nal consistency of the data by the method set forth by Birge.[7] Starting with the seven LiCl/AgCl weight ratios one may compute the most probable errors of these ratios, and make a least-squares propagation of these errors to the final lithium atomic weight values. If the probable errors of the atomic weight of lithium based on the seven determinations are computed on the basis of external and internal consistency and then their ratio is taken, the value, 1.94, is obtained. Now theory predicts that this ratio should deviate from unity by 18%; however, it varies by over five times that amount. This clearly shows the presence of systematic errors in the work even though the experimental work was performed with great precision. A partial explanation may be in the fact that one of the great problems for various workers at that time was the elimination of sodium impurity in their lithium chloride. In fact Richards and Willard[6] state that the purer they got their materials with respect to sodium impurity, the lower was their computed atomic weight for lithium. It should, therefore, not be surprising that a lower value is obtained in the present determination by the X-ray–density method which is practically insensitive to sodium impurities in the lithium fluoride.

The great consistency of the X-ray and density data employed in the present work is shown by the highly consistent results obtained in the previous application of it by the writer[2] to the determinations of atomic weights and by Birge[8] in his use of the data for the determination of the now best values for the Avogadro number and electronic charge. Thus, the value obtained for the atomic weight of lithium in the present determination is mainly dependent on the mass value of fluorine obtained from nuclear reaction data.

It may be noted that the present value for the atomic weight of lithium must be assumed in order to achieve agreement of the atomic weight of fluorine[2] from density and X-ray data with the atomic weights of fluorine obtained from chemical, mass spectrographic and nuclear reaction determinations.

(7) R. T. Birge, *Phys. Rev.*, **40**, 207 (1932).

(8) R. T. Birge, *Am. J. Phys.*, **13**, 63 (1945).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BRISTOL UNIVERSITY]

Solid Solutions of Lithium Oxide in Nickel Oxide

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RECEIVED AUGUST 3, 1953

The effect of gaseous atmosphere and temperature of diffusion on the solid solution of lithium oxide in nickel oxide has been studied. It is shown that the partial pressure of oxygen present during the solid solution determines its character and extent. The absence of excess oxygen prevents the formation of a vacancy free solid solution. The interoxide reaction proceeds to some extent at 600° but at this temperature it is probably limited to the surface layers. Even at 1100° the reaction within the interior of the oxide particles proceeds slowly.

Introduction

Mixed oxides have proved to be catalysts of very wide applicability and considerable interest has been shown in attempts to systematize their behavior and character. Huttig[2] and his co-workers have made intensive studies in which the physical state of such catalysts under varying temperature treatment were correlated with their subsequent catalytic activity. The greatest catalytic activity was found when intermediate states in the interoxide reaction were present. In these states, diffusion of one species over or into the other was occurring with the production of defect structures.

Verwey,[3] in studying mixed oxide systems with regard to their electrical properties, has made use of the principle of induced valence semiconductivity. For example, he has shown that the semiconductivity of nickel oxide can be altered markedly and in a controlled fashion by incorporating in the lattice lithium ions. The mixtures appeared to be homogeneous of composition $Li_\delta Ni_{1-2\delta}^{2+} Ni_\delta^{3+}O$, and up to 10 at. %, the Ni^{3+} was equivalent to the lithium added.

Hauffe[4] has used this principle as the basis of his theory of the corrosion of metal alloys and both he and Parravano have extended this to the general problem of oxide catalysis itself. Parravano[5] has shown that a correlation exists between the activation energy for the oxidation of carbon monoxide over a nickel oxide catalyst and the nature of the added ion. Hauffe[6] has used similar catalysts for the decomposition of nitrous oxide but the correlation in this case was not so simple.

The formation of these catalysts involves a high temperature diffusion of both lithium and oxygen ions into the nickel oxide matrix. Accordingly, some experiments have been carried out to investigate how the resulting solid solution depends on the temperature and the gaseous atmosphere of the diffusion process.

Experimental

Preparation of Solid Solutions.—A series of mixtures of nickel oxide and lithium oxide (containing in turn 0.00, 0.5, 1.0, 5.0, 10.0 and 50.0 atomic % lithium oxide) were prepared as follows. Finely ground nickel carbonate (80 mesh) was made into a smooth paste with the appropriate amount of a solution of lithium carbonate in very dilute acetic acid. These mixtures, with the exception of half the 5.0 at. % Li mixture, were then heated in air at 600° for three hours to decompose the carbonates. The second half of the 5.0 at. % Li mixture was heated at 600° for three hours under continuous evacuation. The seven decomposed mixtures were

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(1) Psychology Laboratory, Cambridge University, Cambridge, England.

