

ADSORPTION AND ELECTRICAL CONDUCTIVITY STUDIES ON CERIC OXIDE IN OXYGEN ATMOSPHERES

by V. SITAKARA RAO, *Department of Chemistry, Indian Institute of Technology, Kharagpur*

(Received 13 December 1976)

Adsorption isotherms have been obtained on ceric oxide in the temperature range 100°C to 400°C and a pressure range of 0 to 10 cms Hg. The adsorption behaviour is well defined by Freundlich adsorption isotherm and monolayer coverage is attained at a pressure of 81.3 cm Hg. The values of n and c , the constants in Freundlich adsorption isotherms, and the heat of adsorption are found to decrease with increase of temperature.

Electrical conductivity measurements on ceric oxide at different temperatures (50°, 100°, 150°, 200°, 300° and 400°C) both in vacuum and in an atmosphere of oxygen upto a pressure of 60 cm Hg show that a linear relationship exists between $\log \sigma$ and $1/T$. The conductivity decreases sharply immediately after the first few additions of oxygen showing it to be an n -type semi-conductor. The specific conductivity (σ) of ceric oxide obeys the relation $\sigma = KP_{O_2}^{-1/X}$ (where K and X are constants) when held at a constant temperature in an atmosphere of oxygen at various pressures (P_{O_2}).

A probable mechanism for the adsorption process has been suggested.

INTRODUCTION

Ceric oxide is used fairly extensively in many heterogeneous catalytic processes either in the pure form (Rienacker & Wu 1962; Minachev & Khodakov 1965; Mandle & Mandle 1966; Dimitur 1969; and Breyse *et al.* 1972) or in the form of mixed catalysts (Rienacker & Wu, 1962; Komarewsky & Wernik 1957) or in the form of a promoter (Or & Orzechowskii 1952 *a, b*). However, no comprehensive studies on the chemisorptive properties in presence of various gases like oxygen have been reported except for a very few papers published on the electron spin resonance study of ceric oxide in presence of oxygen (Dufax *et al.* 1969; Steinberg 1970; and Gideoni & Steinberg 1972). The present paper deals with the chemisorptive properties and electrical conductivity studies on ceric oxide in the presence of oxygen under different experimental conditions.

EXPERIMENTAL

Ceric hydroxide was precipitated from ceric ammonium nitrate (A.R.) by the addition of ammonium hydroxide at a pH of 2.0 to 2.5. The precipitated hydroxide was dried at 110°C and then decomposed at 450°C. The resulting oxide was activated at 500°C for 6 hours. The ceric oxide was found to be of more than 99% purity as evidenced by the volumetric estimation with arsenious oxide using ferroin

as the indicator. 100 to 150 mesh size (B.S.S) powder was used in the adsorption and electrical conductivity measurements reported here.

Oxygen was prepared by heating potassium permanganate (A. R.) and was freed from moisture by using anhydrous magnesium perchlorate.

The adsorption of oxygen was measured in a volumetric adsorption apparatus described earlier (Bhattacharyya *et al.* 1977). About 10 g of the catalyst were taken in the catalyst tube, degassed at 500°C for 6 hours and finally maintained at the experimental temperature. Known quantities of oxygen were admitted at noted intervals and after equilibration, the amounts of oxygen adsorbed at (N.T.P) at different pressures were found out from a knowledge of manometric space, dead space and the volume of oxygen admitted into the apparatus. The adsorption experiments were performed at 100°C, 200°C, 300°C and 400°C at various pressures of oxygen upto 15 cm Hg.

The electrical conductivity measurements were carried out on ceric oxide pellets (1 cm diameter, 0.5 to 0.6 cm thickness) made by compressing about 2 g of ceric oxide between two platinum discs under a pressure of 50 kg wt. cm⁻². This pelleted sample was kept in between two platinum foil electrodes of the conductivity cell and was pressed with a stainless steel cylinder kept in glass (Fig. 1). The temperature of the pellet was measured by a Pt. and Pt-Rh thermocouple. Special insulated and grounded electrical cables were used for electrical connections, especially when resistances greater than 0.1 megohm were measured. A potentiometer (Fig. 1C) was employed for measuring resistances lower than 0.1 megohm and a megohm bridge (G.E.C. make) was used for measuring higher resistances. The resistance readings were accurate upto within $\pm 3\%$ from 0.1 to 100 megohms and $\pm 5\%$

