

Selectivity and Stoichiometry of Copper Oxide in Propylene Oxidation*

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The oxidation of propylene to acrolein on the surface of a cuprous oxide crystal was studied. Simultaneous *in situ* measurements were carried out of the catalytic activity, the electrical conductance, and the optical properties of the catalyst. The results indicate that the most active solid phase for acrolein formation is stoichiometric or copper-rich cuprous oxide. Oxygen-rich cuprous oxide and cupric oxide, on the other hand, favor complete oxidation of propylene to carbon dioxide and water. A mechanism is postulated that is based on a solid-state model with surface state energy levels.

INTRODUCTION

Cuprous oxide catalysts have been used for some time to oxidize propylene selectively to acrolein. Because of its industrial importance several investigators have carried out kinetic studies of this reaction (1, 2). The most recent evidence suggests that the reaction proceeds by way of a π -bonded allyl surface intermediate (3). The ultimate yield of acrolein, however, is highly dependent on temperature and partial pressure of oxygen. Belousov *et al.* (4) showed that an increase in catalyst temperature from 320 to 380°C resulted in an approximately twofold decrease in selectivity, probably because of enhancement in the rate of acrolein oxidation.

In addition to kinetic studies, a number of attempts have been made to identify the active phase in selective copper oxide catalysts. *In situ* X-ray diffraction of unsupported material indicated that the bulk of the catalyst was composed largely of metallic copper under reaction conditions (5). However, electron diffraction studies of thin film catalysts by the same investigators suggested that cuprous oxide is the active phase. A recent study of carborundum-

supported catalysts, in which the overall composition of the catalytic material was determined on samples from the reaction vessel, showed that selective catalysts were composed mainly of cuprous oxide or of cuprous oxide and metallic copper (6).

The results of these investigations do not characterize unequivocally the selectively active phase of a copper oxide catalyst for acrolein formation. It was of interest, therefore, to investigate further the composition of the solid phase of such a catalyst under reaction conditions. This study was carried out by making *in situ* measurements of the solid-state properties of a copper oxide crystal while it catalytically oxidized propylene in a differential flow reactor. Simultaneous measurements of the kinetics of acrolein formation permitted correlation of the catalytic and the solid-state properties of the crystal.

EXPERIMENTAL TECHNIQUE

To eliminate or reduce possible effects of pore diffusion, support interactions, crystal-lite boundaries, etc. on catalytic and electrical measurements, a catalyst in the form of a large crystal was selected. This crystalline catalyst was situated in a 1-in. i.d., fused-quartz, differential-flow reactor provi-

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ded with suitable electrical connections for conductivity measurements and with appropriate instrumentation for examination of the reflectance spectrum. The apparatus is depicted schematically in Fig. 1. All electrical leads were shielded from contact with the reactants or products in the reactor by means of ceramic coatings. Oxygen, propylene, and helium were metered and mixed before passing through the reactor at a total pressure of 1 atm with a total flow rate of 110 cm³/min. The concentrations of reactants and products were determined by chromatography employing a 6-ft column of 15 wt % Ucon 300 on Chromosorb P at 60°C. Sampling valves were used to withdraw aliquots of the entering and effluent streams.

mation of a polycrystal, containing less than a dozen distinct crystal grains, which exhibited values of electrical resistivity comparable to those reported in the literature (8) for single crystals of Cu₂O. Cuprous oxide is reported to be an intrinsic semiconductor at temperatures greater than 305°C (9). Hence, the catalytic experiments were carried out at 350°C even though a reduced selectivity of acrolein formation was likely at this temperature (4).

In the absence of the copper oxide crystal, no measurable conversion of propylene was detectable. Consequently, no correction had to be made for gas-phase reaction or for catalytic reaction on the interior surfaces of the reactor.

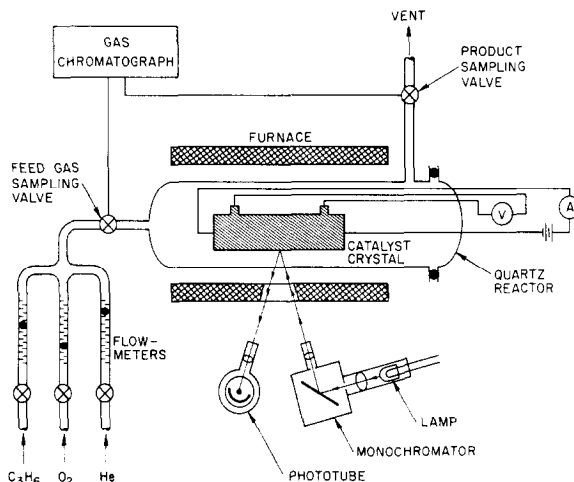


FIG. 1. Schematic diagram of apparatus.