(2) G. Huttig, *J. chim. phys.*, **36**, 84 (1939).

(3) E. J. W. Verwey, *Phillips Res. Rep.*, **5**, 173 (1950).

(4) K. Hauffe, *Werkstoffe u. Korrosion*, **2**, 131, 221, 243 (1951).

(5) G. Parravano, THIS JOURNAL, **75**, 1452 (1953).

(6) K. Hauffe, *Z. physik. Chem.*, **201**, 223 (1952).

TABLE I

ELECTRICAL RESISTANCE (OHM CM.) AT 22°

Heat treatment	% of lithium (at. %)						
	0.0	0.5	1.0	5.0		10.0	50.0
				air dec.	vac. dec.		
Vacuum anneal	1.45×10^6	1.10×10^6	1.00×10^5	7.60×10^4	9.80×10^5	1.10×10^6	6×10^7
Oxygen anneal	6.15×10^4	5.30×10^4	3.25×10^4	4.10×10^4	6.15×10^4	7.60×10^3	4.20×10^5
Partial oxygen anneal	4.75×10^6	2.35×10^6	1.15×10^6	7.25×10^5	1.40×10^6	3.1×10^6	$\sim 10^8$

then compressed into pellets (3800 lb. in.$^{-2}$) and a portion of each of them subjected to the following heat treatments.

Firstly, a set consisting of a sample of each of the mixtures was heated at 1100° (±20°) for eight hours under continuous evacuation (10^{-4} mm.), after which rapid cooling to room temperature was carried out.

Secondly, a set of the mixtures was heated at 1100° for eight hours in an excess of oxygen, and then similarly quenched.

Finally, the remaining set of the mixtures was treated under similar temperature conditions in the presence of a limited supply of oxygen. The pressure of oxygen in the system was initially 16 mm. and during the course of the eight-hour period this value dropped to 9.5 mm. The rate of uptake was very slow at the end of the period. The amount of oxygen which is required to convert the 50 at. % Li mixture alone to the defect formula of Verwey would have produced a pressure of 237 mm. The amount of oxygen available and that actually used up is considerably less than this.

During the three heat treatments, each pellet was covered with a thin layer of its own powder in an attempt to prevent volatilization of lithium from it. Similar precautions were taken by Verwey and in his case there seemed to be little loss of lithium. However, if such a loss did occur, it may well account for some of the low Ni^{3+} values which were obtained in the present work.

Properties of Solid Solutions.—These three sets of seven mixtures were examined physically for their lattice structure, semiconductivity and magnetic susceptibility; and the following results were obtained.

A Debye–Scherrer X-ray photograph (using CuKα radiation) was taken of each mixture and from it, the nickel oxide lattice parameter could be calculated. Within each heat treatment, the parameter decreased with increasing lithium content up to 5 at. % Li. For example, the values of a, the lattice parameter of the nickel oxide, were 4.181, 4.180, 4.179 and 4.178 Å. when the lithium content had the values 0.0, 0.5, 1.0 and 5.0 at. %, respectively. Above 5 at. % Li, there was considerable line broadening which indicated distortion of the lattice; and for both the vacuum and partial oxygen treatments, the presence of a second phase of metallic nickel appeared on the photographs.

For measuring the electrical resistance of the mixtures both a.c. and d.c. methods were employed, and also resonance methods using frequencies up to 25 mc. sec.$^{-1}$. Provided the applied voltage was greater than 5 volts, all the methods gave approximately the same value. The resonance method did show a decrease in resistance above 10^6 c. sec.$^{-1}$; but the type of behavior which was observed by Verwey and others[7] for barrier layer capacitors was not obtained. This seems to indicate that, in the present case, the bulk resistance is greater than that of the surface layers. It is a resistance characteristic of these regions, that has been measured. These resistances are given in Table I.

