NOTES

Photoenhancement of the H_2–D_2 Reaction
Catalyzed by Zinc Oxide

We wish to report that the rate of the H_2–D_2 exchange reaction catalyzed by ZnO was greatly enhanced while the catalyst was being irradiated with near-ultraviolet light. The photoactivation of the catalyst was shown to be reversible with respect to the light at the three temperatures studied: $-196°$, $80°$, and $110°C$.

With one exception (1), all heterogeneously catalyzed photosensitive reactions reported involve oxygen as one of the reactants. Many catalyst-reactant systems employing catalysts suspended in liquids have been reported (2) to have photosensitive rates, but only five systems involving gaseous reactants, $O_2^{16} + O_2^{18}$ over ZnO (3), $CH_3OH + O_2$ over ZnO (4), $CO + O_2$ over CuO (5), $H_2 + D_2$ over MgO (1), and $CO + O_2$ over ZnO (6), have been reported.

Numerous studies have been carried out in an attempt to correlate the catalytic and electronic properties by comparisons of diversely doped semiconductors. An especially interesting example of doping effects, because the rate measurements were made at low temperature, was the study of the ZnO catalysis of H_2–D_2 exchange reported by Harrison and McDowell (7). They showed that the rate of the exchange reaction at $-196°$, presumably in the dark, was increased 81-fold by doping ZnO with the free radical α,α-diphenyl-β-picryl hydrazyl. In the present experiments we considered that a reversible photoenhanced rate could be due to reversible doping in the sense that charge carriers can be added by the action of light. Assuming a correlation between electronic properties and catalysis the largest catalytic photoenhancements would be expected to be found at low temperatures, since the per cent change in the number of electronic charge carriers upon illumination of a semiconductor is greater at low temperatures.

Our experiments, designed to study photoenhanced catalysis, were carried out at approximately atmospheric pressure in a 350 cc recirculating system employing a fluidized bed of 4 g of analytical reagent grade ZnO. The pretreatment history of the ZnO was such that it was largely freed of carbon dioxide and water and finally was exposed to hydrogen gas at about 100°. The light source employed was a General Electric H-400 mercury bulb whose radiation was restricted to wavelengths above 300 mμ. In order to ensure that the photoenhancement was reversible and was not due to a gradual changing activity of the catalyst with time, the experiments were conducted, at a given temperature, in the sequence: dark, light, dark. In all cases the rates for the two dark periods, separated by the light period, agreed within experimental error. We wish to emphasize that the dark and light rates reported at each of the temperatures demonstrate photoenhancement but that no temperature-dependence for either the light or dark rates should be inferred from our data. We did not demonstrate that the catalytic activity of our sample was the same for each of the series of experiments conducted at

the three different temperatures. Molinari and Parravano (8) have examined in detail the extreme sensitivity of the dark reaction to the activation procedure. Our experimental results including the maximum estimated error, given in Table 1, are expressed in terms of the rate constant employed by Harrison and McDowell (7) for the dark reaction rate:

$$k = [1/(t_2 - t_1)] \log_{10} (\Delta x_1/\Delta x_2)$$

where Δx_i is the per cent difference of HD from equilibrium at time, t_i in sec.

TABLE 1

Series	Temp (°C)	Rate constant		$k \times 10^{-7}$ (sec^{-1})
		Dark		Light
A	−196	0 ± 1		5 ± 1
B	80	0 ± 1		6 ± 1
C	110	1.5 ± 0.5		3 ± 0.5

One may speculate about the mechanism responsible for the reversible photoenhanced rate. One possibility is that the active sites induced by the light are similar to those responsible for the enhancement of the dark reaction which can be achieved by chemical doping. Parravano (8) has shown that Ga doping (Ga increases the number of electron carriers) of ZnO resulted in an increase of the dark rate measured above room temperature.

