BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2475—2479 (1969)

Kinetics of the Adsorption of Water and Electrical Conduction in Amorphous Ferric Oxide

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(Received February 19, 1969)

Amorphous ferric oxide was prepared by precipitation in a mixture of ammonium hydroxide and ferric nitrate at 90°C, after which it was calcinated in air at a constant rate of 10°C/min up to 200°C. The rate of the adsorption on the amorphous oxide was measured by a gravimetric method. An equation of the Elovich type was obtained: $dq/dt=k'p^{0.63}\exp(-\alpha'q/\boldsymbol{R}Tp^{0.5})$, where k' and α' are constants; q, the amount of adsorbed water, and p, the pressure. This kinetics can be interpreted by a model of a two-stage adsorption process, the van der Waals adsorption and the charge-transfer adsorption, the latter stage being assumed to be rate-determining. The effect of adsorbed water on the direct-current conductivity of the oxide, i, is formulated as $i=i_0\exp(aq)$. Assuming that the adsorbed water is acting as a donor-type impurity and that the ionization energy decreases with the concentration of impurity, the relation between i and q can be derived from the theory of the semiconduction of an n-type conductor.

Many investigators have reported the adsorption of water on ferric oxide.[1–6] Jurinak,[6] drawing a line between chemisorption and physical-adsorption, measured the amounts of water in the two adsorption states. Blyholder and Richardson[4] have shown, in a study of the infrared absorption, that the water molecule chemisorbs by dissociating to form an OH^- ion and an H^+ ion, the latter of which reacts with a surface O^{2-} ion to form another OH^- ion. Onoda and DeBruyn[7] have suggested the possibility of the transformation of anhydrous ferric oxide to goethite in a study of proton adsorption at the ferric oxide/aqueous solution interface. Kawasaki, Minowa, and Inamatsu[8] found, in studying the "Metallic Oxide Electric Hygrometer," that electrical resistance of oxide decreased with an increase in the relative humidity in the range from 50 to 100%. On the other hand, with various kinds of proteins the effect of adsorbed water on the electrical conductivity has been studied[9,10]; it has been found that the electrical conductivity, i, increased with an increase in the amount of adsorbed water, q, obeying an empirical equation, $i=A\exp(\alpha q)$, where A and α are constants.

It is to be noticed that the water adsorption affects the conductivity in a similar fashion in both inorganic and organic materials. The semiconductivity of inorganics is known to play an important role in the catalytic activity of the inorganic solids.

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[1] A. G. Foster, *J. Chem. Soc.*, **1945**, 360.

[2] K. S. Rao, *J. Phys. Chem.*, **45**, 500 (1941).

[3] F. H. Healey, J. J. Chessick and A. V. Fraioli, *ibid.*, **60**, 1001 (1956).

[4] G. Blyholder and E.A. Richardson, *ibid.*, **66**, 2597 (1962).

[5] S. J. Gregg, "Chemisorption," ed. by W. E. Garner, Butterworths Scientific Publications, London (1957), p. 68.

[6] J. J. Jurinak, *J. Colloid Sci.*, **19**, 477 (1964).

[7] G. Y. Onoda, Jr., and P. L. DeBruyn, *Surface Science*, **4**, 48 (1966).

[8] T. Kawasaki, Z. Minowa and T. Inamatsu, *J. Appl. Phys. Japan*, **35**, 355 (1966).

[9] D. D. Eley and R. B. Leslie, "Advances in Chemical Physics," Vol. VII, ed. by J. Duchesne, Interscience Publishers, New York (1964), p. 238.

[10] B. Rosenberg, *J. Chem. Phys.*, **36**, 816 (1962).

In the present experiment, the kinetics of water adsorption on the amorphous ferric oxide prepared by heating the ferric oxide gel at 200°C, and the effect of water on the semiconductivity of the oxide, were investigated in an attempt to elucidate the interaction between the oxide and the adsorbed water.