The product analysis gave the quantities of propylene and acrolein leaving the reactor. The quantity of carbon dioxide in the effluent stream was computed by difference, assuming that CO₂, H₂O, and acrolein were the only products of reaction. The conductance of the crystal was computed from the measured values of voltage and current, using the standard four-point technique.

The catalyst crystals were prepared by oxidizing 1 × 2-cm rectangular pieces of copper foil in air at 1030°C, then annealing at 1115°C. In principle, this technique (7) is capable of forming single crystals of Cu₂O; in fact, visual inspection indicated the for-

In addition to the electrical and chemical measurements, reflectance spectra of the catalyst were obtained by viewing the crystal through a 6 × 35-mm opening in the side of the furnace (Fig. 1). A single-grating monochromator* equipped with 0.8-mm entrance and exit slits was arranged so that the emerging light beam from the monochromator illuminated the crystal at an angle of about 20° from the normal. The source of illumination was a tungsten lamp. Light reflected off the crystal was picked up by an RCA 1P21 phototube whose out-

* Model 103420, Farrand Optical Company, New York.

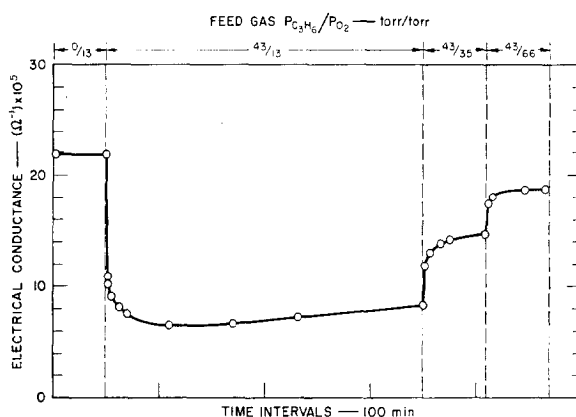


FIG. 2. Effect of feed gas composition on electrical conductance of copper oxide catalyst.

put was recorded on one channel of the dual-channel recorder. The other channel simultaneously recorded the voltage drop across a 5-ohm helipot connected to the wavelength drive of the monochromator, and this wavelength-analog voltage was used for wavelength calibration.

After the reflectance spectrum of the crystal was measured under various reaction conditions, a reference spectrum was made from the crystal whitened with a coating of MgO (10). Wavelength calibration of the monochromator was then carried

out with a 60-W Na-K lamp. Wavelength dispersion at the Na-D line was approximately 75 Å (line width at half-height).

An additional optical measurement on the catalyst was an evaluation of its emissivity under various conditions of feed-stream composition and chemical activity. These measurements were made with a Huggins Infra-Scope infrared thermometer that measures total radiation in the spectral range from 1.8 to 2.7 μ .

EXPERIMENTAL RESULTS

Under the conditions of these experiments, changes in the composition of the

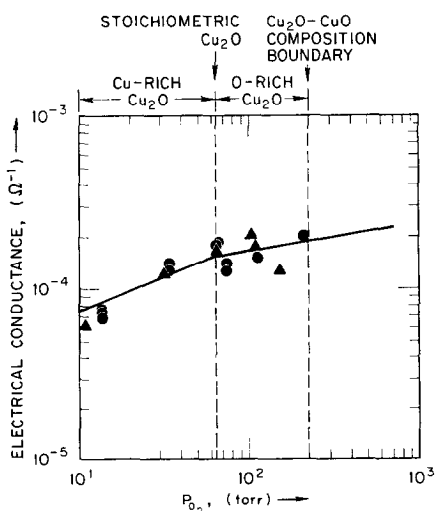


FIG. 3. Variation of electrical conductance with oxygen pressure: composition boundaries based on values of Bloem (12) normalized to present experimental data; crystal thickness: ▲, 0.0051 cm; ●, 0.0143 cm.

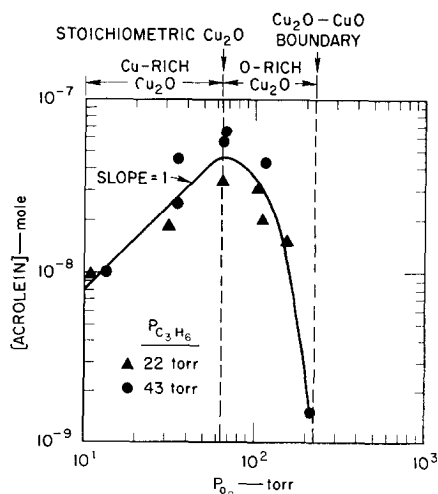


FIG. 4. Catalytic activity for acrolein formation as a function of oxygen pressure: indicated composition boundaries are derived from conductance data of Fig. 3.