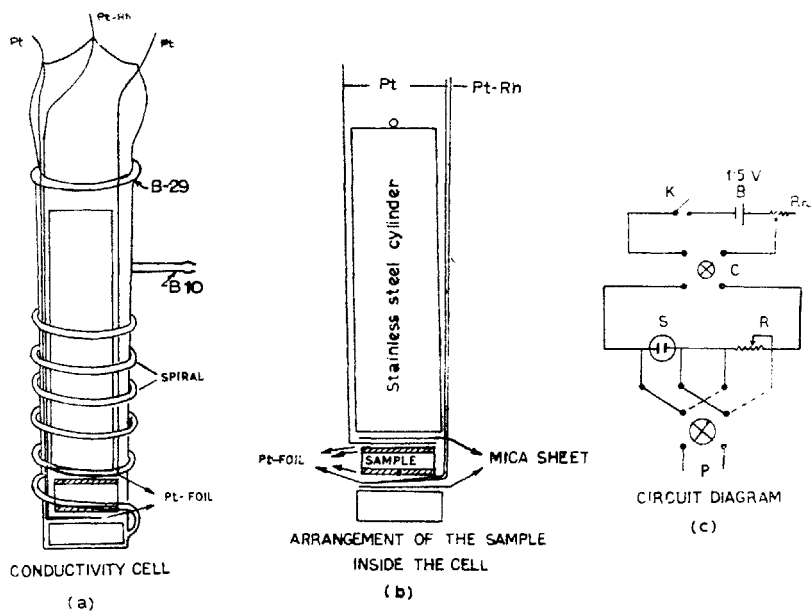


FIG. 1. Conductivity cell and circuit diagram

beyond 100 megohms. The conductivity of ceric oxide was determined at various temperatures (50°C, 100°C, 200°C, 300°C and 400°C) both in vacuum and in an atmosphere of oxygen upto a pressure of 60 cm of Hg.

RESULTS AND DISCUSSION

Adsorption Isotherms—The conformity of the different amounts of oxygen adsorbed (q) at various pressures (p) at 100°C, 200°C, 300°C and 400°C to Langmuir, Fredundlich and Temkin adsorption isotherms was tested as follows : plots of p/q vs. p , $\sqrt{p/q}$ vs. \sqrt{p} and q vs. $\log p$ were drawn. These did not give straight lines showing that these data do not obey either Langmuir or Temkin adsorption isotherms. Plots of $\log p$ vs. $\log q$ gave good straight lines at different temperatures studied (Fig. 2). Further, these straight lines converge and meet at one point. This shows that the adsorption of oxygen on ceric oxide obeys the Freundlich adsorption isotherm. viz.,

$$q = cp^{1/n}, \quad \dots(1)$$

where c and n are temperature dependent constants. The amount of oxygen adsorbed at monolayer coverage (q_m) is found from the point of intersection of the isotherms to be 109.6 $\mu\text{moles/g}$. Further, the pressure ($p_m = 1/a_0$) required for the formation of a monolayer is 81.3 cm Hg. The heat of adsorption at $\theta = 0.37$ is calculated from the expression