Experimental

Materials. Ferric oxide gel was prepared by mixing 54 m*l* of a 6N NH_4OH solution and 750 m*l* of a 0.1 M $Fe(NO_3)_3$ solution at 90°C. The pH of the solution in which the hydroxide gel was suspended was 9.05. The precipitate obtained as above was carefully washed with distilled water and dried for two days at room temperature and for 6 hr at 100°C in 20 mmHg. After drying, it was calcinated in air at a fixed heating rate of 10°C/min up to 200°C and kept at this temperature for 10 min. The sample to be studied was ground to a powder with a mesh size of 200—300. This oxide was found to be amorphous by X-ray diffraction examination, and its surface area was 162 m^2/g (BET method).

Measurements. The rate of the adsorption of water vapor was measured gravimetrically using a quartz spring microbalance and a cathetometer. The water vapor was supplied by a sulfuric acid solution placed in a constant-temperature bath, while the pressure was controlled by changing the concentration of the acid solution. Before the adsorption experiment, the specimen was evacuated at 150°C for 3 hr at 10^{-5} mmHg. The cell used for the measurement of the electrical conductivity was of the sandwich type, with two platinum electrodes (contact area, 0.95 cm^2) and a stainless-steel spring to press the oxide between electrodes at a pressure of 1 kg/cm^2. The voltage supplied across the cell was 10 V d. c., and the conducting current was measured in a vacuum of 10^{-6} mmHg at various fixed temperatures ranging from 5°C to 50°C. The conducting current was measured by an electrometer (Ohkura Electric Co.). Before the measurement of the conductivity, the specimen was subjected to the adsorption of water vapor in a desiccator containing the sulfuric acid solution for various periods of time in order to change the amount of adsorbed water which could be determined by weighing the specimen before and after the adsorption.

Results

Kinetics of Adsorption. Typical adsorption-time curves are shown in Fig. 1, in which the amount of water adsorbed, *q*, is represented in units of mg H_2O per m^2 of the oxide surface and the time, *t*, in minutes. The *q* values in the initial stage of the adsorption, *i.e.*, for 1 or 1.5 min after the introduction of water vapor into the adsorption chamber, are not so accurate as in the later stage because of the oscillation of the quartz spring.

To analyze these adsorption-time curves in the figure, *q* is plotted against $\log(t+t')$ in Fig. 2, where t' is chosen to linearize the q-$\log t$ relation by a trial-and-error method. It may be seen in Fig. 2 that the kinetics of water adsorption on the amorphous ferric oxide obeys the Rozinsky-Zeldovich or Elovich equation, which can be formulated as follows in the differential and integrated forms respectively:

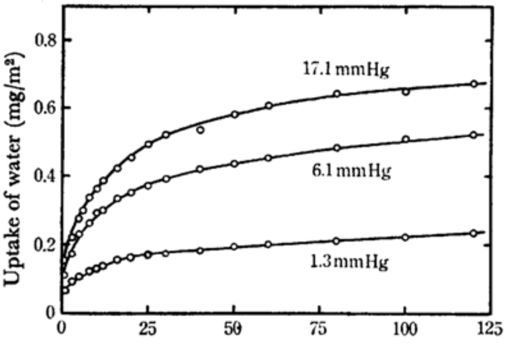

Fig. 1. Adsorption-time curves for amorphous ferric oxide at 30°C at various pressures.

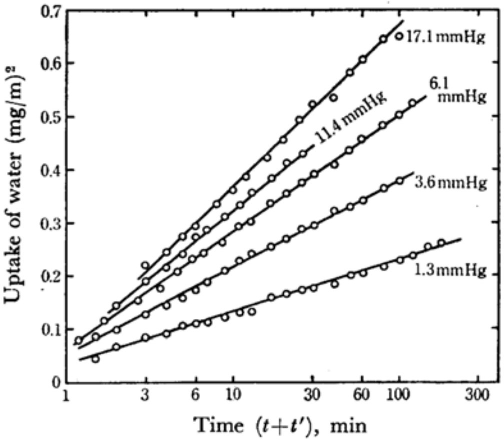

Fig. 2. Kinetics of the water vapor uptake at 30°C at various pressures.