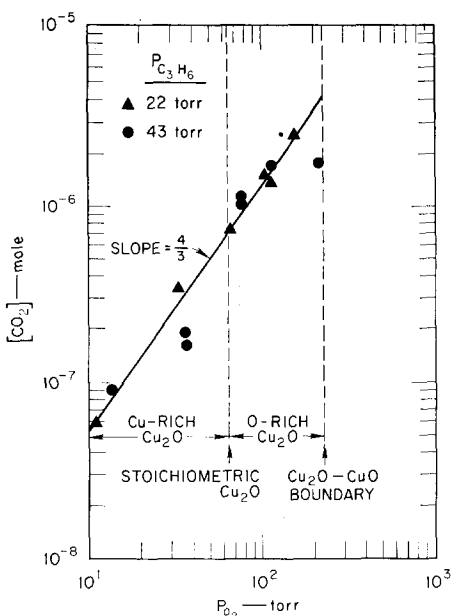


FIG. 5. Catalytic activity for CO_2 formation as a function of oxygen pressure: indicated composition boundaries are derived from conductance data of Fig. 3.

feed gas caused profound changes in the electrical conductance of the catalyst. The addition of propylene to the oxygen-containing feed stream diminished the conductance of the copper oxide crystal (Fig. 2), but for a fixed partial pressure of the olefin, increasing the oxygen pressure resulted in a corresponding increase in the electrical conductance (Figs. 2 and 3). The yields of acrolein (Fig. 4) and of carbon dioxide (Fig. 5) are presented as functions of the

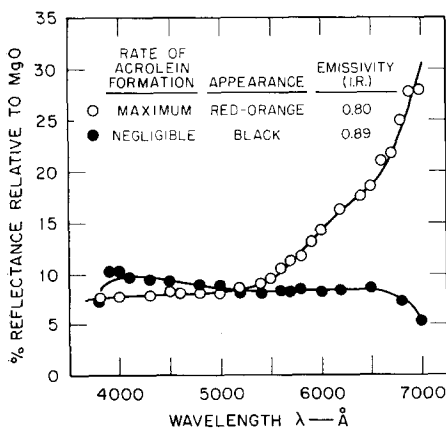


FIG. 6. Reflectance spectra of catalyst.

partial pressure of oxygen in the feed stream. The total gas-flow rate through the reactor was approximately constant, hence the yields are proportional to the rate of formation of the respective products.

The reflectance measurements demonstrated only two distinct spectra for the copper oxide catalyst (Fig. 6). One, in which the catalyst had a dull black appearance and exhibited a featureless spectrum, was characteristic of a surface condition where no acrolein formation could be detected. The other, in which the catalyst was of a reddish-orange color and demonstrated a strong reflectance at long wavelengths, was characteristic of a catalytic surface active for acrolein production.

DISCUSSION

It has been established that the conductivity of Cu_2O is a sensitive function of the partial pressure of oxygen in accordance with the behavior of a *p*-type semiconductor (11). Such an effect on the defect structure was observed in the present study when the ratio of oxygen to propylene in the feed stream was varied. Propylene behaves as a reducing agent, and an increase in its partial pressure over the catalyst has an effect on the catalyst comparable to a reduction of the partial pressure of oxygen. These observations, which are summarized in Fig. 2, suggest that only a relatively thin surface layer participates in these interactions, since large effects on the magnitude of the conductivity occur quite rapidly after a change in the oxygen/propylene ratio is imposed. This conclusion is further supported by the fact that the variation of conductance with gas composition is independent of the thickness of the crystal (Fig. 3). In addition, under the conditions of our experiments, the distance traversed by Cu^+ diffusing through Cu_2O amounts to a fraction of the crystal thickness, as calculated from published diffusion data (11). Consequently, the observed variations in conductance are attributed to changes in the conductivity of the surface layer in contact with a bulk crystal of relatively high resistance.

The observed variation of electrical con-

ductance with partial pressure of oxygen exhibits the same characteristics as those reported for a cuprous oxide single crystal (12). In particular, the copper-rich region is distinguished from the oxygen-rich region by a change in the exponent relating conductivity to oxygen pressure. The solid curve in Fig. 3 is derived from the equilibrium conductivity data of Bloem (12) by extrapolation to 350°C and by superposition onto our conductance data measured during propylene oxidation. This entailed a translation of Bloem's curve to higher values of oxygen pressure, since conductances of the magnitude shown in Fig. 3 would normally be exhibited by a Cu_2O crystal in contact with O_2 at much lower pressures. However, under surface-reactive conditions in the presence of oxygen and a reducing agent (propylene), the partial pressures of reactants near the surface of the catalyst are greatly reduced relative to the gas phase. The surface-catalyzed reaction, therefore, allows stabilization of cuprous oxide even at relatively high partial pressures of oxygen in the feed stream.

