

Oxygen Depletion of Oxide Catalysts

When some oxides are heated in vacuum, an appreciable depletion of oxygen can take place. The depletion can be easily measured by recording the pressure increase of the liberated oxygen with time. The diffusion coefficient of oxygen in the lattice can thus be determined from the curves obtained. The bismuth molybdates are of particular interest as catalysts for oxidation. It has been stated (1-3) that the lattice oxygen is the oxidation agent, the role of the external oxygen being simply to replenish the oxygen consumed in the lattice. Hence, information about the diffusion of oxygen in the bismuth molybdate lattice might be of some significance in the interpretation of the catalytic process.

EXPERIMENTAL METHODS

The materials used were of ultrapure quality. The Bi_2O_3 and MoO_3 were supplied by Ventron Alfa Corp. The 1:1 and 2:3 bismuth molybdates were obtained from Climax Molybdenum Corp. and the 2:1 bismuth molybdate was prepared by us by melting Bi_2O_3 and MoO_3 in corresponding proportions. Measurements of the melting point and the X-ray powder diffraction confirmed that the product obtained was indeed the 2:1 bismuth molybdate. Measurements of specific surface area, density and depletion of oxygen from the catalyst were carried out using an Orr surface area-pore volume analyzer (Model 2100D) supplied by Micromeritics Instrument Corp. The density was determined by measuring the expansions of a known amount of dry helium gas in a container when filled in part with catalyst and when empty. During

each experiment, the desired amount of material was introduced in a specimen holder. The surface area and density were determined both before and after oxygen depletion. The measurement of oxygen depletion from the samples consisted of the following steps:

1. Introduction of the oxide in the sample flask. Evacuation of the catalysts at 400°C and at 10^{-4} Torr for 15 min followed by saturation, at the same temperature, with pure O_2 at 800 Torr overnight.

2. Cooling down the sample to 120°C and subsequent evacuation under high vacuum overnight in order to desorb moisture and air.

3. Maintaining the specimens at the desired temperature in vacuum and recording the increase in pressure with time in a closed volume (the distribution manifold of the Orr surface area-pore volume analyzer).

Kinetic Equation

The time dependence of the oxygen depletion can be described by taking into account the diffusion of oxygen in the lattice as well as the "vaporization" and "condensation" processes which occur at the solid-gas interface.

The diffusion is described by the differential equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \quad (1)$$

where c is the concentration of oxygen at the spatial coordinate x and at time t , and

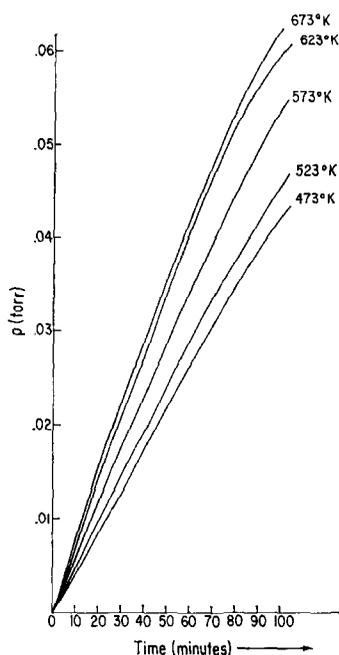


FIG. 1. Oxygen depletion isotherms for the 2:1 bismuth molybdate heated at various temperatures. Sample weight = 7.176 g.

D is the diffusion coefficient of oxygen ions through the lattice.

At the gas-oxide interface the diffusional flux has to be equal to the difference between the rates of "vaporization" and "condensation," therefore

$$D\left(\frac{\partial c}{\partial x}\right) = K_1 c_s - K_2 p, \quad \text{for } x = 0, \quad (2)$$

where the rate of vaporization is assumed proportional to the concentration c_s at the solid-gas interface while the rate of condensation is assumed proportional to the pressure p .