$$\mathrm{d}q/\mathrm{d}t = k\exp(-\alpha q/\boldsymbol{R}T) \tag{1}$$

$$q = 2.303(\boldsymbol{R}T/\alpha)\log(t+\boldsymbol{R}T/\alpha k) - 2.303(\boldsymbol{R}T/\alpha)\cdot\log \boldsymbol{R}T/\alpha k \tag{2}$$

where k is the initial rate when q is zero and α is constant. The value of t' on the abscissa $\log(t+t')$ in Fig. 2, therefore, corresponds to the $\boldsymbol{R}T/\alpha k$ term, and the slope of the straight lines, to $2.303(\boldsymbol{R}T/\alpha)$ in Eq. (2). Accordingly, α and k can be calculated from the values of t' and the slope of the lines. However, it has been shown by Taylor and Thon[11] that the initial rate of adsorption, k, calculated t' is smaller than the experimentally-measured rate

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[11] H. A. Taylor and N. Thon, *J. Am. Chem. Soc.*, **74**, 4169 (1952).

in many cases. In the present paper, because of the difficulty in measuring the initial velocity, the calculated k has been assumed to be the initial rate of adsorption.

As may be seen in Fig. 2, the solpe of the line, that is $2.303(\boldsymbol{R}T/\alpha)$ in Eq. (2), increases with the pressure of the water vapor, p. The slope of the line, when plotted as in Fig. 3, is seen to increase linearly with $p^{0.5}$, so α can be writted as $\alpha=\alpha'/p^{0.5}$. To examine the pressure-dependence of k, which can be calculated from Eq. (2), log k is plotted as a function of log p in Fig. 4. Thus, the relation between k and p can be represented as $k=k'p^{0.63}$. The substitution of new pressure-dependent parameters, α and k, into Eq. (1) yields:

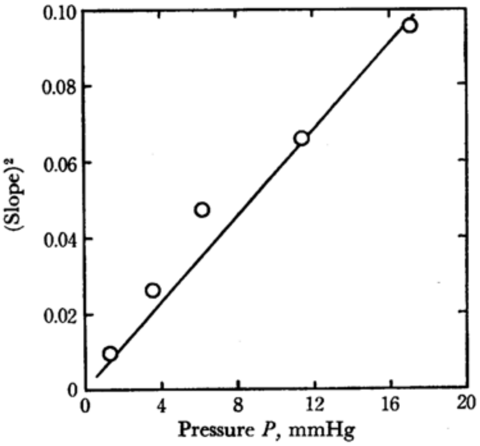

Fig. 3. Pressure dependence of the slope of lines in Fig. 2.

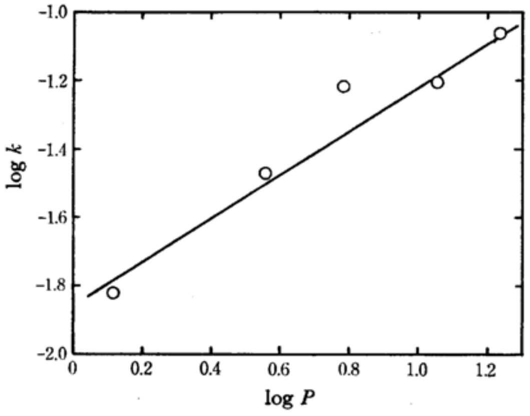

Fig. 4. Pressure dependence of the initial velocity calculated from the data in Fig. 2.

$$dq/dt = k'p^{0.63} \exp(-\alpha' q/\boldsymbol{R}Tp^{0.5}) \tag{3}$$

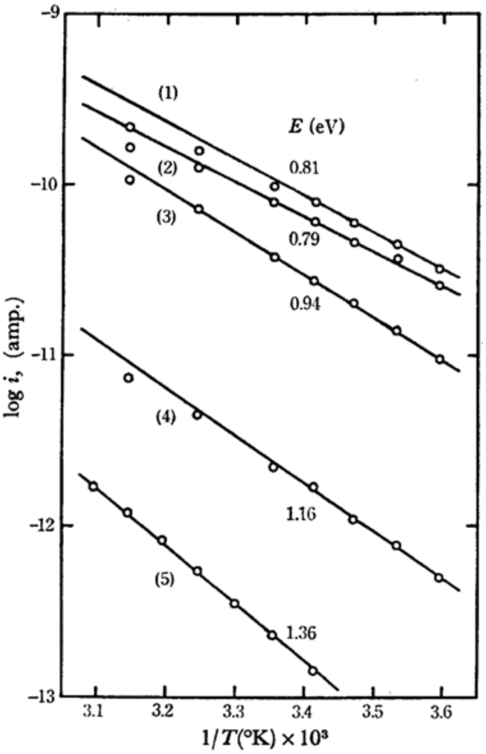

Fig. 5. Conductivity of amorphous ferric oxide as a function of temparature. Curves (1), (2), (3), (4) and (5) correspond, respectively, to the conductivity of samples containing 0, 4.9, 8.7, 12.0 and 14.5 wt% of adsorbed water.

