JOURNAL OF CATALYSIS 3, 387–389 (1964)

NOTE

Photocatalytic Oxidation of Ammonia on Zinc Oxide Catalysts

We report here the reaction between gaseous ammonia and oxygen, occurring at room temperature on ultraviolet-irradiated zinc oxide catalysts, yielding nitrous oxide, nitrogen, hydrogen, and water; or nitrogen, hydrogen, and water, depending upon the pretreatment of the catalyst. The photocatalytic behavior of zinc oxide suspensions is well known, however few examples have been reported of vapor-phase photocatalytic reactions. Equilibration of oxygen isotopes at 25°C (*1*) and the oxidation of carbon monoxide at 400° and 0°C (*2*, *3*) have been carried out on zinc oxide catalysts. Cuprous oxide films on Cu metal are also photocatalytically active at 25°C for oxidation of CO (*4*).

Direct exposure of gaseous ammonia to ultraviolet radiation results in decomposition to N_2, and H_2 for ammonia pressure to 1 atm (*5*).

Hydrazine is obtained as a product in flow systems upon irradiation at 1849 Å, however no hydrazine is obtained upon static photolysis of NH_3 (*6*). The photochemical reaction of ammonia with oxygen gas has been reported to yield only N_2, H_2, and H_2O as products (*7*). It has also been reported that this reaction yields some ammonium nitrate and nitrite, but that these compounds decompose upon prolonged irradiation into N_2, H_2O, and O_2 (*8*).

The reaction of ammonia gas with oxygen is reported to yield nitrous oxide as principal product on several oxide catalysts (*9*, *10*), notably those of Bi, Mn, Co, Cu, and Fe. Krauss suggests that these oxides contain excess oxygen as lattice defects, and operate to form N_2O because of this active oxygen. Optimum yields of N_2O are obtained with these catalysts above 200°C. It is also reported that *p*-type semiconductor oxides are more effective catalysts for this reaction than *n*-type oxides (*11*).

EXPERIMENTAL

Anhydrous ammonia gas and dried cylinder oxygen were passed at flow rates of 40 ml/min into a quartz tube of 400 ml capacity, the inside of which was coated with zinc oxide. The zinc oxide coating was deposited by suspending approximately 5 g of ZnO in 25–30 ml of absolute ethanol, followed by removal of ethanol by vacuum evaporation while continuously rotating the quartz tube. The ZnO formed a uniform coating about 0.05 mm thick. The quartz reaction tube and quartz tube containing the Hanovia 550 watt Hg arc lamp were immersed in cooling water maintained at 23–25°C. The distance between the lamp and the reaction chamber was 5 cm. The reaction tube was then irradiated with the full Hg spectrum for 1 hr, after which samples were collected for analysis. Water and unreacted ammonia were removed with a cold trap and solid oxalic acid. Analysis of products was carried out by gas–solid chromatography (*12*). The presence of N_2O was further confirmed by its infrared spectrum.

RESULTS

The results of several experiments are summarized in Table 1. The photolytic reaction of NH_3 and O_2 and the homogeneous photolytic dissociation of NH_3 occurred to a large extent on ZnO (B).

TABLE 1
RESULTS OF PHOTOCATALYTIC OXIDATION OF NH_3 ON ZNO SAMPLES

Catalyst[a]	Products found (not removed by Dry Ice-acetone trap)	Other products found	Conditions of reaction
ZnO (A)	N_2O – 77% N_2 – 14% H_2 – 5 to 10% Unreacted O_2 also observed.	H_2O HNO_3 (traces) Unreacted NH_3	Continuous irradiation of catalyst
ZnO (A)	No reaction O_2 only	No reaction Unreacted NH_3 only	No irradiation of catalyst
ZnO (B)	H_2 – 45 to 50% N_2 – 30 to 35% Unreacted O_2 also observed.	H_2O Unreacted NH_3	Continuous irradiation of catalyst

[a] ZnO (A): Sample prepared by decomposition of $ZnCO_3$ at 550°C, followed by heating under flowing H_2 at 250°C for 2 hr prior to use.

ZnO (B): Sample prepared as (A), H_2 treatment followed by heating under flowing O_2 at 300°C for 2 hr prior to use.

Analysis of samples by EDTA titration, Eriochrome Black T indicator: Calc.; Zn 80.60%, O 19.40%. ZnO (A); Found Zn 81.40%, ZnO (B); Found Zn 79.95%.

With ZnO (A), less than 15% of the NH_3 was consumed by gas phase, homogeneous dissociation or homogeneous reaction with O_2. The zinc oxide coating was not entirely opaque to passage of ultraviolet radiation, and it appears that N_2 was formed by the homogeneous gas-phase photolysis of the NH_3–O_2 mixture. The compositions shown in Table 1 are analyses of samples removed from the gas stream after removal of H_2O, unreacted NH_3, and other products condensable at —78°C. From estimation of the relative amount of oxygen leaving the reaction chamber, more than 75% of the NH_3 was consumed, either by homogeneous photolytic decomposition or oxidation, or by the competing pathway yielding N_2O. No evidence of reaction could be found in the absence of irradiation. Upon irradiation, only those ZnO samples which had been pretreated with H_2 displayed catalytic activity for N_2O formation. NO and NO_2 could not be detected as reaction products. The catalysts could not be activated by heating *in vacuo*, treatment reported to activate ZnO for hydrogenation of ethylene (*13*).