A second possibility is that the active sites are chemical intermediates formed during the course of the chemical changes which are known to accompany photoinduced electron conductivity. To explain the reversibility of the photoenhanced catalysis the active sites created during the illumination must rapidly disappear upon turning off the light. The nature of the chemical changes have been deduced from conductivity measurements on single crystals of ZnO. It has been shown (9) that the photoproduced holes (holes and electrons are formed in equal numbers by the light) neutralizes negative charges of the oxygen anions residing on the surface. We suggest that the active sites result

from the partial neutralization of surface oxygen anions and are species intermediate between an oxide ion similar to a lattice anion (O^{2-}) and a sorbed diatomic oxygen molecule. Hence we propose that large numbers of these partially neutralized species, e.g., $O_{(s)}^-$, $O_{2(s)}^{2-}$, $O_{2(s)}^-$, are present only during the illumination period, and when the light is turned off the active sites react to form inactive stable species, such as $O_{(s)}^{2-}$ and $O_{2(s)}$.

Several other possible mechanisms should be considered including those not involving the creation of a new pathway for the photoreaction. In view of the known surface photochemistry (9) it is more difficult to support mechanisms in which the light functions to increase the rate of the slow step in the dark reaction pathway.

Infrared (10) and electron paramagnetic resonance measurements (11, 12) appear to be promising tools and are currently in progress in an attempt to distinguish whether the photoinduced catalysis is directly related to the increase in the number of charge carriers or is the result of chemical changes accompanying the increase in the number of electrical carriers.

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Heterogeneous Catalysis of a Dilute Solution of Sodium in Liquid Ammonia

INTRODUCTION

It is well known that platinum catalyzes the decomposition of alkali metal solutions in liquid ammonia (*1, 2*). The purpose of this note is both to present some quantitative data on the reaction

$$Na + NH_{3(liq)} \xrightarrow{Pt} NaNH_2 + \frac{1}{2} H_2$$
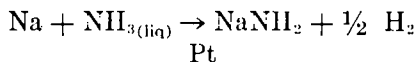
at −78°C and to consider the effect of initial treatment of this system on the rate of decomposition. Because the initial treatment significantly alters the rate of decomposition of metal-ammonia solutions, it is necessary to consider the initial purification of the glass surface prior to its contact with the blue solution (*3, 4*).

EXPERIMENTAL

A simple procedure for the preparation of a dilute solution of sodium in liquid ammonia at −78°C has been described previously (*5*). This procedure was used to wash the surface of the ampule including a platinum foil (4.3 × 2.5 × 0.015 cm) for varying lengths of time. After washing the system with the blue solution, the ammonia was distilled into another ampule on the vacuum line. Then the system was flamed (while pumping) to distill out any volatile residue. The above procedure was repeated to prepare 4.0 cc of the sodium-ammonia solution at −78°C, and its de-

composition was studied in the presence of the platinum foil. Pressure measurements of the evolved hydrogen were made by means of a calibrated McLeod gauge, which had a trap with a liquid nitrogen bath around it between the McLeod gauge and the ampule containing the blue solution. (The volume of the system was 1.74 liters.) At convenient time intervals the pressure of the evolved hydrogen was measured by replacing the dry ice-acetone bath with a liquid nitrogen bath. After each pressure measurement, the evolved hydrogen gas was pumped out of the system. When the final pressure measurement of each "run" was made, the blue coloration had completely faded. The initial concentration of sodium was calculated from the total pressure of evolved hydrogen (at room temperature) (Fig. 1).

RESULTS AND DISCUSSION

Figure 1 summarizes the kinetic data, including the effect of washing the system with the blue solution at −78°C. The data plotted (pressure vs. time) seem to indicate that two reactions occur: (1) reaction at the glass–liquid interface due to the presence of adsorbed water (*5*), (2) reaction at the platinum–liquid interface (*1*). The effect of washing the system with a blue solution for increasing lengths of time appears to be a decrease in the evolution of hydrogen in the first reaction. This trend is to be expected if adsorbed water is