For each of the heat treatments, the addition of the lithium to the nickel oxide decreased the electrical resistance by a small factor up to 10 at. % Li. The resistance of those mixtures which were annealed in oxygen is appreciably less than the corresponding ones in the other heat treatments, although the change with increasing lithium content is least within this set. Above 10 at. %, the appreciable quantity of the insulating lithium oxide begins to predominate. The vacuum decomposed mixture containing 5 at. % Li has a higher resistance than the air decomposed mixture of the same composition under all three heat treatments.

The color of the mixtures was in general agreement with the resistance measurements. In each set, the color changed progressively from gray-green to black with increasing lithium content. The common statement that nickel oxide is an insulator when green and a semiconductor when black is thus supported.

The activation energy for the conductivity was calculated from the $\log_e$ (resistance) against $1/T$°K. plot for each mixture. It was found that, with the exception of the 50 at. % Li mixture which gave a low value, the activation energy was approximately constant within each heat treatment. The average values for the vacuum, oxygen and partial oxygen anneals were 0.43, 0.38 and 0.53 e.v., respectively. The error in these energies is ±0.02 e.v.

When the magnetic properties of the mixtures were investigated by the Gouy method, it was found that the mass susceptibility was always field dependent, and this indicated the presence of ferromagnetic material. This effect was greatest for the vacuum annealed set of mixtures; and within each set, greatest for the vacuum decomposed mixture. The amount of ferromagnetism in general increased with the lithium content; but even the pure nickel oxide mixtures in each heat treatment showed it to a small extent. The ferromagnetism, however, showed practically no remanence and this suggested a very fine state of division for the ferromagnetic particles. By an investigation of the temperature dependence of the susceptibility, it was shown that the ferromagnetism was due to metallic nickel. All ferromagnetism was lost suddenly at 360° which is the Curie point of nickel.

Owing to the presence of the metallic nickel, no magnetic analysis of the Ni^{2+} and Ni^{3+} ion concentrations present in the mixtures was possible. However, this method of analyzing induced valence states still offers great possibilities in other systems, and could be applied in the present case if all the nickel was oxidized.

Attempts to analyze chemically for the amount of Ni^{3+} which was formed during the solid solution were complicated and always gave values much lower than that which would be equivalent to the lithium added. This can be ascribed in two ways. The metallic nickel interferes in the analysis by reducing the oxidative power of the Ni^{3+}. More fundamentally, the low values are thought to be due to incomplete solid solution. This incomplete solid solution is apparent from all the above results. For example, while the resistance effects are in general agreement with those of Verwey, the magnitude of the effects is considerably less.

Discussion

The metallic nickel is probably produced by partial reduction during the decomposition of the carbonates, and in the case of the vacuum and partial oxygen annealed mixtures by reduction of some of the nickel oxide by the lithium oxide. The small nuclei of the metal are probably imbedded in the oxide particles, since they withstand complete oxidation even in the oxygen anneal.

Anderson[8] and others have suggested that bulk diffusion in ionic compounds only becomes appreciable above 0.5 T_m, where T_m is the melting point in degrees absolute. Further, if defects of the Verwey type (as shown in Fig. 1) are produced during the solid solution, the lattice will have a minimum number of vacant lattice sites and diffusion will be slow, if a vacancy mechanism is assumed. This seems likely since the ions involved are of approximately equal size.

The heating temperature in the present experiments was 1100° which is 0.58 T_m and the attain-

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(7) E. J. W. Verwey, "Semiconducting Materials," Butterworth Scientific Publications Ltd., London, 1951, p. 151.

(8) D. J. M. Bevan, J. P. Shelton and J. S. Anderson, *J. Chem. Soc.*, 1729 (1948).

ment of true equilibrium and a uniform distribution would be very slow processes. This is borne out by the oxygen uptake in the partial oxygen anneal.

There is a difference between the properties of the mixtures of 5 at. % Li for the vacuum and air decompositions. Again, the vacuum annealed mixtures showed all the effects of solid solution, at least to some extent. Hence it is evident that the interoxide reaction does occur at 600°. However, at this temperature it appears that the reaction is restricted to the surface layers.