The kinetic data suggest that the rates of formation of both acrolein and CO_2 are a function of the oxygen pressure, but are relatively independent of the pressure of propylene (Figs. 4 and 5). This kinetic dependence of the acrolein formation rate on the feed gas composition, however, is observed only over the lower one third of the investigated oxygen pressure range. At higher oxygen partial pressures, the acrolein formation rate diminishes rapidly. On the basis of the relationship between electrical conductance, oxygen pressure, and chemical composition reported by Bloem (12), one can assign stoichiometric limits for the copper oxide catalyst as a function of the oxygen pressure. These are indicated in Figs. 3-5. The resulting relationship between the composition of the catalyst and the measured kinetic data suggests that copper-rich Cu_2O is an effective catalyst for acrolein formation from propylene (Fig. 4), while oxygen-rich Cu_2O favors complete oxidation of the propylene to CO_2 (Fig. 5).

The reflectance measurements provide

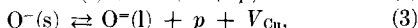
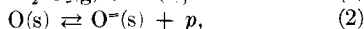
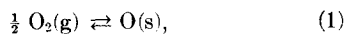
further evidence for such a relationship between catalytic selectivity and catalyst stoichiometry. The existence of a strong absorption band edge at 7200 Å has been reported (13) for Cu_2O at 370°C. Our results indicate a sharp rise in the reflectance signal in the region from 6900 to 7000 Å when the catalyst is selectively active for acrolein formation. (The observed wavelength discrepancy may be attributed to the magnitude of the dispersion of the monochromator and to the reduced sensitivity of the phototube in this spectral region.) The values of emissivity (indicated in Fig. 6) obtained under conditions of both high and low catalytic activity for acrolein formation are high and typically characteristic of nonmetallic materials such as metal oxides. These observations of the optical properties of the catalyst further suggest the presence of a Cu_2O surface phase during the period in which catalytic activity for acrolein formation is high.

Comparison of the chemical rate data with the physical measurements of the crystalline catalyst indicates strongly that acrolein formation is very sensitive to the stoichiometry of the surface phase of the catalyst. Maximum selectivity for oxidation of propylene to acrolein demands that the cuprous oxide catalyst possess a copper-oxygen ratio on the copper-rich side of stoichiometric composition. Oxygen-rich cuprous oxide favors the formation of CO_2 from propylene and oxygen. This observed requirement of copper-rich stoichiometry for acrolein selectivity in a propylene oxidation catalyst is in qualitative agreement with other investigators' reports that copper and cuprous oxide are frequently found together as components of such catalysts (1, 5, 6).

It is of interest to speculate on the mechanism of the oxidation of propylene that favors acrolein formation in the presence of cuprous oxide. In recent publications the selectivity of metal oxide catalysts was attributed to the strengths of the metal-oxygen bond (14, 15). In these studies the

correlations with experimental data considered the binding of the lattice oxygen and not the adsorbed oxygen to be of significance. Our results point out that the valence state of the catalyst is a function of the gaseous environment during the process of propylene oxidation. But the strikingly different behavior of the two cation valence states in the case of copper oxide cannot be interpreted simply in terms of the metal-oxygen bond, or in terms of the heat of formation of the metal oxides, as was suggested in Ref. (16). We suggest that the relationship between specificity and valence state of the cation in the present system is to be interpreted in terms of the electronic properties of the semiconductor catalyst, which controls the nature of the adsorbate.

We interpret our results in terms of the densities of different oxygen species present on the catalytic surface. Solid-state studies (12) of Cu_2O showed that in contact with gaseous molecular oxygen the conductivity of the crystal increases as a result of formation of holes (p) associated with the formation of surface and lattice oxygen species such as those indicated in the following reaction sequence:



where V_{Cu} represents a copper vacancy and

(s) and (l) refer to surface and lattice species, respectively. The relative distribution of the oxygen species associated with the solid, viz., $\text{O}(\text{s})$, $\text{O}^-(\text{s})$, and $\text{O}^-(\text{l})$, depends not only on the partial pressure of O_2 but also on the defect structure of the catalyst. In copper-rich Cu_2O , the lattice has a high affinity for oxygen and the equilibrium in Eq. (3) lies to the right. As the lattice becomes oxygen-rich, however, the high hole densities in the solid will shift the equilibria to the left, resulting in a predominance of $\text{O}(\text{s})$ on the surface. Ultimately the oxidation of Cu^+ to Cu^{2+} will take place.

