Oxide–Water Vapor System. Mechanism of Adsorption from Electrical Conductivity Studies

The information in the literature on the chemisorption of water vapor on zinc oxide is not sufficient to explain the various observations about the shift reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ in the presence of catalysts containing zinc oxide as one of the major components. Atherton *et al.* (*1*) concluded from ir measurements that the chemisorption is dissociative in nature:



$$Zn^{+2}—O^{-2} + H_2O \rightarrow \overset{OH^-}{\overset{|}{Zn^{+2}}}—\overset{H^+}{\overset{|}{O^{-2}}}$$

However, ir measurements cannot be carried out with shift catalysts which are reduced and activated before reaction and which become opaque to infrared radiation. To obtain more information about the mechanism of adsorption, we have studied the effect of water vapor adsorption upon the electrical conductivity of zinc oxide.

Zinc oxide was obtained by oxidation of zinc metal and was cured at 500°C for 10 hr in air. The sample was pressed into 4 × 8 mm pellet and held between two spring loaded platinum discs. Platinum and platinum-rhodium thermocouples were welded to the platinum discs to measure the temperature and resistance. The conductivity cell could be evacuated to 10^{-5} Torr. The conductivity measurements were carried out with an ac (3 kc/s) bridge and the sample temperature was measured to ±1°C by means of a potentiometer. Hydrogen was purified by a Deoxo catalyst and dried at −196°C. Air was passed over soda lime and phosphorous pentoxide to remove carbon dioxide and moisture. Water was deaerated by repeated freezing and thawing in a vacuum. The pressure was measured by means of a mercury manometer (for pressure greater than 1 Torr) and a thermocouple gauge (for $1\text{–}10^{-3}$ Torr).

The sample was activated by reduction in a flow of hydrogen at 250°C for 12 hr followed by evacuation at 386°C for 3 hr and then subjected to the various treatments indicated below:

(1) cooling in vacuum to 75°C;

(2) treatment with $10 \times 10^{-3}\text{–}20 \times 10^{-3}$ Torr dry air at 386°C for various intervals of time, evacuated till the conductivity became constant and cooled in vacuum to 75°C;

(3) treatment with dry air as in (2) but at 75°C;

(4) treatment with 10 Torr hydrogen for 1 hr at 75°C after treatment (1) and evacuated for 1 min.

Water vapor at a pressure of 24 Torr was introduced into the sample chamber at 75°C after every treatment and the conductivity at different intervals of time was noted. The change in conductivity is given by $\Delta\sigma = \sigma_0 - \sigma_t$ where σ_0 = initial conductivity and σ_t = conductivity after time t. After each adsorption, the sample was regenerated by the activation process outlined above. From the results presented in Figs. 1 and 2 it can be seen that the conductivity continuously decreased upon adsorption of water vapor, but if the sample is subjected to pretreatment (3) there is initially a sharp increase in conductivity. The phenomenon can be explained if it is assumed that the H_2O molecule is dissociatively adsorbed as OH and H

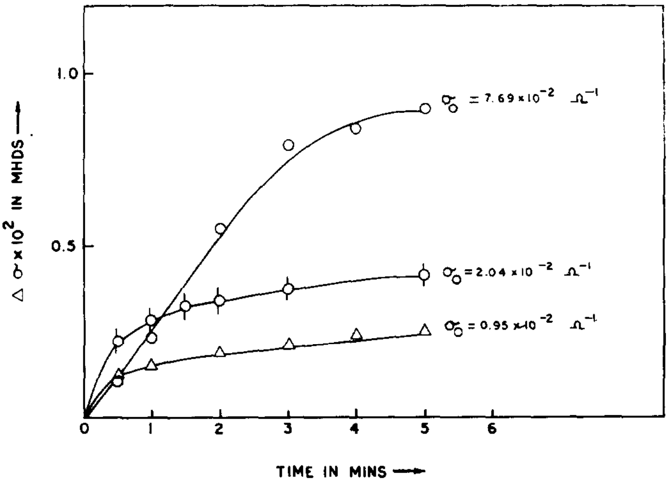


FIG. 1. Change of conductivity with time in presence of water vapor at 75°C after treatment (1) (—○—), and (2) (—ϕ—) (—△—).

radicals on a $Zn^+ \cdot Zn^+$ ion pair site. The unpaired electron of the OH radical combines with the free electron of the Zn site forming a strong covalent bond and the trapping of the free electron will cause a decrease in conductivity. The chemisorption of the H radical takes place on the other Zn^+ site of the ion pair as Zn^+ H. Such adsorption (*2*) without involving electron transfer occurs below 100°C and does not affect the electrical conductivity of zinc oxide. If hydrogen is preadsorbed as in treatment (*4*) adsorption of water vapor is inhibited and no change in conductivity takes place.