DISCUSSION

We are unable to state, at this time, the extent to which a difference in light transmission of the ZnO coatings (A) and (B) is responsible for the greater N_2 concentration obtained on (B). Since nearly equal amounts of ZnO were used the thickness of the ZnO coatings is comparable, and it appears that the difference in relative amounts of N_2 obtained on (A) and (B) is a result of the competing reaction yielding N_2O.

These results may be interpreted with respect to photoelectric processes occurring on zinc oxide. Oxygen gas, under the conditions of this experiment, is desorbed during irradiation of zinc oxide (*14*). Since the value of the photoconductivity of zinc oxide decreases with increasing pressure of oxygen (*15*), chemisorbed oxygen is released from the ZnO surface by capture of electrons or holes, and released in an active form. The reactive oxygen may either de-

sorb, or in the presence of ammonia may react with ammonia forming nitroxyl (HNO) and H_2O. N_2O may then be formed by combination of two HNO molecules, which is in agreement with the mechanism proposed by Krauss for the catalytic formation of N_2O from NH_3 and O_2 on oxide catalysts at 300°C (*10*), i.e.,

$$h\nu + ZnO(s) \rightarrow {}^{+}(ZnO) + e^{-}(ZnO) \quad (a)$$

$$e^{-}(ZnO) + O_2 \rightarrow O_2^{-}(ZnO) \quad (b)$$

$$HN_3(g) + O_2^{-}(ZnO) \rightarrow e^{-}(ZnO) + HNO + H_2O \quad (c)$$

$$HNO + HNO \rightarrow N_2O + H_2O \quad (d)$$

Reaction (b) appears to be involved in many reactions with irradiated ZnO and O_2. Evidence for reaction (c) is the formation of N_2O from gaseous NH_3 and O_2 on metal oxide catalysts which contain excess oxygen (MnO, CoO, NiO, Fe_2O_3), this oxygen presumably existing as lattice defects (*11*). Krauss reports a uniform rise in catalytic activity for these oxides with increase in concentration of excess oxygen (*10*). However zinc oxide treated with oxygen is not an effective catalyst for this reaction. Similarly our oxygen-treated ZnO (B) is not an effective photocatalyst for oxidation of NH_3 to N_2O. Irradiation of partially reduced zinc oxide [as in ZnO (A)] may make possible a release of chemisorbed oxygen as a reactive species similar to *p*-type oxides previously found to be active catalysts for this reaction in the absence of irradiation.

Formation of N_2O by way of a primary step involving photolysis in the gas phase of either NH_3 or O_2, followed by photocatalyzed reaction steps on the ZnO surface remain as a possible mechanism.

References

1. Barry, T. I., and Stone, F. S., *Proc. Roy. Soc. (London)* **A255,** 124 (1960).
2. Romero-Rossi, F., and Stone, F. S., *in* "Actes du Deuxieme Congr. Intern. Catalyse 2e Paris, 1960," Vol. II, p. 1481. Éditions Technip, Paris, 1961.
3. Nagarjunan, T. S., and Calvert, Jack G., *J. Phys. Chem.* **68,** 17 (1964).
4. Ritchey, W. M., and Calvert, J. G., *J. Phys. Chem.* **60,** 1465 (1956).
5. Wiig, E. O., and Kistiakowsky, G. B., *J. Am. Chem. Soc.* **54,** 1806 (1932).
6. McDonald, C. C., Kahn, A., and Gunning, H. E., *J. Chem. Phys.* **22,** 908 (1954).
7. Berthelot, D., and Gaudechon, H., *Compt. Rend.* **150,** 1327 (1910).
8. Bacon, H. E., and Duncan, A. B. F., *J. Am. Chem. Soc.* **56,** 336 (1934).
9. von Nagel, A., *Z. Electrochem.* **36,** 754 (1930).
10. Krauss, W., *Z. Electrochem.* **53,** 320 (1949).
11. Johnstone, H. F., Houvouras, E. T., and Schowalter, W. R., *Ind. Eng. Chem.* **46,** 702 (1954).
12. Marvillet, L., and Tranchant, J., Qualitative and Quantitative Analysis, By Gas-Solid Chromatography, Of Mixtures Containing Nitrogen Oxides, *in* "Gas Chromatography" (R. P. Scott, ed.) pp. 321–332. Butterworths, Washington, D. C., 1960.
13. Aiguesperse, J., and Teichner, S. J., *J. Catalysis* **2,** 359 (1963).
14. Fujita, Y., and Kwan, T., *Bull. Chem. Soc. Japan* **31,** 379 (1958).
15. Heiland, G., Mollwo, E., and Stockmann, F., *Solid State Phys.* **8,** 278 (1959).

I. E. Den Besten
M. Qasim

Department of Chemistry
Bowling Green State University
Bowling Green, Ohio

Received March 3, 1964