Qualitatively the variation in density of surface species with changes in the partial pressure of oxygen can be predicted in terms of a solid-state model in which surface state energy levels are associated with adsorbed species. At the surface of the catalyst we may consider an energy level located somewhere between the valence band and the Fermi level E_F (Fig. 7). The energy E_S is the energy of the electron when this level is occupied. As a result of the adsorption of gaseous oxygen and the process of charge transfer at the gas/solid interface, an equilibrium distribution between charged and uncharged species will be established. In Fig. 7 we are considering $\text{O}^-(\text{s})$ as the particle of interest, but the existence of other electronegative species such as $\text{O}_2^-(\text{s})$

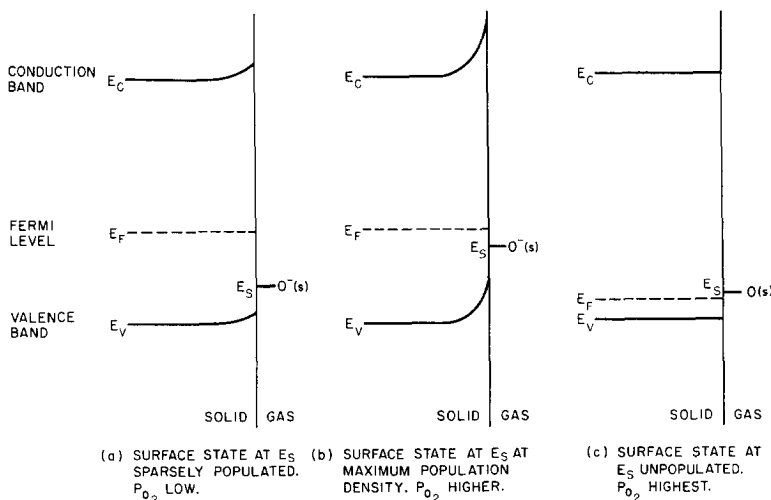


FIG. 7. Band model of Cu_2O catalyst with surface state energy level.

cannot be excluded. The degree of band bending associated with the excess negative charge on the surface is determined by the surface-density ratio $O^-(s)/O(s)$. Since the energy separation between the edge of the valence band at the surface and the surface state remains constant, the upward band bending causes a corresponding shift of the same magnitude and direction in the location of the surface state energy level (Fig. 7b). With increasing partial pressures of oxygen the $O^-(s)$ density will rise in accordance with the Fermi distribution function, which yields (17)

$$O^-(s)/O(s) = \exp[-(E_F - E_s)/kT].$$

This describes in quantitative terms the equilibrium relationship given by Eq. (2) and demonstrates the attainment of a limiting surface density of $O^-(s)$ that becomes independent of the oxygen partial pressure (Fig. 7b).

However, concurrent with these surface effects, oxygen migrates into the Cu_2O lattice (Eq. 3) where the formation of $O^-(l)$ results in the generation of holes and a lowering of the Fermi level. Depression of the Fermi level, of course, reduces the steady-state population of the $O^-(s)$ surface state. When the Fermi level drops below the surface state level, the surface state empties (Fig. 7c). The net result of these processes is that as the pressure of oxygen is increased, the surface density of $O^-(s)$ first increases, attains a maximum value, then decreases. This type of behavior appears to be reflected in the rate of formation of acrolein. We conclude that sorbed charged oxygen species, associated with a surface energy level are the active intermediate in the selective oxidation of propylene to acrolein on cuprous oxide. Under conditions in which the surface state is empty, the predominant oxygen species sorbed on the surface is an uncharged entity such as $O(s)$, which presumably is the precursor for complete oxidation to carbon dioxide.

This solid-state model offers some insight into the role played by promoters in the selective oxidation of propylene. It has been reported (1) that additives such as halogens, alkyl halides, selenium, or sulfur com-

pounds improve the activity and specificity of the catalyst for acrolein formation. A characteristic common to all these promoters is their high electron affinity. Their presence as surface state occupants could lead to control of the Fermi level at the surface (17). By charge transfer between solid and additive, the degree of band bending in the catalyst and the relative surface densities of the two valence states of the additive will attain some equilibrium value and, in effect, anchor the Fermi level at the surface regardless of the presence of other reactants, such as oxygen. Such control of the Fermi level may be responsible for a high specificity for acrolein formation.

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