

# ADSORPTION OF WATER VAPOUR ON ZINC OXIDE

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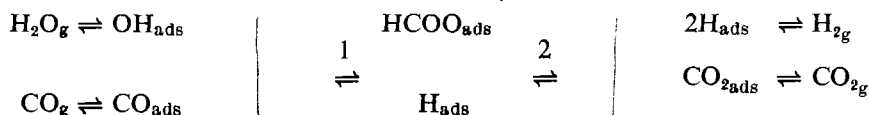
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The adsorption of water vapour on zinc oxide has been studied by electrical conductivity, to understand the role of zinc oxide in low temperature water gas shift reaction. Water molecule is dissociatively adsorbed as OH· and H· radical on Zn<sup>+</sup> and O<sup>-2</sup> sites of zinc oxide surface, and changes in electrical conductivity depends on the temperature of adsorption. A mechanism of adsorption has been suggested to explain the findings.

## INTRODUCTION

The system zinc oxide-copper oxide is the precursor of an active catalyst for the low temperature water gas shift reaction. Before the reaction, the catalyst is activated by careful reduction with hydrogen which converts copper oxide to finely dispersed copper. According to Temkin in Cheredinik *et al.* (1969) the mechanism of the reaction is the alternate oxidation—reduction of the dispersed copper. However, from direct measurement of the rates of oxidation and reduction of the surface, Yureva *et al.* (1969) have shown that the conversion does not take place through alternate oxidation-reduction of copper surface but through an active complex including both carbon monoxide and water molecule.

But in none of these proposed mechanisms the exact role played by zinc oxide and copper individually during adsorption of the reactants and subsequent surface reaction has been clearly established. In particular the fact that zinc oxide itself can provide active sites for surface reaction between water molecules and carbon monoxide seems to have been neglected. Ueno *et al.* (1969, 1970) have carried out IR spectroscopic studies on zinc oxide in water vapour + carbon monoxide and hydrogen + carbon di-oxide atmosphere. They could detect the presence of adsorbed OH group and carbon monoxide in the former case and surface HCOO group in the latter. Comparing the rate of the overall reaction  $H_2 + CO_2 \rightarrow H_2O + CO$  with that of the dehydration decomposition of surface formate (formed by adsorbing formic acid vapour) they concluded that the mechanism of the water gas shift reaction is :—



the step (1) being slow and rate determining.

However the IR data of Tamaru and co-workers do not help us to get a detailed understanding of the mechanism of dissociative adsorption of water vapour. From the above mechanism it can be seen that H<sub>2</sub>O molecule dissociates on the surface into OH· radical which is an electron acceptor and H· radical which is an electron

donor. Adsorption of these species on zinc oxide which is a *n*-type semi-conductor will effect its electronic properties. In view of this the present investigation has been taken up to study the interaction between the active sites on zinc oxide surface and adsorbed radicals through electrical conductivity measurements.

#### EXPERIMENTAL

Zinc oxide used for the experiment was pigment variety and according to the manufacturer's [M/s. Hindustan Pigments Ltd.] specification it has been prepared by the oxidation of zinc metal. Chemical analysis indicated a purity better than 99.9 per cent. It was cured at 500°C for 10 hours. The surface area determined from nitrogen adsorption was 24 m<sup>2</sup>/gm. The sample was pressed under a pressure of 700 kg/cm<sup>2</sup> into a cylindrical pellet of 4 × 8 mm size and was charged in the conductivity cell. The conductivity cell is fitted with two spring loaded Platinum discs between which the pellet is held tightly. Platinum/Platinum-Rhodium thermocouples were welded to the platinum discs to measure the temperature, resistance, temperature difference and thermal e.m.f. between the two faces of the pellet. The conductivity cell was attached to an all glass vacuum apparatus and could be evacuated to 10<sup>-5</sup> torr. by means of a three stage oil diffusion pump backed by a rotary pump. Water was de-aerated by repeated freezing and thawing in vacuum. The conductivity measurements were carried out with an A.C. (3 Kc/s) conductivity bridge [Toshniwal type CLOI/OIA, accuracy ± 2 per cent] and the temperature of the sample was measured to ± 1°C by means of a potentiometer. The same potentiometer was used to measure the thermal e.m.f. and temperature difference.

The sample was reduced at 250°C in a flow of hydrogen for 24 hours, evacuated at 300°C to 10<sup>-5</sup> torr for 3 hours and cooled to 100°C measuring resistance and Seebeck coefficient at intervals of 25°C. The temperature was again raised to 250°C and water vapour added. After equilibration for 4 hours in water vapour the temperature was brought down to 100°C measuring resistance and Seebeck coefficient at same temperature intervals.

