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.

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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]

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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 semiconductors, so a catalyst which is also a semiconductor 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).

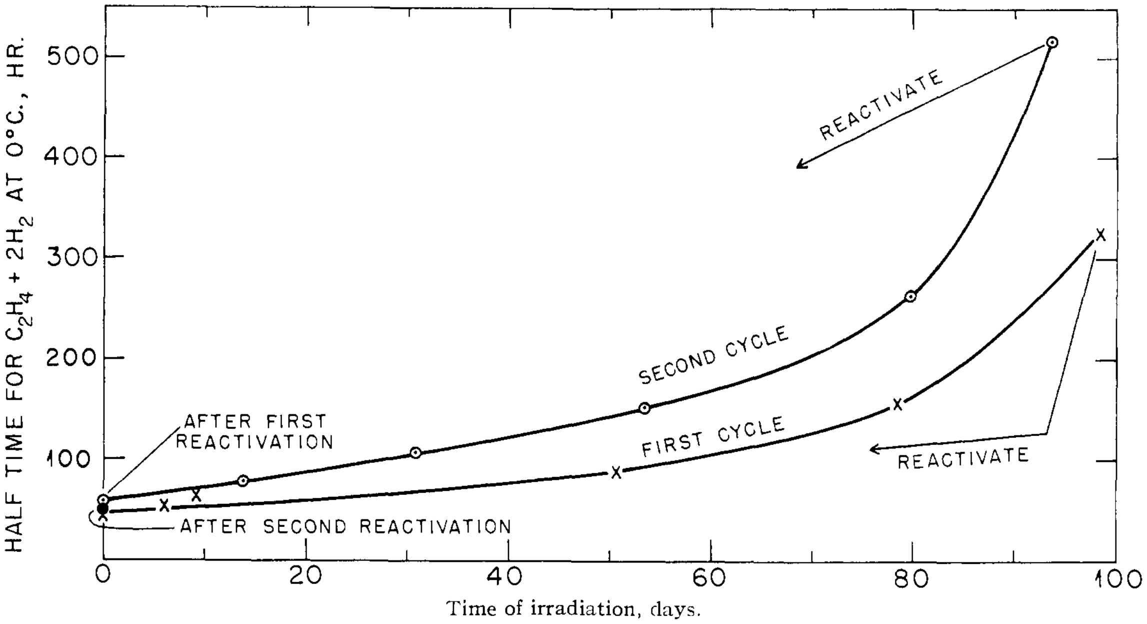

Fig. 1.—Effect of irradiation on the activity for ethylene hydrogenation of a ZnO catalyst. (Co^{60} γ-rays at *ca.* 10,000 roentgen/min.)

of 91.2 mm. by difference. If the C_2H_6 were frozen out in liquid N_2, the residual pressure should be that of H_2 only, reduced by the temperature ratio, 77/303, or 23.2 mm. The sample bulb (at least 95% of the volume) was so frozen, and the pressure observed was 23.5 mm. If the reaction were polymerization, the final total pressure should be the same, but this, being mostly H_2, would be reduced only to 184.9 × 77/303 = 47.0 mm. by liquid N_2.

Samples were evacuated at a constant temperature between runs, and the reproducibility of successive runs was entirely adequate after (in most cases) a preliminary period of declining activity, particularly noticeable when the evacuations were at 100°. One sample thus had successive half-times measured at 0° of 22, 25, 29 and 28 hr. after activation at 360° and inter-run evacuations at 100°. The continual decrease in activity from run to run noted by Woodman[2] was not observed, presumably because of differences in the catalyst or in the inter-run pumping.

The ionizing radiation was supplied by a Co^{60} source delivering γ-rays at about 6000 to 10,000 roentgen/min., depending on position. The samples were irradiated *in vacuo* in the reaction tubes at 15 ± 5°. They were evacuated before irradiation at the temperature used for inter-run evacuations in the particular series, usually 0° but sometimes 100°.

Results and Discussion

Supporting experiments established connections between activity and conditions of preparation which strengthen the analogy with semi-conduction. Evacuation at temperatures up to about 200° produced no activity; increasing temperature above that produced increasing activity up to a plateau around 450°. Half-times (measured at 26°) after a series of successive overnight evacuations of the same sample were: 200°, 105 hr.; 300°, 9.4 hr.; 400°, 6.5 hr.; 450°, 4.9 hr.; 500°, 5.3 hr. The role of oxygen in activation was shown by heating a sample of ZnO in O_2 overnight at 360°, the usual activation temperature. The sample was essentially inactive (half-time at 0° over 1000 hr.). Subsequent overnight evacuation at 396° produced a moderately active catalyst, half-time 42 hr. at 0°. Addition of O_2 to an active catalyst diminished the activity, a particular sample going from a half-time at 0° of 23 to 80 hr. on treatment at room temperature with air for 0.5 hr. It is clear that the catalytic activity, like the electrical conductivity[3] is closely related to oxygen deficiency in the oxide. Another indication in the same direction was an experiment in which a sample of half-time 2.9 hr. (at 26°) was essentially unchanged by two successive overnight heatings at 400° with Zn vapor (half-times 3.2 and 3.1 hr.).