The chemisorption of H_2O molecules on $Zn^+ \cdot Zn^+$ ion pair sites is also inhibited if such sites are occupied by strongly adsorbed oxygen due to pretreatment (2) (Fig. 1). According to Kokes (*3*), at 350°C and above oxygen is adsorbed as the O^{2-} ion on Zn^+ sites and it is quite possible that $Zn^+ \cdot Zn^+$ ion pairs can also be involved. However, as suggested by Uchida and Ogino (*4*), if the temperature of oxygen adsorption is 100°C or less oxygen is weakly held by $Zn^+ \cdot Zn^+$ ion pairs as $\overset{O^-}{Zn^+ \cdot Zn^+}$ species; in that case it is possible that the

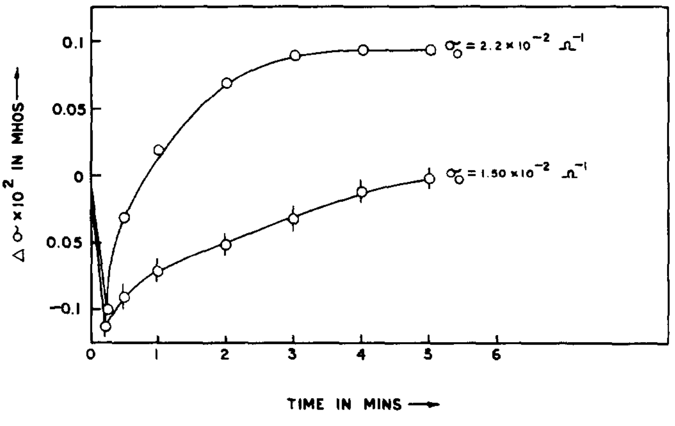


FIG. 2. Change of conductivity with time in presence of water vapor at 75°C after treatment (3).

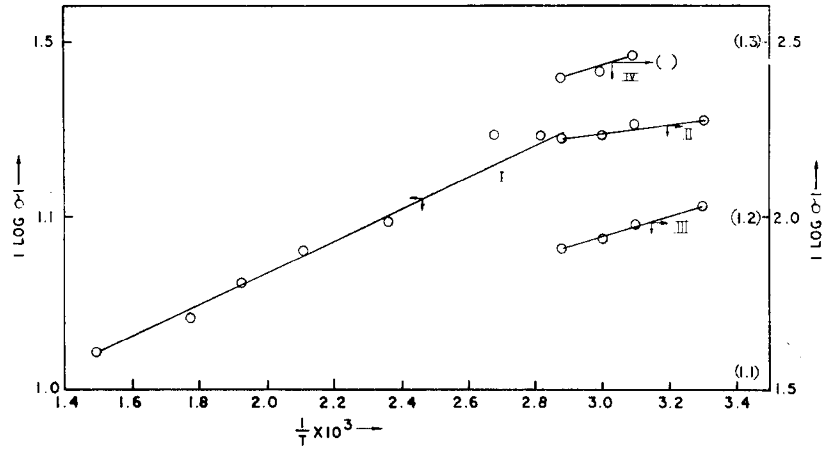
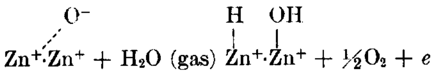


FIG. 3. Arrhenius plots for zinc oxide after different type of treatment (see Table 1).

water molecules can displace the weakly adsorbed oxygen ions and become adsorbed:



$$\overset{O^-}{Zn^+}\cdot Zn^+ + H_2O\ (gas)\ \overset{H}{Zn^+}\cdot\overset{OH}{Zn^+} + \tfrac{1}{2}O_2 + e$$

The liberation of the electron trapped by the O^- ion causes an initial rise in conductivity as can be seen Fig. 2.

The conductivity of the sample was measured in vacuum at various temperatures and under the conditions indicated in Table 1. From the plots of log σ vs $1/T$ (Fig. 3), the activation energy ϵ shown in Table 1 was calculated.

The low activation energy (0.02 eV) of conduction for the vacuum activated sample is due to ionization of Zn·Zn atom pairs as suggested by Miller (*5*). A similar value of ϵ is obtained after water vapor adsorption on the evacuated surface because in this case $Zn^+ \cdot Zn^+$ ion pairs are occupied and Zn·Zn atom pairs remain free. But oxygen adsorption at 75°C (treatment (3)) traps the free electron of the Zn·Zn atom pairs. Conductivity can then take place through ionization of $Zn^+ \cdot Zn^+$ ion pairs since oxygen is weakly held at the latter sites. Consequently the activation energy is increased to 0.26 eV. However, water vapor adsorption after treatment (3) increased the activation energy still further to 0.59 eV: we consider that the free electrons of $Zn^+ \cdot Zn^+$ ion pairs are also trapped in this case and ionization of interstitial Zn atoms provides the conduction electrons.

TABLE 1

Curve no.	Nature of sample treatment	ϵ in eV
I	Treatment (1)	0.02
II	Treatment (2)	0.26
III	H_2O adsorption at 75°C after treatment (3). Evacuation at 75°C	0.59
IV	H_2O adsorption at 75°C after treatment (1). Evacuation at 75°C	0.018

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