Electrical Conductivity. The results of the measurement of the electrical conductivity as a function of the temperature are shown in Fig. 5, in which the logarithm of the conducting current through the cell has been plotted against the reciprocal absolute temperature. Five curves, denoted in this figure by (1) to (5), represent the conductivity of specimens containing different amounts of adsorbed water, that is 0, 4.9, 8.7, 12.0 and 14.5 wt% of water respectively. The results in Fig. 5 show that the conducting current, i, at a given temperature, T, can be formulated by Eq. (4);

$$i = i_0 \exp(-E/\boldsymbol{k}T) \tag{4}$$

where i_0 and E are constants and $\boldsymbol{k}$, the Boltzman constant. Furthermore, it was found that, although no variation in the current with time occurred at 5°C in a vacuum, some decrease in the current did occur when air entered the conductivity cell. These results imply that the ferric oxides are n-type semiconductors. Accordingly, the slope of the lines Fig. 5 is considered to give the activation energy, E, for semiconduction. At higher temperatures the conducting currents of the wet oxides, as seen in Fig. 5, deviates downward from the stright line, probably because of the desorption of the adsorbed water.[10)]

It may also be seen in Fig. 5 that as the amount of adsorbed water increases, E decreases and i

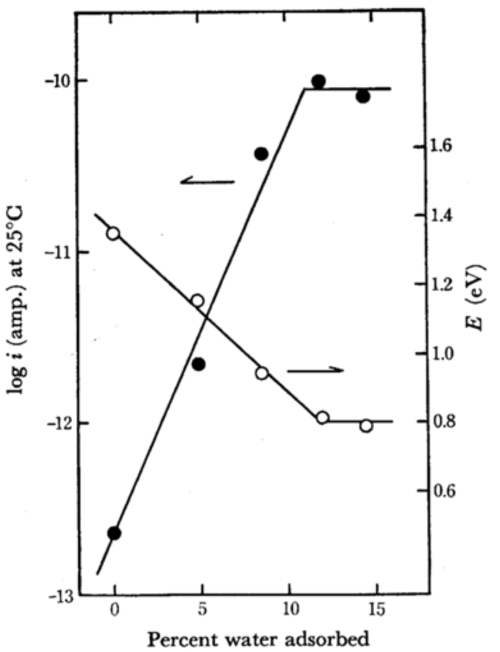

Fig. 6. Relation between conducting current at 25°C, activation energy and amount of adsorbed water.

increases in the temperature range examined. This is quantitatively shown in Fig. 6, in which the values of the conducting current at 25°C are given as examples. The change in the conducting current, i, with the amount of adsorbed water, q, at a fixed temperature is seen to obey the equation:

$$\log i = i' + aq \tag{5}$$

where i' and a are constants. Furthermore, the activation energy of semiconduction, E, can be expressed by:

$$E = E_0 - bq \tag{6}$$

where E_0 corresponds to the activation energy of the dried oxide and where b is constant.

From Eqs. (5) and (6) the relation:

$$\log i = \text{const.} - \text{const.} \times E \tag{7}$$

can be obtained. Equation (7) satisfies Mayer's rule,[12] which, in general, has been interpreted as follows: the activation energy of electronic conduction in semiconductors decreases with an increase in the concentration of carriers and donor centers. Accordingly, it may be concluded that the adsorbed water acts as a donor-type impurity in the oxide, the oxide being a semiconductor of the n type.

