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Selectivity in Ammonia Oxidation on a Cuprous Oxide Crystal

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Experimental measurements have been carried out on the oxidation of ammonia on a crystalline catalyst of cuprous oxide. By simultaneous measurements of electrical conductance and product distribution, it has been found that the electronic defect structure of the catalyst can be related to catalytic specificity. Nitrogen is favored in the presence of a catalyst that has oxygen deficiency while nitrous oxide is the predominant product with a catalyst containing oxygen excess. Kinetic studies demonstrate certain similarities between propylene oxidation to acrolein and ammonia oxidation to nitrogen.

INTRODUCTION

It has been observed in a number of cases that those mixed oxide catalysts which exhibit high specificity for acrolein during propylene oxidation also show high specificity for acrylonitrile during propylene ammoxidation. This specificity toward two entirely different products may be the result of a reaction mechanism involving acrolein as an intermediate in the ammoxidation or of some common steps in the partial oxidation of propylene and ammonia. To elucidate the process of propylene ammoxidation and its relationship to the solid state properties of the catalyst, we embarked on a study of the oxidation of ammonia and of ammonia and propylene in admixture (*1*).

In earlier experiments (*2*) we examined the relationship between the defect structure of cuprous oxide and its catalytic properties in propylene oxidation. In these measurements we employed a crystal of cuprous oxide as the catalyst. By simultaneous determination of product distribution and electrical conductance, we were able to show that a copper-rich cuprous oxide surface favors the formation of acrolein whereas oxygen-rich cuprous oxide and cupric oxide lead to complete oxidation of propylene. In the experiments to be described, we used the same experimental technique for ammonia oxidation.

EXPERIMENTAL DETAILS

Single Crystal Studies

The continuous-flow apparatus employed in the study of ammonia oxidation was identical to that previously used for propylene oxidation (*2*). The cuprous oxide catalyst was grown in the quartz reactor in accordance with the procedure described by Trivich and coworkers (*3*). Measurements of electrical conductivity of the cuprous oxide catalyst were carried out by means of a four-point probe; simultaneously the product distribution was monitored as a function of reaction variables, such as temperature, reactant composition, and gas velocity. The reactants* (NH_3 and O_2) were diluted with a carrier gas** (helium) and the total flow velocity maintained at 120 cm^3/min and a total pressure of 1 atm. The concentrations of reactants

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** Gas purity: NH_3 (99.99 Vol %), O_2 (99.95 Vol %), He (99.95 Vol %). Source: Matheson Co., Newark, CA.

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and products were determined by gas chromatography. Sampling valves were provided for the withdrawal of aliquots of the gas stream entering and leaving the reactor. In the absence of the catalyst, no measurable oxidation of ammonia or propylene occurred under our experimental conditions.

Product Analysis

The following column materials were employed for gas chromatographic analysis of the product distribution. A 15-ft column of 15 wt % Ucon 300 on Chromosorb W gave satisfactory separation of propylene, acrolein, and acrylonitrile at 75°C. A 6-ft column of Poropak Q and a 6-ft column of molecular sieve (Linde 5A) operated at 25°C with a switching valve were employed during the studies of ammonia oxidation. The Poropak Q was used for analysis of N_2O, and the molecular sieve 5A for N_2 and O_2. The helium carrier flow rate was maintained at 30 cm^3/min.

RESULTS

For the oxidation of ammonia the experimental measurements with crystalline cuprous oxide demonstrated a marked change in product distribution with the mixture ratio of O_2/NH_3. As shown by the data presented in Fig. 1, at low partial pressure of oxygen, nitrogen appeared as the predominant product at 548°K. However, its rate of formation went through a maximum, with nitrous oxide becoming predominant at high oxygen partial pressures. A similar effect was noted at 573°K (Fig. 2) and at 623°K. Of special interest are the electrical conductivity data obtained during the catalytic oxidation of ammonia (Fig. 3). In this logarithmic plot,

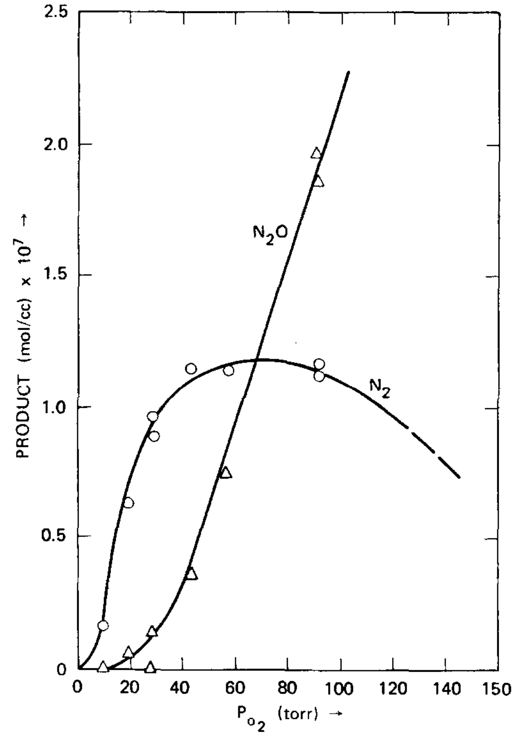

FIG. 1. Ammonia oxidation catalyzed by cuprous oxide at various oxygen pressures and 548°K (initial partial pressure of ammonia = 50 Torr).