The sample was again evacuated at 300°C for 3 hours and then cooled to 100°C. Water vapour was added at 100°C and change of resistance with time was measured. The experiment was repeated at 150°C, 200°C and 250°C after evacuation at corresponding temperatures, i.e., 150°C, 200°C and 250°C.

#### RESULTS AND DISCUSSION

From Fig. 1 it can be seen that upon adsorption of water vapour the resistance (*R*) of zinc oxide changes markedly. The resistance increases with time at 100°C, 150°C and 200°C although the increase at 200°C is much less. These phenomena can be explained if it is assumed that H<sub>2</sub>O molecule is dissociatively adsorbed on zinc oxide at all temperatures in the form of OH· and H· radicals (the indicates an unpaired electron). The adsorption of OH· radical can take place on a Zn<sup>+</sup> site (which are present on a zinc oxide surface). The unpaired electron of OH· radical will combine with the free electron associated with Zn<sup>+</sup> site resulting in a strong homopolar bond (cf. Volkenstein 1963, p. 40). Localisation of the free electron of zinc oxide will increase the electrical resistance.

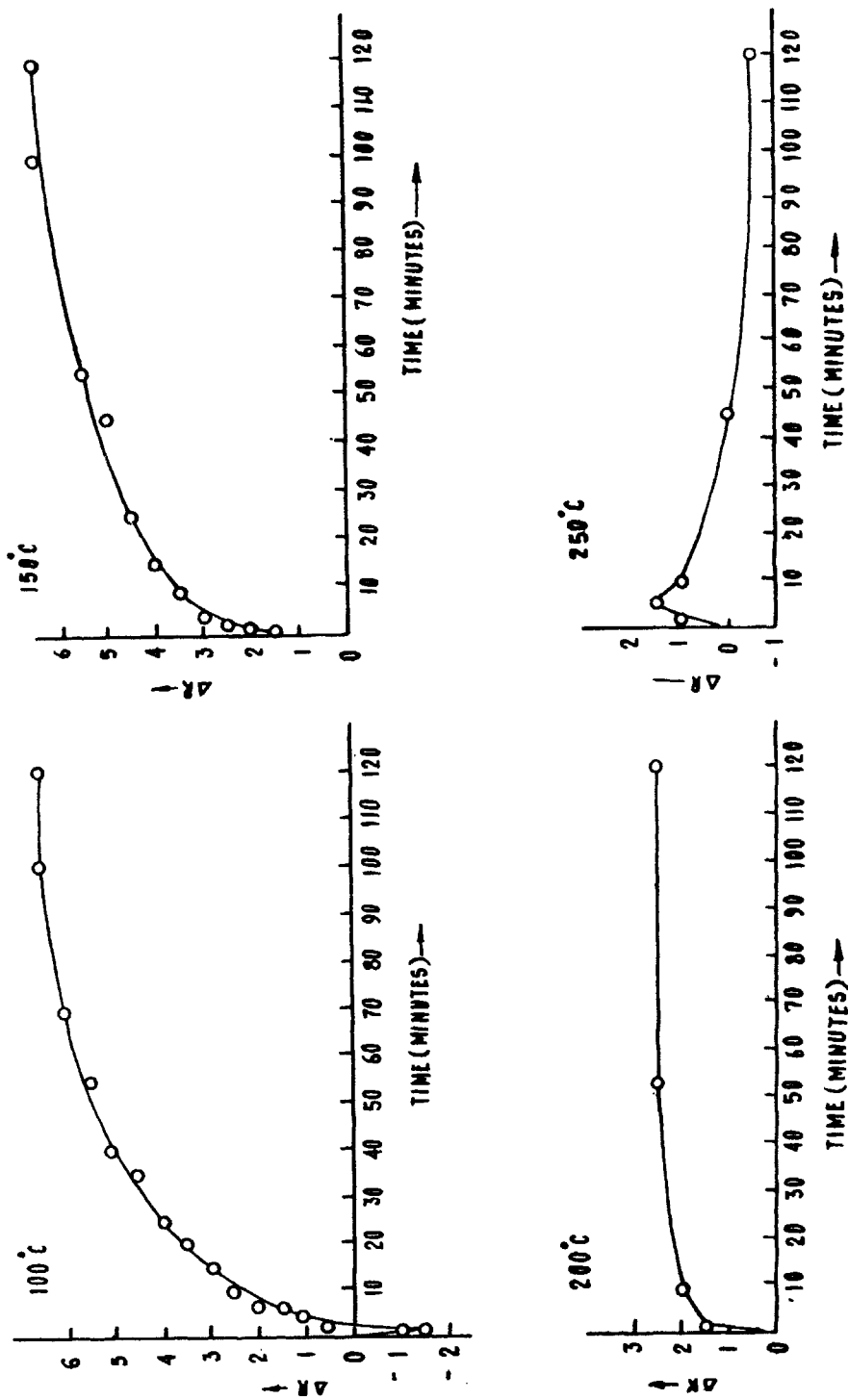


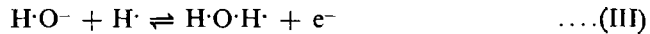
FIG. 1. Change in resistance with time upon water vapour adsorption at different temperatures.

