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WATER CHEMISORPTION AND ELECTRICAL CONDUCTIVITY OF ZINC OXIDE

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Abstract

The effect of adsorption of water vapour on the electrical conductivity was investigated on zinc oxide, both pure as well as doped, containing 0.05, 0.1 and 1 mole percent of gallium and lithium. Water was found to undergo chemisorption at temperatures varying from 150~250°C. At 230°C and above chemisorption was accompanied by evolution of gas which was identified as hydrogen. The electrical conductivity decreased on water chemisorption and the volume of gas evolved subsequent to chemisorption was found to be related to the decrease in electrical conductivity. The experimental observations were interpreted to suggest that on n-type ZnO semiconductor, water undergoes dissociative chemisorption leading to the formation of O²⁻ and H⁺ ions and that the hydrogen ions subsequently get attached to quasi-free electrons and are liberated as gaseous hydrogen.

Introduction

The main constituents of low temperature shift reaction catalysts are the oxides of zinc and copper. In a previous publication¹⁾ it was shown that the oxide of copper is responsible for chemisorption of carbon monoxide—an intermediate step in the shift reaction. In the present investigation an attempt has been made to study the role of zinc oxide, the other important ingredient of the shift catalyst. In view of the fact that the oxide of copper is responsible for carbon monoxide chemisorption it was but logical to suppose that zinc oxide is likely to interact with water vapour, another probable intermediate step in the overall reaction.

Several workers have reported correlation between electrical conductivity and catalytic activity of non-stoichiometric n-type zinc oxide²⁻⁵⁾. The work of CIMINO *et al.*⁶⁾, HECKELSBURG *et al.*⁷⁾ and others^{8,9)} demonstrated direct correlation between electrical conductivity and catalytic activity for hydrogen chemisorption on pure and doped zinc oxide. From literature survey it

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appersars that several workers^{4,10~14)} have studied water chemisorption on ZnO, TiO₂ and α -Fe₂O₃, but no one has so far reported the influence of adsorption of water on electrical conductivity of these oxides.

In the present work, zinc oxide, pure as well as doped, containing 0.05, 0.1 and 1.0 mole percent of lithium and gallium was used for investigating the electrical conductivity and the water chemisorption characteristics.

Experimental

The zinc oxide was prepared by the well-known technique of precipitation followed by thermal decomposition⁷⁾. Zinc oxalate was precipitated from a hot solution of zinc nitrate by the addition of oxalic acid (B.D.H. Analar), the excess of oxalic acid being removed by washing with hot water. The zinc oxalate thus prepared was heated at 400°C for 4 hrs. to produce zinc oxide. Impregnation method was used for doping, according to which weighed quantities of zinc oxide samples were soaked in dilute solutions of the nitrates of lithium and gallium, the volume and the strength of the solutions being so adjusted that the soaked mass on drying contained definite mole percentages of respective doping agents. The soaked mass was dried on water bath and finally heated to 400°C (Hüttig temperature for zinc oxide). Prior to measurements of either electrical conductivity or adsorption of water, every sample of zinc oxide, either doped or pure was degassed in vacuum at 400°C for about 5 hrs. The above treatment was considered sufficient to introduce non-stoichiometry in ZnO.

A standard B.E.T. assembly¹⁾ was used, with minor modification for adsorption of water. There was a separate limb connected to the apparatus and this contained one bulb for storage of pure water and a second bulb directly connected with the first one which was used as a condenser for the distillation of water. During distillation of water the condenser bulb was put in a liquid nitrogen bath and the entire assembly was connected to vacuum so as to ensure removal of dissolved gases from water. A stopcock was introduced in between this attachment and the main apparatus. The apparatus and procedure used for the measurement of electrical conductivity have been described elsewhere¹⁾. The apparatus was however slightly modified in this case for measurement of electrical conductivity of zinc oxide on chemisorption of water vapour. The conductivity apparatus was connected with a separate bulb containing pure water and attached to main unit through a stopcock.

Results and Discussion

The electrical conductance data for zinc oxide compacts are presented in Figs 1, 2 and 3. The conductance data presented in Figures were obtained with cylindrical compacts of almost identical dimension (6~7 mm diam. and 2~3 mm thickness).