The principal result of the work was the observation of a definite effect of γ-irradiation upon catalytic activity. Previous reports[4] on such effects have tended to be inconclusive. In some, metal catalysts have been used, in which one would not expect storage of energy, and in others the radiation has been applied during the activity measurement, leaving the possibility that any effect was due to radiation-induced reaction of the substrate. In the present work, a total of 19 separate irradiations of 10 samples of ZnO produced measurable decreases in activity, demonstrated most clearly by Fig. 1 which shows the effect of successive irradiations of the same sample. In no instance did sufficient radiation fail to produce this effect.

That the effect was not a gross sintering was shown by surface area measurements[5] that were unchanged by irradiation, the sample used having an area (measured by N_2) of 4.1 meter²/g. originally, 4.3 after activation, and 4.4 and 4.3 after 10 and 23 days total irradiation, respectively. Nor was it poisoning by air admitted through a radiation-produced pinhole, for several of the runs were checked by duplicates before further irradiation.

The most attractive explanation for this behavior is of course that it is the result of the electronic

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[3] D. J. M. Bevan and J. S. Anderson, *Faraday Soc. Disc.*, No. 8, 238 (1950).

[4] P. Guenther, *Ergebnisse tech. Roentgenkunde*, **4**, 100 (1934).

[5] Measurements by P. R. Kuehn of the K-25 Plant, Carbide and Carbon Chemicals Company.

dislocations in the catalyst produced by the irradiation. This has not yet been conclusively demonstrated, but the only plausible alternate hypothesis is that it is a poisoning by radiation-polymerized reactants (or products) not removed by pumping prior to irradiation. This is rendered unlikely by two lines of evidence. First, a copper catalyst, presumably unable to store energy from the radiation but capable of retaining some residual gases for later polymerization and poisoning, was essentially unaffected by an irradiation sufficient to reduce by one-third the activity of a ZnO catalyst. The half-time was changed only from 16 to 17 min. by 312 hr. of irradiation. Second, a ZnO sample which had been increased in half-time from 45 to 326 hr. by irradiation was restored to 57 hr., and again after further increase to 518 restored to 48 hr. by the usual activation. One would not expect a high molecular-weight polymer to be removed so completely, while one would expect an annealing of effects on the catalyst itself.

A consideration of the magnitude of the observed effect relative to the radiation dose leads to an equivocal conclusion, namely, that one cannot thereby distinguish between the electronic-dislocation and the poisoning-by-polymerization hypotheses. In the first place, the total dose corresponding to the lowest activity of the first curve of Fig. 1 is about 40 to 50% of that required to polymerize all of any residual ethylene, assuming a dose rate of 6.2×10^{17} e.v./min., cm.[3] H_2O,[6] a yield for ethylene polymerization equal to that observed with alpha rays in the gas, 5 to 6 molecules/ion pair[7] (= *ca.* 15 to 18 molecules/100 e.v.), a time of irradiation of 2362 hr., and a mass absorption coefficient for C_2H_4 greater than that for H_2O in the ratio of the respective electron densities (ratio = 1.03). This dose reduced the catalytic activity to about 13% of its initial value, implying a considerably greater fraction of C_2H_4 immobilized by polymerization than the 40 to 50% estimated above. Since this calculation is only rough and the actual dose might be considerably higher, one should not argue that it makes the polymerization hypothesis untenable. On the other hand, it is unlikely that much C_2H_4 remains on the surface after evacuation (the effect of radiation was observed whether the evacuation was at 0° or 100°), and whatever amount does remain must be strongly held and hence be unlikely to polymerize with a yield anywhere near as large as the gas phase value assumed above.

Another approach in trying to decide between poisoning and electronic changes in the solid is a comparison of the rate of loss of catalytic activity with the rate of production of some of the typical physical effects with which it is hoped ultimately to establish an experimental connection. The most striking and best understood of these, the production of color centers in alkali halide crystals, indeed seems quite distinct in time scale from the present effects, reaching saturation in less than a day in radiation of the intensity used in this work. On the other hand, there are more complex effects observable in glow spectra and in electrical conductivity[8] which seem to continue to intensify over irradiation periods as long as those under consideration here. These slower effects presumably involve not simply trapping of the electrons at pre-existing defects, but the migration of entities of atomic dimensions to create new defects or new arrangements of multiple defects.

These results suggest that interesting information about the nature of non-metallic catalysts can be obtained through the use of ionizing radiation to produce subtle changes in structure. The utility of such an approach hinges on the possibility of correlation of the activity changes with changes in those physical properties which are beginning to be understood in some detail, electrical conductivity, Hall effect, luminescence, etc. If, as suggested, the correlation is with some of the secondary effects that are presently less well understood than, say, the formation of F-centers in alkali halides, the interpretation will be more difficult, but, it may be hoped, none the less fruitful.

Heavy particle radiation (fast neutrons, protons, etc.) may have similar uses, the changes there including not only those produced by gamma rays, but also dislocations of the lattice of the catalyst. Finally, irradiation of certain elements with slow neutrons could be used to produce significant amounts of homogeneously distributed transmutation products, and might therefore be useful in the study of promotion and poisoning, where one of the present difficulties is the preparation of homogeneously promoted or poisoned catalysts.

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(6) J. A. Ghormley and C. J. Hochanadel, personal communication.

(7) S. C. Lind, D. C. Bardwell and J. H. Perry, THIS JOURNAL, **48**, 1556 (1926).

(8) J. A. Ghormley and C. M. Nelson, personal communications.