The closed volume into which oxygen-gas accumulates is composed of two parts: One is at the desired temperature T and has the volume $V = 10$ ml of the sample flask and the other, the distribution manifold of the Orr surface area-pore volume analyzer, is maintained at the constant temperature $T_1 = 307^\circ\text{K}$ and has the volume $V_1 = 28.4$ ml. From the ideal gas

law, a mass balance for the gas phase leads to

$$\frac{1}{A}\left(\frac{V}{RT} + \frac{V_1}{RT_1}\right)\frac{dp}{dt} = K_1 c_s - K_2 p. \quad (3)$$

where A is the total surface area of the sample and R and p have their usual meaning. The initial conditions are

$$c = c_0 \quad \left. \vphantom{c = c_0} \right\} \text{ for } t = 0. \quad (4)$$

$$p = 0 \quad \left. \vphantom{p = 0} \right\} \text{ for } t = 0. \quad (5)$$

The pellet behaves like a semi-infinite solid if the depth of penetration by diffusion of the oxygen atoms is sufficiently small in comparison to the thickness of the pellet. Using the Laplace transform, the solution to the above system of equations can be obtained as

$$p(t) = \frac{K_1}{K_2} c_0 + \frac{K_1}{K_2} c_0 \left[\frac{N}{M - N} e^{Mt} \operatorname{erfc}(Mt^{1/2}) + \frac{M}{N - M} e^{Nt} \operatorname{erfc}(Nt^{1/2}) \right], \quad (6)$$

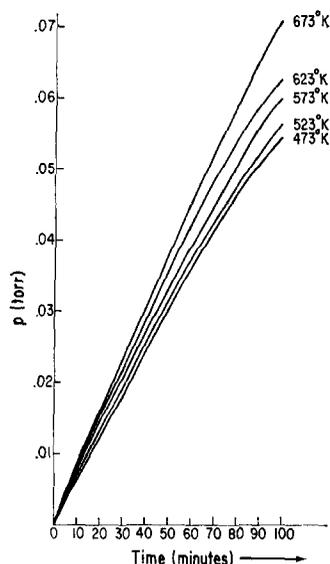


FIG. 2. Oxygen depletion isotherms for the 1:1 compound heated in vacuum at various temperatures. Sample weight = 6.674 g.

TABLE I
Diffusion Coefficients of Oxygen in Bismuth-Molybdates^a

Sample	Temperature (°K)	$K_1 \times 10^8$ (cm/sec)	$K_2 \times 10^{13}$ (moles/cm ² sec/mm Hg)	$D \times 10^{15}$ (cm ² /sec)	Activation energy for diffusion E_D (kcal/mole)	$D_0 \times 10^{13}$ (cm ² /sec)
Bi ₂ O ₃ MoO ₃ Melting pt = 1248°K Density = 6.949 g/cm ³ Surface area = 0.4 m ² /g	473	3.3	1.1	1.4		
	523	4.2	1.3	2.7		
	573	4.7	1.5	4.8	4.01	1.1
	623	5.0	1.6	7.5		
	673	5.1	1.7	11.2		
Bi ₂ O ₃ 2MoO ₃ Melting pt = 1000°K Density = 6.39 g/cm ³ Surface area = 0.14 m ² /g	473	3.9	1.2	0.9		
	523	4.8	1.4	1.1		
	573	5.3	1.6	1.3	1.81	0.08
	623	5.6	1.7	1.5		
	673	5.7	1.8	1.6		
Bi ₂ O ₃ 3MoO ₃ Melting pt = 922°K Density = 5.76 g/cm ³ Surface area = 0.29 m ² /g	473	4.9	0.57	0.55		
	523	5.7	0.69	0.64		
	573	6.4	0.79	0.72	1.42	0.03
	623	7.0	0.87	0.79		
	673	7.4	0.92	0.86		