The relation between electrical conductance and temperature for pure zinc oxide as well as doped samples is presented in Fig. 1, where $\log \sigma$ is shown to be a linear function of $1/T$ and conductance increases exponentially with temperature. This indicates the semi-conducting properties of the

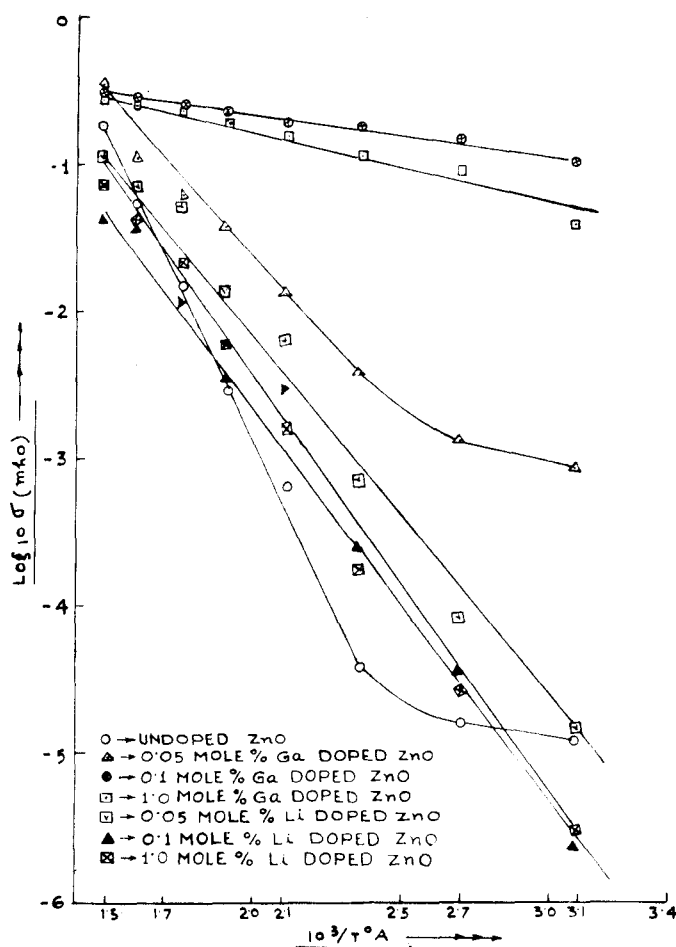


Fig. 1. Relation of electrical conductance to temperature.

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samples. The sharp change in the slope of the two curves (undoped zinc oxide and 0.05 mole percent gallium doped zinc oxide) at higher temperature indicates that in this region of temperature the conductance is essentially intrinsic, whereas at lower temperature it is dominated by impurity⁵⁾.

The electrical conductivity of zinc oxide containing different mole percentage of altrivalent ions are shown in Fig. 2. The increase in conductivity from addition of trivalent Gallium and decrease with monovalent lithium clearly indicates the *n*-type character of zinc oxide¹⁰⁾.

Fig. 3 shows the changes in electrical conductance of zinc oxide on chemisorption of water vapour. The conductance decreases with increasing partial vapour pressure of water at 250°C. This phenomenon clearly indicates depletive chemisorption in this temperature range.

Kinetics of adsorption of water vapour on zinc oxide was studied at three different temperatures, namely, 215, 230 and 250°C. It was observed that water vapour undergoes chemisorption on zinc oxide at 215°C, but at higher temperatures (230 and 250°C), adsorption was followed by the evolution of gases in the system. This interesting observation was subsequently studied in details. During the measurement of adsorption it was observed that on introduction of water vapour to the system containing zinc