$$H_m = n R T. \quad \dots(2)$$

The constant c is evaluated from the values of q_m , a_0 and n by the relation

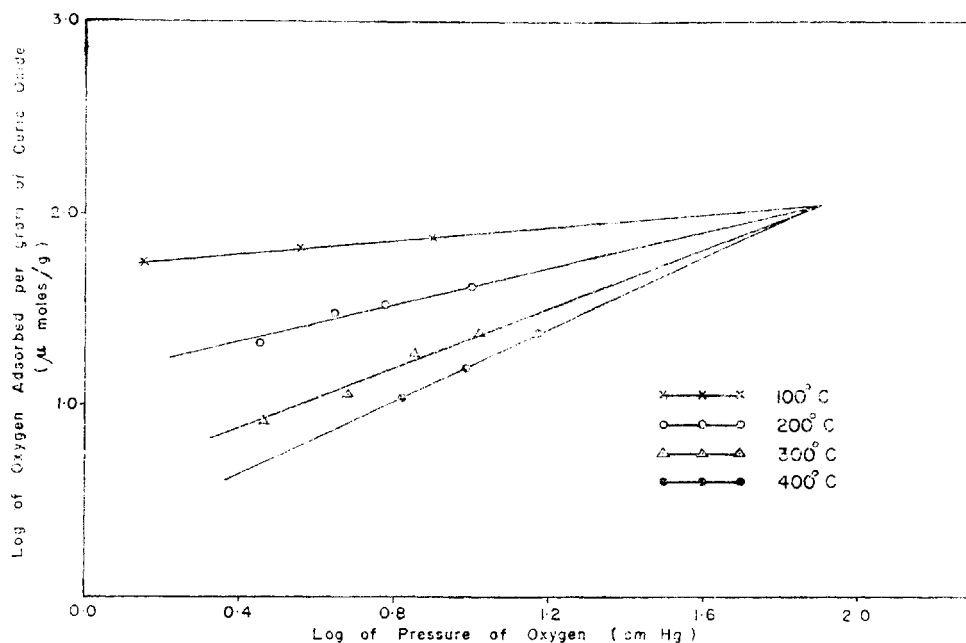


FIG. 2. Freundlich adsorption isotherms for oxygen chemisorption on ceric oxide

$$\log c = \log q_m + \frac{1}{n} \log a_0 \quad \dots(3)$$

TABLE I
Coefficients of Freundlich Isotherms for Oxygen Adsorption on Ceric Oxide

Temperature <i>T</i> (°K)	<i>n</i>	<i>nT</i>	<i>H_m</i> = <i>nRT</i> (kcal mole ⁻¹)	<i>c</i> (μmoles/g)
373	0.66	2484	4.94	56.7
473	1.91	903	1.80	11.0
573	1.31	750	1.49	3.8
673	1.07	719	1.43	1.8

The values of *n*, *H_m* and *c* at different temperatures, as evaluated from the above expressions, are given in Table I. It is seen that both *n* and *c* decrease with increase of temperature, which is the usually observed behaviour (Otto & Shelef 1970; and Gandhi & Shelef 1972, 1973). The higher values of *n* and *nT* at 100°C compared to other values point out that probably oxygen has greater affinity to the surface of ceric oxide at this temperature. According to the derivation of the Freundlich adsorption isotherm from statistical thermodynamics, the product *nT* should be a constant, but it is experimentally quite frequently observed that the product decreases with increase of temperature. These results also show a decrease of *nT* with temperature.

Electrical Conductivity—The conductivity values of ceric oxide in the temperature range of 50°C to 400°C in vacuum and in an atmosphere of oxygen at a pressure of 60 cm Hg showed that linear relationships exist between log σ and 1/*T*, where σ is the specific conductivity and *T* is the temperature in absolute scale (Fig. 3). The activation energy, as calculated from the expression

$$\sigma = Ae^{-E/kT} \quad \dots(4)$$

is found to be 10.85 kcal mole⁻¹ in vacuum and 12.9 kcal mole⁻¹ in oxygen respectively.

No change in conductivity of ceric oxide is observed at 50°C at different oxygen pressures. However, at higher temperatures, viz. between 100°C and 400°C, there is a sudden and steep decrease in conductivity on first introducing small quantities of oxygen (Fig. 4). This shows that ceric oxide is an *n*-type semiconductor. On further additions of oxygen, the conductivity decreases very slowly in the temperature range 100°C to 400°C.

Gideoni and Steinberg (1972) have suggested from their electron spin resonance study during the oxygen adsorption on ceric oxide that the ESR signal I (*g_{av}* = 1.96) is due to quasifree electrons (*e*⁻) present in ceric oxide as per the equation



where *Ce_i* stands for an interstitial quadrivalent ceric cation. Simultaneously with the adsorption of oxygen, the intensity of signal I decreases because of the depletion of quasifree electrons in the conduction band according to the equations,

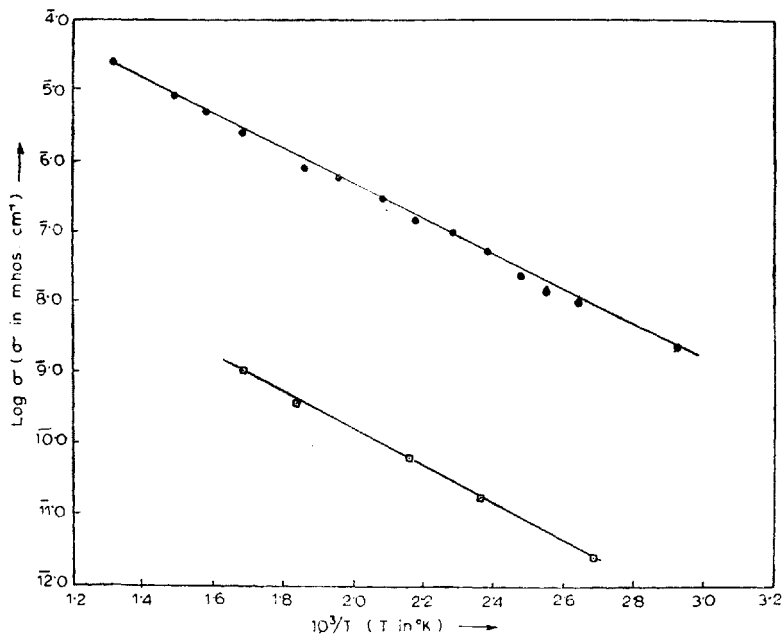


FIG. 3. Variation of electrical conductivity of ceric oxide with temperature in vacuum (●—●—●) and in oxygen at a pressure of 60 cm of Hg (□—□—□).