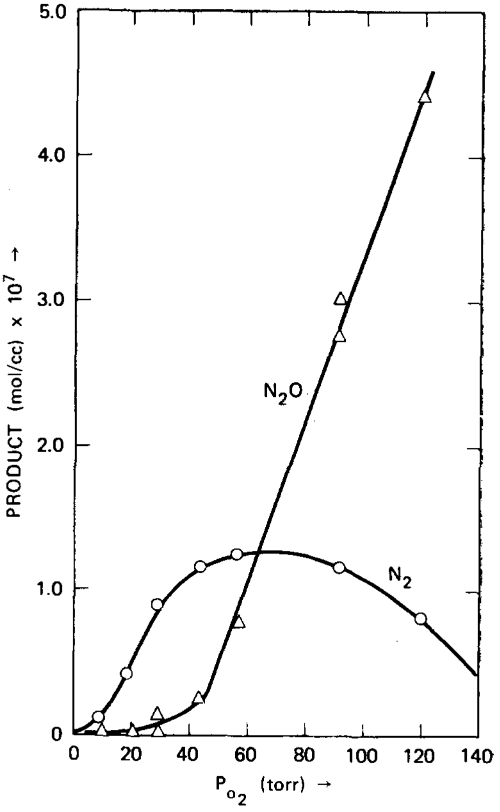

FIG. 2. Ammonia oxidation catalyzed by cuprous oxide at various oxygen pressures and 573°K (initial partial pressure of ammonia = 50 Torr).

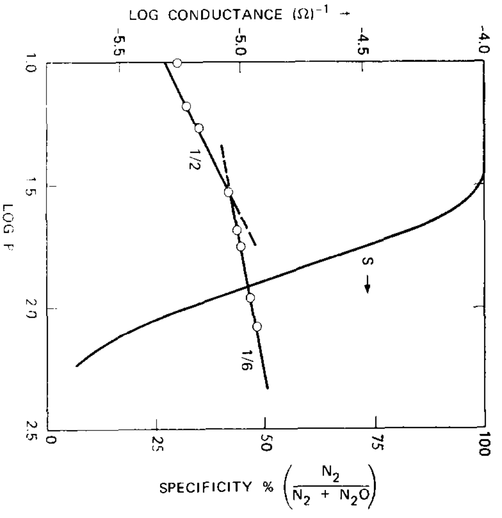

FIG. 3. Electrical conductivity of cuprous oxide and product specificity at 573°K for various oxygen partial pressures (initial NH_3 pressure = 50 Torr).

the slope of the conductivity curve changes from ½ to ⅙ at a specific partial pressure of oxygen, indicative of changes in the defect structure of the cuprous oxide. While the region exhibiting the ½-power dependency is characteristic of the copper-rich phase of cuprous oxide, the region with ⅙-power dependency (theoretically ⅛ power is predicted) is indicative of the oxygen-rich cuprous oxide phase (*2*, *4*). Also shown in Fig. 3 is the variation in product specificity for nitrogen calculated on the basis of the data presented in Fig. 1. The constant and high value in N_2 selectivity up to the region near the stoichiometric cuprous-oxide composition, as evidenced by the conductivity data, is an interesting demonstration of the relationship between catalytic specificity and the solid-state properties of the catalyst surface.

DISCUSSION

Of special significance is the striking similarity observed in the specificity of the catalyst for both ammonia and propylene (*2*) oxidation. If we consider the nitrogen produced in the reaction involving ammonia equivalent to the acrolein produced in the partial oxidation of propylene, we find that in each case the product concentration of N_2 and C_3H_4O, respectively, goes through a maximum as the catalyst surface changes its defect structure from a copper-rich to an oxygen-rich composition. Similarly, the higher oxidation products, nitrous oxide in ammonia oxidation and carbon monoxide and dioxide in propylene oxidation, begin to form under identical solid-state conditions of the surface, i.e., oxygen-rich cuprous oxide. Consequently, the interpretation of the reaction mechanism advanced for the propylene system (*2*) may be applicable to ammonia. On the basis of the physical (electrical conductance) and chemical measurements (product analysis), we concluded that charged oxygen species may be responsible for the observed pattern in specificity. The surface density of this oxygen species is controlled by the relative difference between the surface-state energy level associated with the oxygen and the Fermi level. In an application of this concept to olefin oxidation, the role of catalyst moderators, such as halogen compounds, was evaluated (*5*). It was found to be compatible with the theoretical model involving "anchoring" of the Fermi level due to specific surface states associated with the moderator molecule.