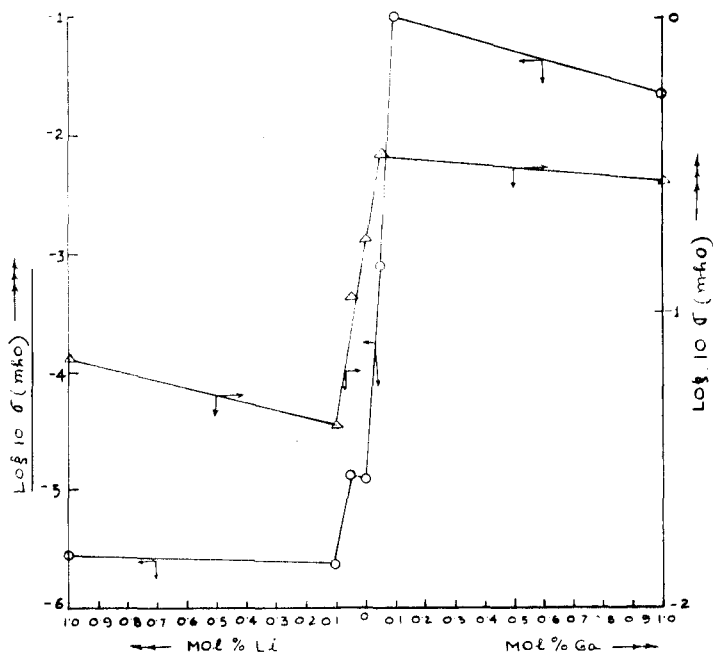


Fig. 2. Electrical conductance at 50°C (●) and 400°C (Δ).

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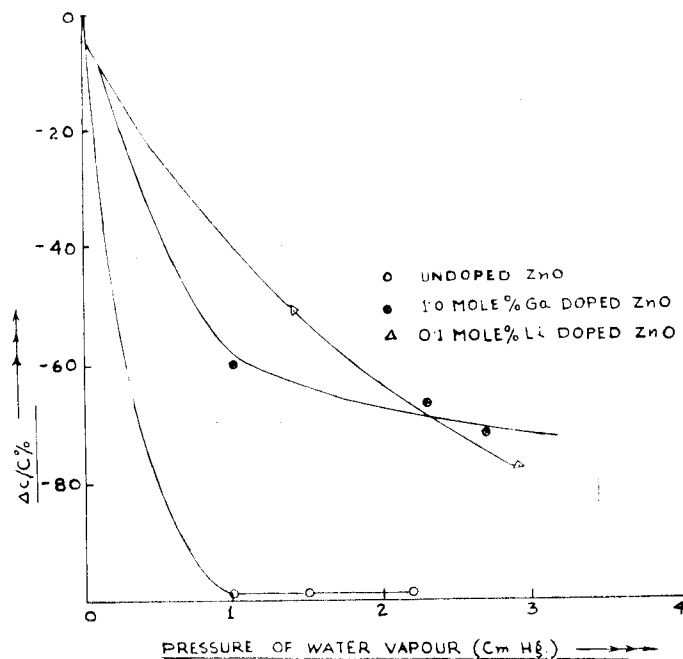


Fig. 3. Relation between partial pressure of water vapour in cm. and change in electrical conductance at 250°C.

oxide, the pressure recorded a steady decrease as was to be expected, for a minute or so because of expansion of water vapour into the dead space as well as due to adsorption. Subsequently however the pressure in the system became steady showing attainment of a pseudo-equilibrium. This was followed by gradual development of pressure in the system as recorded in the manometer. It is thus clear that hydrogen evolution was preceded by a period of induction. The results are presented in Table 1. It will be seen that the pressure that developed subsequent to chemisorption is related to the nature of alervalent ions added to zinc oxide. In the present case, gallium doped sample records the maximum development of pressure while lithium doped sample shows a fall in pressure due to adsorption. Further, it was noted that the development of pressure subsequent to chemisorption depends on the partial pressure of water vapour in the system upto a certain limit beyond which any further increase in the vapour pressure of water does not result in further development of pressure in the system. This is evident from the data recorded in lower three horizontal columns of Table 1. Here ZnO was brought into contact with water vapour in three successive

TABLE 1.