The higher conductivity values of ceric oxide in vacuum compared to different oxygen pressures at the same temperature are due to the increased concentration of quasifree electrons as formed according to the forward reaction (5) during evacuation. Initial addition of oxygen consumes most of the conduction electrons and forms O_2^- , O^- and O^{2-} ions as per the mechanisms in equations (6), (7) and (8) respectively. This results in an initial steep decrease in conductivity of ceric oxide due to the first addition of small amounts of oxygen. Further additions of oxygen may now fill up the very few remaining sites, thereby causing a very slow decrease in conductivity. At a temperature, as low as 50°C , the oxygen molecules are probably physically adsorbed and therefore do not consume the conduction electrons causing no change in conductivity.

In an n -type oxide semiconductor, in which an equilibrium exists between the point defects and the ambient gaseous atmosphere, the conductivity (σ) and the oxygen partial pressure (P_{O_2}) at a constant temperature are related by the following

relation, viz.,

$$\sigma = K P_{O_2}^{-1/X}$$

$$\text{or } \log \sigma = \log K - \frac{1}{X} \log P_{O_2}, \quad \dots(9)$$

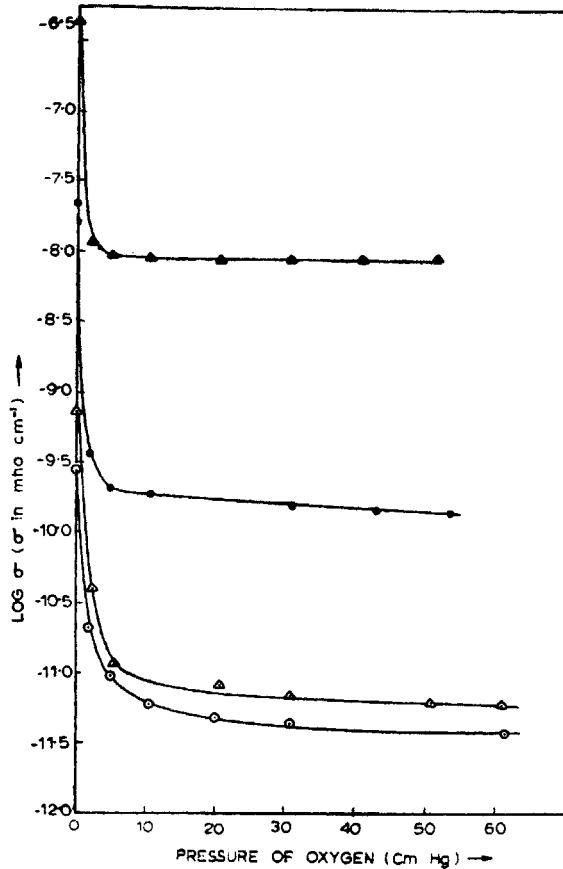


FIG. 4. Variation of logarithm of electrical conductivity of ceric oxide with pressure of oxygen at different temperatures. ○—○—○ 100°C; △—△—△ 200°C; ●—●—● 300°C and ▲—▲—▲ 400°C

where K and X are constants. Equation (9) shows a linear relationship between $\log \sigma$ and $\log P_{O_2}$. Such plots have been drawn for different temperatures (Fig. 5)

and, as expected, straight line behaviour is observed at each of the temperatures.

Thus the electrical conductivity measurements on ceric oxide during oxygen chemisorption point out that ceric oxide behaves like an n -type semiconductor. Physical adsorption of oxygen takes place at 50°C, while chemisorption is responsible for changes in conductivity at higher temperatures, viz., 100°C, 150°C, 200°C, 300°C