An interesting similarity between the catalytic oxidation of propylene and ammonia is to be found in the reaction kinetics In the copper oxide system the rate of disappearance of propylene was found to be zero-order in propylene and first-order in oxygen (*2*, *7*). An analogous dependence on reaction order obtains in the ammonia–oxygen system. As shown by the data in Fig. 4, the rate of conversion of ammonia appears to be essentially independent of the ammonia concentration and first-order in oxygen concentration. Over the narrow temperature range of 548–623°K, one finds from an analysis of the rate data that the activation energy for ammonia oxidation is less than 10 kcal/mole. It is noteworthy that this value is of the same magnitude as the temperature coefficient of the electrical conductance. This observation suggests that, irrespective of the type of product

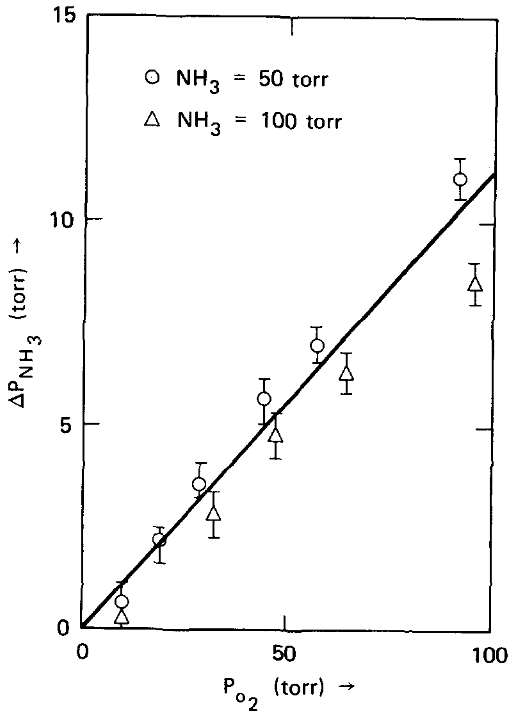

FIG. 4. Kinetics of ammonia oxidation catalyzed by cuprous oxide at 548°K (○ $NH_3 = 50$ Torr, △ $NH_3 = 100$ Torr).

formed (N_2 or N_2O), the initial step in the oxidation of ammonia may be controlled by the electronic properties of the catalyst surface.

The experimental results obtained for the copper oxide system also relate to the ammonia-oxidation studies with nickel oxide (*8*) and other metal oxides (*9*), and to the nitrous oxide decomposition studies on chromia–alumina catalyst (*10*). For ammonia oxidation the presence of "extra-lattice" oxygen in the catalyst was found to favor the formation of nitrous oxide (*9*), as did the presence of lower valence metal oxide additives in the case of nickel oxide (*9*). Qualitatively the defect structure associated with extralattice oxygen or Ni^{2+} vacancies is similar to that of the oxygen-rich (or copper deficient) cuprous oxide encountered in our experiments. The chromia–alumina experiments (*10*) have been interpreted on the basis of oxygen-anion vacancies (or chromium-cation excess) as a key factor in the nitrous oxide decomposition. Again we encounter a system analogous to cuprous oxide which favors the production of nitrogen when the catalyst surface exhibits an oxygen-deficient stoichiometry, i.e., cuprous ion excess. One may ask whether, in the ammonia oxidation catalyzed by cuprous oxide, nitrous oxide is formed under all conditions of catalyst composition and whether the subsequent nitrous oxide decomposition rate is fast enough in the case of copper-rich cuprous oxide to yield nitrous oxide concentrations too low for detection by our technique. Several experiments with nitrous oxide as the reactant demonstrated that under our experimental conditions of temperature (<623°K) and residence time ($<10^{-2}$ sec) the nitrous oxide did not decompose to any measurable extent.

In conclusion, the variable governing the catalytic selectivity for ammonia and propylene oxidation appears to be the hole carrier-density at the catalyst surface. Formation of nitrogen and acrolein are favored by initial low hole densities so that charged oxygen species may be produced by reactions such as:

$$O_{2(g)} \rightleftarrows 2O^- + 2p \rightleftarrows 2O^{2-} + 4p.$$

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