Adsorbent	Temp. of Adsorption (°C)	Partial pressure of water vapour before adsorption (cmHg)	Volume of water vapour adsorped at S.T.P./gm. of catalyst. (cc)	Pressure on attainment of Pseudo-equilibrium (cmHg)	Final pressure (cmHg)	Pressure buildup (cmHg)	Vol. of H ₂ evolved (S.T.P.)/gm. of catalyst. (cc)
1. ZnO (1.71 gm.)	240	2.0	0.27	1.6	1.75	0.15	0.11
2. ZnO+1 mole % Ga (1.55 gm.)	240	2.0	0.33	1.6	1.90	0.30	0.25
3. ZnO+1 mole % Li (2.24 gm.)	240	2.0	0.21	1.6	1.20	-0.40	No gas evolution
4. ZnO (1.71 gm.)	240	0.6	—	0.45	0.55	0.10	—
ZnO (1.71 gm.)	240	2.0	0.27	1.5	1.55	0.05	0.11
ZnO (1.71 gm.)	240	2.15	—	2.0	2.0	—	—

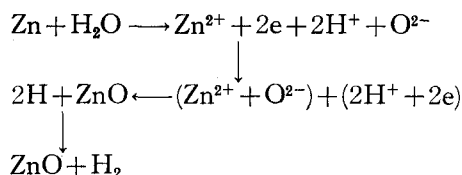
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stages at partial pressures of 0.6, 2 and 2.15 cmHg, respectively and the corresponding build up of pressures are shown in the last three figures in the vertical column. It will be observed that the maximum cumulative pressure developed in the system is $0.10 + 0.05 = 0.15$ cmHg which is same as obtained in case of the first sample. In other words an equilibrium appears to be attained with respect to the evolution of gas when the partial pressure of water vapour reaches an upper limit (1.5 cmHg). The evolved gases were analysed by a Gas Chromatograph (Podbielniak gas chromatograph, model No. 9870 USA) and hydrogen gas was identified in all cases. The volume of hydrogen evolved in different cases is shown in the last vertical column (Table 1). The gradual decline in the electrical conductance of zinc oxide on water chemisorption (Fig. 3) coupled with the fact that chemisorption of water is followed by hydrogen evolution strongly suggests that water undergoes dissociative chemisorption leading to the formation of either O^{2-} and H^+ ions or OH^- and H^+ ions, and the hydrogen ions once formed remove quasi free electrons from the interstitial position of zinc oxide lattice and is finally evolved as hydrogen gas. To check the above hypothesis, the electrical conductivity of undoped zinc oxide was measured once again at 250 and 100°C in vacuum as well as in presence of water vapour (partial pressure 3.0 cmHg). The conductance values dropped to 1/10th on adsorption of water. This strongly suggests that water adsorption has got close relation with removal of quasi-free electrons which are responsible for the electrical conductance. Further, it was argued that if the above mechanism, namely, removal of electrons by hydrogen ions leading to the evolution of hydrogen gas is operative then once all the quasi-free electrons are removed there should not be any further evolution of gas on exposing the zinc oxide to water vapour. To check the above contention, undoped zinc oxide after degassing was exposed to water vapour at 250°C at a partial pressure of 3.0 cmHg. The system approached a pseudo-equilibrium at a pressure of 2.1 cmHg. Gas evolution began at this point till an equilibrium pressure of 2.3 cmHg. was attained. This indicated that the extra pressure generated due to evolution of gas was $2.3 - 2.1 = 0.2$ cmHg pressure. The sample was degassed at this stage at 250°C and the whole process was repeated once again. It was observed that during the second operation there was no evolution of gas in the system. From above observations it is obvious that once *n*-type zinc oxide semiconductor loses quasi-free electrons as a result of interaction between hydrogen ions and electrons, it loses its semiconducting property as well and there is no scope for any further dissociative chemisorption of water which ultimately give rise to evolution of hydrogen.

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The process may be visualized as follows: Let us represent excess zinc in the *n*-type ZnO semiconductor lattice as $(\text{Zn}^{2+} + 2e)$. Then,



Once ZnO is formed according to the above mechanism, the non-stoichiometry of ZnO is removed and as a result it loses semiconductor properties as well as its capacity for dissociative chemisorption of water.

The above mechanism is apparently at variance with the observations of ATHERTON¹⁰ *et al.* who demonstrated the presence of surface hydroxyl groups on zinc oxide which was exposed to water vapour at 673°K. From *ir* adsorption data the above authors identified four different types of hydroxyl groups. It appears likely that unlike our samples which were deliberately heated in vacuum at high temperature in order to impart non-stoichiometry, the samples used by ATHERTON *et al.* were probably stoichiometric oxide of zinc.

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