Discussion

As has been mentioned above, the amorphous ferric oxide is an n-type semiconductor and the adsorption of water on it causes the electrical conductivity to increase. Therefore, the adsorption which, in the present case, may be referred to as the cumulative or cationic chemisorption must be accompanied by the charge transfer. Hauffe, Morrison and Stone[13] have discussed the kinetics of the cationic adsorption on the basis of the boundary-layer theory of chemisorption. On the other hand, Eley and Leslie[14] postulated in their recent study that the adsorption kinetics of water vapor on proteins may be regarded as a two-stage process: the van der Waals adsorption and the charge-transfer adsorption, with the rate-determining step being the latter. On the basis of this adsorption model, they derived theoretically the equation indicated by Eq. (8) and gave a qualitative description of the rate of adsorption experimentally obtained (Eq. (9)):

$$\mathrm{d}q/\mathrm{d}t = K'N_{\mathrm{VW}}p^{0.6}\exp[-(E_0 + \beta q - \gamma p)/RT] \tag{8}$$

$$\mathrm{d}q/\mathrm{d}t = Kp^{0.6}\exp(-\alpha' q/RTp) \tag{9}$$

where K, K', β, γ nad α' are constants; N_{VW}, the number of sites on the surface of the adsorbent, E_0, the energy barrier of the charge-transfer step at $q=0$. In Eq. (8), the activation energy, E, is assumed to increase linearly with the amonut of adsorbed water, the additional term, γp, is the contribution to E of the dipole moment of water molecules in the van der Waals adsorption state. By comparing Eq. (3) with Eq. (9), it can easily be seen that these two equations are almost the same except for a difference in the exponent of p in the exponential term. Accordingly, the adsorption of water on the amorphous ferric oxide may be explained by the two-stage model proposed for the adsorption on protein. On the basis of the above discussion, the adsorption process can be represented as follows:

$$\begin{aligned} \mathrm{H_2O} + \text{oxide} &\rightleftarrows [\mathrm{H_2O}\cdots\text{oxide}]_{\mathrm{VW}} \\ &\xrightarrow{\wedge} [\mathrm{H_2O} \rightarrow {}^{-}\text{oxide}]_{\mathrm{CT}} \end{aligned}$$

Pearson and Bardeen[15] found, for boron in silicon, that the ionization energy, E_{D}, of the donors decreased with an increase in the concentration of the donors, n_{D}, in the semiconductor. Assuming the interaction energy between the impurity atoms to be inversely proportional to the average distance between these atoms, they derived this relation between E_{D} and n_{D}:

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[12] W. Meyer, *Z. Physik*, **38**, 1014 (1937); F. A. Kroger, "The Chemistry of Imperfect Crystals," North-Holland Publishing Co., Amsterdam (1964), p. 475.

[13] K. Hauffe, "Advances in Catalysis," Vol. VII, Academic Press, New York (1955), p. 213; S. R. Morrison, *ibid.*, p. 259; F. S. Stone, "Chemistry of the Solid State," ed. by W. E. Garner, Butterworths Scientific Publications, London (1955), p. 367.

[14] D. D. Eley and R. B. Leslie, *Trans. Faraday Soc.*, **62**, 1002 (1966).

[15] G. L. Peason and J. Bardeen, *Phys. Rev.*, **75**, 865 (1949).

$$E_D = E_{DC} - n_D^{1/3} \tag{10}$$

If it can be assumed that, as has been described above, the adsorbed water is acting as an impurity producing donor centers, and that the amount of adsorbed water, q, is proportional to n_D to the one-third power, the change of E with q in Eq. (6) can be interpreted in terms of the interaction between the adsorbed waters. Moreover, the conductivity[16] is given by the theory of the impurity mechanism of semiconduction:

$$\sigma = e\mu(4n_D)^{1/2}(2\pi mkT/h^2)^{4/3}\exp(-E_D/2kT) \tag{11}$$

where e is the electronic charge, and μ, the mobility, while the others are well-known symbols. By substituting Eq. (10) into Eq. (11), and by assuming $n_D^{1/3}$ to be proportional to q, the logarithm of σ can be given by:

$$\log\sigma = \text{const.} + \log q^{3/2} + \text{const.}\times q \tag{12}$$

Neglecting log $q^{3/2}$ term, Eq. (12) fits the relation between i and q in Eq. (5) obtained experimentally in the present investigation.

One of the authors (R. F.) especially wishes to thank the Sakkokai Foundation for his scholarship.

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[16] N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," Clarendon Press, Oxford (1948), p. 165.