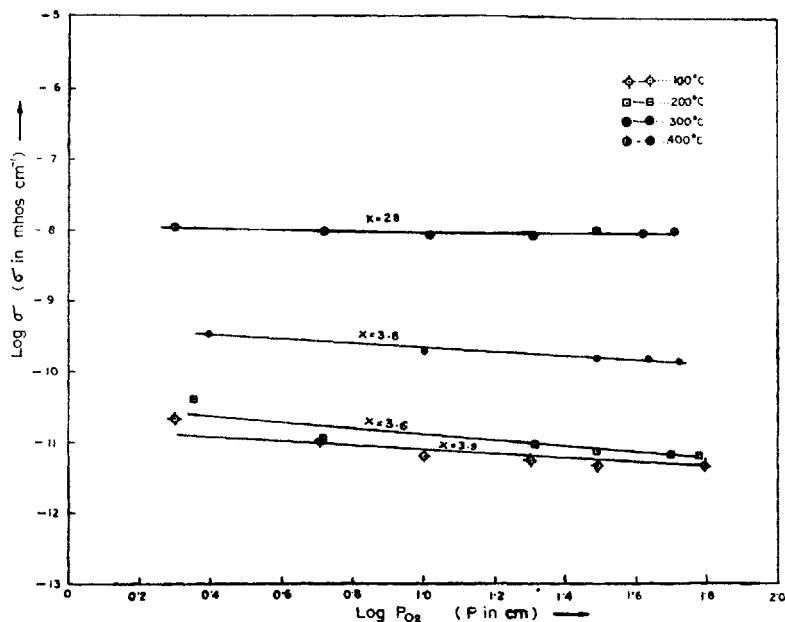


FIG. 5. Log σ —Log P_{O_2} plots for oxygen chemisorption on ceric oxide at different temperatures.

and 400°C. These results also suggest that a defect mechanism of the type mentioned above is probably responsible for oxygen adsorption on ceric oxide.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. S. K. Bhattacharyya, Dr. D. Sen, Dr. K. S. De and Dr. H. S. Maiti for their interest in the course of this work. He is also thankful to Mr. S. K. Chattopadhyay for his help during the adsorption isotherm measurements.

REFERENCES

- Bhattacharyya, S. K., Sitakara Rao, V., and De, K. S. (1977). Studies of chemisorption of hydrogen on ceric oxide. *Proc. Indian natn. Sci. Acad.*, **43**, A, No. 2, 89-95.
- Breyse, M., Guenin, M., Claudel, B., Latreille, H., and Veron, J. (1972). Catalysis of carbon monoxide oxidation by cerium dioxide. Correlation between catalytic activity and electrical conductivity. *J. Catal.*, **27**, 275-280.
- Dimitur, K. (1969). Oxidation of methyl alcohol to formaldehyde on cerium dioxide. *Z. Chem.*, **9** (10), 394-396.
- Dufaux, M., Che, M., and Naccache, C. (1969). Electron paramagnetic resonance study of the adsorption of oxygen onto supported molybdenum and cerium oxides. *C. r.*, **268** C, 2255-2257.
- Gandhi, H. S., and Shelef, M. (1972). The adsorption of nitric oxide and carbon monoxide on nickel oxide. *J. catal.*, **24** (2), 241-249.
- (1973). The adsorption of nitric oxide on copper oxide. *J. catal.*, **28** (1), 1-7.
- Gideoni, M., and Steinberg, M. (1972). The study of oxygen sorption on cerium (IV) oxide by electron spin resonance. *J. solid State Chem.*, **4**, 370-373.
- Komarewsky, V. I., and Wernick, M. (1957). Catalytic properties of the rare earths. *Proc. Congr. intern. Chim. pure et Appl.*, 16e Paris, 249-255.

- Mandle, H. L., and Mandle, R. M. (1966). In : *Progress in the Science and Technology of the Rare Earths*, (Ed. LeRoy Eyring). Pergamon Press, Oxford, 1, p. 447; 2, p. 225.
- Minachev, Kh. M., and Khodakov, Yu. S. (1965). Catalytic activity of the rare earth elements in the conversion of butane. *Kinet. Catal.*, 6, 89-94.
- Or, L. D., and Orzechowski, A. (1952a). Promotion in heterogeneous Catalysis. *C. r.*, 235, 368-70.
- (1952b). Further studies on promotion in heterogeneous catalysis. *C. r.*, 235, 430-432.
- Otto, K., and Shelf, M. (1970). The adsorption of nitric oxide on iron oxides. *J. catal.*, 18, 184-192.
- Rienacker, G., and Wu, J. (1962). Effect of additives on oxide catalysts. XI. Properties of cerium-Lanthanum mixed oxides especially as catalysts for the oxidation of carbon monoxide. *Z. Anorg. U. allgem. Chem.*, 315, 121-135.
- Steinberg, M. (1970). ESR study of cerium (IV) oxide in vacuum, air and hydrogen. *Israel J. Chem.*, 8, 877-881.