$$^a D = D_0 e^{-E_D/RT}$$

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where

$$\operatorname{erfc}(\eta) = 1 - \frac{2}{(\pi)^{1/2}} \int_0^\eta e^{-s^2} ds,$$

$$M = \frac{K_1}{2(D)^{1/2}} - \left(\frac{K_1^2}{4D} - \frac{K_2 RA}{\alpha} \right)^{1/2}, \quad (7a)$$

$$N = \frac{K_1}{2(D)^{1/2}} + \left(\frac{K_1^2}{4D} - \frac{K_2 RA}{\alpha} \right)^{1/2},$$

$$\alpha \equiv \frac{V}{T} + \frac{V_1}{T_1}. \quad (7b)$$

Evaluation of the Parameters from the Depletion Curve

From the experimental pressure-time curve, a least squares estimate of the constants D , K_1 and K_2 were obtained. The numerical technique used was the steepest descent method (4, 5). The objective function to be minimized was $\phi = \sum(\hat{p}_i - p_i)^2$, where \hat{p} and p are the observed and predicted values, respectively, of the pressure.

The steepest descent directions were defined by the quantities $\partial\phi/\partial b_i$ ($i = 1, 2, 3$), where the b_i are the three parameters. After initial trial values for the unknown parameters were assumed, the $(r + 1)$ th

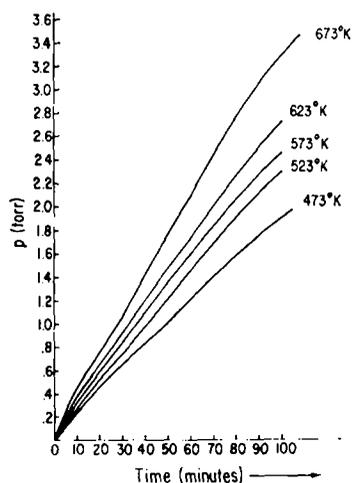


FIG. 3. Oxygen depletion isotherms for the 2:3 compound heated in vacuum at various temperatures. Sample weight = 2.665 g.

trial values could be written

$$b_{i,r+1} = b_{i,r} + \alpha_r N_{i,r},$$

where

$$N_{i,r} = \frac{(1 + b_{i,r}^2)(\partial\phi/\partial b_i)_r}{\left[\sum_{j=1}^3 (1 + b_{j,r}^2)(\partial\phi/\partial b_j)_r^2\right]^{1/2}},$$

$$\alpha_r = \alpha_{r-1}(1 + 0.5 \cos^4 \theta)$$

and

$$\cos \theta = \sum_{j=1}^3 N_{j,r} N_{j,r-1}.$$

This technique ensures rapid convergence for practically all assumed initial values of the parameters.

RESULTS AND DISCUSSION

The oxygen depletion isotherms are given in Figs. 1 to 3 for three bismuth molybdates where the ratios of bismuth to molybdenum are 2:1, 1:1, and 2:3. The depletion isotherms have been obtained only for short times (<100 min) so that the pellet behaves as a semi-infinite solid to enable Eq. (6) to hold.

The results of the computations are given in Table 1 along with some relevant physical properties of the oxides. The diffusion coefficient is the largest for the 2:1 compound and the smallest for the 2:3 compound.

An important question from a catalytic point of view is in what manner the diffusion coefficient of oxygen in the lattice influences the activity of the catalyst. This is a natural question since the lattice oxygen is responsible for the oxidation

process (1-3). Schuit (7) classifies the three bismuth molybdates in the following order as concerns their activity: the 2:3 compound has the lowest activity and the 2:1 compound the highest activity. Because the diffusion of lattice oxygen is the largest in the 2:1 compound and the smallest in the 2:3 compound, the order of the activities is in the same direction as the order of the diffusivities of the oxygen in the lattices.

CONCLUSION

Depletion of oxygen from oxide catalysts can be used to measure the diffusion coefficients of oxygen in the corresponding lattices.

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