Chemisorption of H<sup>•</sup> radical on zinc oxide can take place in following ways depending on temperature of chemisorption as shown by Navarez and Taylor (1965). The type I chemisorption occurring at temperatures of 150°C and below can be represented as—



It can be seen that the electrical resistance of zinc oxide is not affected by type I chemisorption.

The mechanism suggested for type II and III chemisorption by Navarez and Taylor are—



The type II and III adsorption take place above 150°C and cause decrease in electrical resistance of zinc oxide due to release of free electrons.

Thus it can be assumed that when the temperature of water vapour adsorption is 200°C the effect of ‘acceptor’ type adsorption of OH<sup>•</sup> radical is partially balanced by the ‘donor’ type II adsorption of H<sup>•</sup> radical and the net increase in electrical resistance is less than that at 100°C or 150°C. However since the sample had been evacuated at temperatures much less than 350°C after water vapour adsorption, the surface would contain quite appreciable number of Zn-OH<sup>•</sup> groups, because as pointed out by Atherton *et al.* (1971) for complete dehydroxylation of zinc oxide, evacuation at 400°C is necessary. Consequently type II adsorption of H<sup>•</sup> radical can take place to a limited extent only. But type III adsorption (a donor type adsorption) which occur at 250°C and involves surface OH<sup>•</sup> groups is quite appreciable as indicated by the continuous decrease in resistance at 250°C.

The effect of temperature on the resistance in vacuum and in presence of water vapour can be seen from Fig. 2. Upon cooling in water vapour more H<sub>2</sub>O molecules are dissociatively adsorbed, but when the temperature is below 175°C, adsorption of H<sup>•</sup> radical does not affect the electrical resistance which is increased due to adsorption of OH<sup>•</sup> radical.

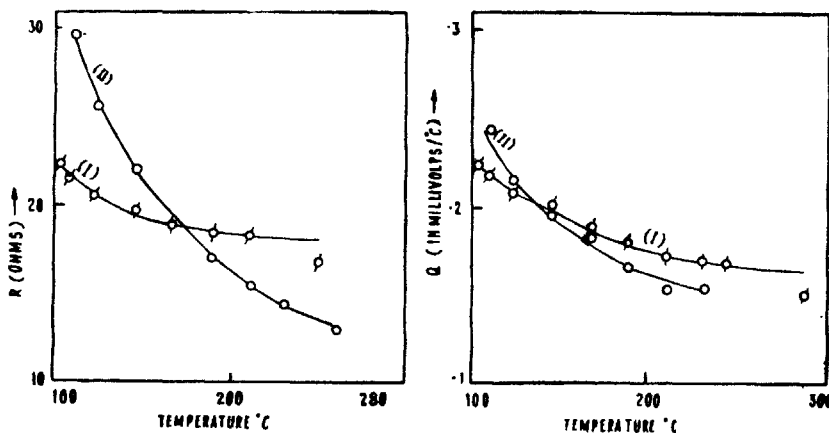


FIG. 2. Variation of resistance (*R*) and Seebeck Coefficient (*Q*) with temperature in vacuum and in presence of water vapour. I—Vacuum; II—24mm H<sub>2</sub>O.

Adsorption of OH· radicals will increase the Fermi energy  $E_F$  (the energy difference between the Fermi level and bottom of the conduction band) at the surface. As the adsorbent is in finely dispersed state this will result in an increase in Fermi energy throughout the crystal (Volkenstein 1963, p. 128). Type III adsorption of H· radical will create positively charged surface layer which will lower the Fermi energy. This is reflected in the change in the Seebeck coefficient  $Q$  with temperature in presence of water vapour as compared to vacuum (Fig. 2), since the relationship between  $E_F$  and  $Q$  is given by :

$$E_F = QT$$

Low and Taylor (1959) have observed that pre-adsorption of hydrogen at 100°C considerably inhibits the adsorption of water vapour at the same temperature and vice versa. The phenomenon can be readily explained by the mechanism suggested that at 100°C the adsorption of both water vapour and hydrogen involved  $Zn^+$  sites on the surface of zinc oxide.

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