The nickel oxide catalysts, which were used by Parravano,[5] were sintered at 600° and probably have a surface concentration of lithium considerably higher than that in the bulk. He observed no reversal in the activation energy trend with increasing concentration, but this is not surprising since he did not use more than 1 mole % Li_2O. Hauffe[6] sintered his catalysts at 900° and did observe a reversal in activation energy above 1 mole % Li_2O. These results agree with the present work, where a reversal in the trend of the physical properties of the mixtures was observed above 5 at. % Li. Verwey,[3] who sintered his nickel oxide mixtures at 1200°, found a monotonic change in properties even for concentrations of lithium above 10 at. %. It appears, therefore, that a sintering temperature of greater than 1100° is necessary to produce complete homogeneity for solid solutions of lithium oxide in nickel oxide.

Ni^{2+}	O^{2-}	Ni^{2+}	O^{2-}	Ni^{2+}
O^{2-}	Li^{+}	O^{2-}	Ni^{2+}	O^{2-}
Ni^{3+}	O^{2-}	Ni^{2+}	O^{2-}	Ni^{2+}
O^{2-}	Ni^{2+}	O^{2-}	Ni^{2+}	O^{2-}

Fig. 1.—Solid solution of lithia in nickel oxide—two dimensions.

Acknowledgment.—The author wishes to thank Professor W. E. Garner and Dr. M. Boudart for their interest and many helpful discussions. Thanks are also due to the Royal Commission for the Exhibition of 1851 for an Overseas Scholarship which made the present work possible.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

The Effects of Ionizing Radiation on Heterogeneous Catalysts—Zinc Oxide as a Catalyst for the Hydrogenation of Ethylene[1]

BY ELLISON H. TAYLOR AND JOHN A. WETHINGTON, JR.

RECEIVED SEPTEMBER 23, 1953

Irradiation with γ-rays lowers the catalytic activity of ZnO for the hydrogenation of ethylene. There is some evidence that this is the result of electronic changes produced in the catalyst by the radiation, although the possibility of poisoning by radiation-polymerization of residual ethylene is not definitely excluded. The possible utility of such experiments in the study of heterogeneous catalysis is indicated.

Introduction

Recent interest in the relation between catalytic properties and electronic structure of heterogeneous catalysts prompts us to report preliminary results of experiments undertaken to try to demonstrate as directly as possible some features of this relation. The hypothesis that led to these experiments was that the changes produced in ionic crystals and semi-conductors by ionizing radiation might include changes affecting catalytic behavior. Since changes produced in this way can be characterized by physical measurements (electrical conductivity, etc.) and since they are beginning to be explicable in terms of the electron theory of solids, the demonstration of an experimental connection with catalytic changes should be interesting. Many experimental tests of the more fundamental ideas about catalysis involve systematic variation of a particular property (*e.g.*, lattice parameter) through a series of catalysts. The well-known irreproducibility of catalysts is a handicap in such programs. The technique of inducing changes by irradiation avoids this difficulty, since measurements can be made on the same sample of catalyst before and after the irradiation. In this respect this approach is similar to studies employing sintering, but has the advantage that the changes are more easily characterized by physical measurements.

The catalyst chosen for this study was ZnO, because it appeared to be likely to show such an effect. A rather close parallel can be noted between the preparation of catalytic ZnO and semi-conducting ZnO, and it was surmised that the catalytic activity is centered at sites related to those responsible for semi-conductor behavior. It is known that irradiation produces marked effects in semi-conductors, so a catalyst which is also a semi-conductor was a natural choice.

Experimental

The reaction used to assess the catalytic activity was the hydrogenation of ethylene, carried out with 1.000 g. of ZnO and 10 cm.³ of ($2H_2 + 1C_2H_4$) in a Pyrex tube 24 mm. o.d. by 125 mm. long, connected to a manometer which contained (including the connecting tubing) less than 5% of the gas volume. The reaction was so slow as to allow omission of stirring. The reaction was followed manometrically, assuming that it was indeed the hydrogenation of ethylene, as observed by Woodman,[2] rather than polymerization. This assumption was confirmed by a cryoscopic analysis of the residual gas from a run allowed to go to completion. A gas mixture comprising 184.9 mm. H_2 and 95.6 mm. C_2H_4 reached a constant total pressure of 186.8 mm. after some 18 hr. over ZnO at 30°. If the reaction was hydrogenation 95.6 mm. should have been C_2H_6, leaving a final H_2 pressure

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[1] This paper is based upon work performed under Contract Number W-7405-eng 26, for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] J. F. Woodman and H. S. Taylor, THIS JOURNAL, **62**, 1393 (1940).