

Selective Propylene Oxidation over a Copper-Tin Oxide Catalyst

The mixed oxide system of copper and tin and the active single oxide, Cu_2O , were compared for reducibility of the copper ion, relative number and type of active sites, and reaction kinetics. The enhanced selectivity of the mixed oxides may result from the formation of highly selective sites at the expense of less selective sites. The reducibility of the copper ion in the mixture is influenced by the oxidation state of the tin ion. The reactant and product reaction orders are the same for both catalysts but the mixed oxides are more sensitive to inhibition by water. The catalyst composition affects the energetics of the reaction over the copper-tin oxide catalysts.

D. E. SELF, J. D. OAKES,
and M. G. WHITE

School of Chemical Engineering
Georgia Institute of Technology
Atlanta, GA 30332

SCOPE

Mixed oxide catalysts are employed in a number of important catalytic conversion processes in the petroleum and petrochemical industries. Most often these complicated catalyst systems have properties unlike those of the constituent metal oxides; the acidity of the silica-alumina cracking catalysts is but one example. The genesis of these catalytic properties in relation to catalyst structure is important to the development of efficient conversion processes.

The properties of the copper-tin oxide, selective propylene oxidation catalyst which favor the high yields of the desired product, acrolein, are studied. A comparison of the copper ion reducibility, types of active surface sites, and the reaction kinetics of the mixed oxide and the single oxides will shed light on the mechanism by which the yield improvement is achieved by the mixed oxide system.

For some selective oxidation catalysts such as copper oxide, there is a relation between the yields of the desired product to the gross oxidation state of the metal ion, e.g., copper ion. Commercially feasible operating conditions for the production

of acrolein (i.e., stoichiometric olefin-oxygen feed) overoxidize the copper phase to the nonselective cupric phase. Thus the oxidation-reduction characteristics are important to the performance of the catalysts. For those catalyst systems where a specific oxidation state of the transition metal ion (t.m.i.) is the selective agent, a successful catalyst will "stabilize" the optimum oxidation state of the transition metal ion.

The types of sites may be characterized by a selective, site poisoning technique in which the reaction rates are measured as the surface sites are covered. In this way one may characterize the type and relative number of sites active for the desired reaction over the catalysts. The kinetics of the reaction may be established in gradientless reactors to measure the orders of reaction, rate constants and activation energies. Controlled oxidation and reduction of the catalysts were studied in a batch reactor in which the activity and selectivity of the acrolein reaction were determined before and after the redox treatments.

CONCLUSIONS AND SIGNIFICANCE

The reaction orders of the acrolein reaction are the same for Cu_2O and the mixed oxide equimolar in copper and tin atoms (first order in oxygen, nearly zero order in propylene, and negative order in products); the cuprous oxide catalyst showed less sensitivity than the mixed oxide to inhibition by water. The energetics of the reaction were a function of catalyst composition such that changes in the preexponential factor compensate for changes in the activation energy. The preexponential factor per unit mass of copper ion, a function of catalyst composition showing a minimum near 16 atom % tin, is greatest for the catalyst containing 50 atom % copper. For all the catalysts under study the specific surface areas were unchanged with pretreatment; the surface area of the samples were $30 \pm 3 \text{ m}^2/\text{g}$ of catalyst.

The oxidation-reduction pretreatment of the mixed oxides was necessary in the activation of reliable, selective catalysts. For propylene-oxygen feeds stoichiometric to the acrolein reaction the catalyst selectivity and activity declined with exposure time; these deactivated catalysts may be regenerated totally by the oxidation-reduction pretreatment. A portion of the activity decline may be restored by evacuation to $1.3 \times 10^{-4} \text{ Pa}$ at room

temperature (298 K) for 1.8 ks; the remainder of the activity-selectivity loss may be restored by reduction in a propylene-helium mixture at 598 K.

A controlled oxidation-reduction experiment showed the reducibility of the copper ion in the mixed oxide may be inhibited under the conditions which favor the formation of the stannic ion whereas the cuprous oxide catalyst, subjected to the same treatment, may be reduced easily. Those mixed oxides which resist reduction are inactive to the acrolein reaction; upon treating these inactive catalysts in a severe reducing atmosphere the selectivity and activity were restored.

Both cuprous oxide and the mixed copper-tin oxide are "poisoned" by the reaction products acrolein and water; these results are interpreted by a two-site model for which acrolein and carbon dioxide are produced at each site. One site (A) shows an affinity for water while the other site (B) apparently does not. The unique characteristics of acrolein, a conjugated pi-electron system and a high dipole moment polarity (2.9 Debye at 298 K), may permit this molecule to sorb to both sites. The mixed oxides show a greater number of the type A sites than the cuprous oxide catalysts. From the acrolein sorption and reaction data, the total site density for the production of acrolein would appear to be the same for Cu_2O and the mixed oxide. Since the mixed oxides are the more selective agent for acrolein, the A site is probably the more selective site over the B site.

D. E. Self is presently with Texaco Research & Development, Port Arthur, TX 77640.
Correspondence concerning this paper should be addressed to M. G. White.

INTRODUCTION

Mixed oxide catalysts have been the object of much research for over two decades (Margolis, 1973; Voge and Adams, 1967). The importance of the propylene selective oxidation reaction is obvious from the number of review articles and patents devoted to the reaction (Keulks et al., 1978). Recent work in this laboratory shows a mixed copper-tin oxide catalyst to be more selective than bulk cuprous oxide for the acrolein reaction (Self, 1979; Oakes, 1981). We report here the method of catalyst preparation, pretreatment, the reaction kinetic data, and the oxidation-reduction characteristics of the mixed oxides to be compared to the performance of a cuprous oxide catalyst.

EXPERIMENTAL

Plug Flow Reactor

A stationary-state, flow reactor of 18 mm O.D. quartz tubing is affixed with a 6 mm O.D. quartz thermowell for an iron-constantan thermocouple, connected to a Honeywell potentiometer, which may sense the temperature along the length of the reactor. The 74 to 105 micron in size catalyst powders were supported in the reactor from above and below by plugs of pyrex wool. Helium, propylene, and oxygen were individually metered through needle valves and the flow rates were measured by Fisher-Porter flowmeters; the reactor pressure was controlled to room pressure. Condensable products were removed from the reactor effluent before the product gases were analyzed in a Hewlett Packard 5720-A gas chromatograph equipped with a 2.13 m of 3.2 mm O.D. stainless-steel column packed with Porapak Q (149-177 micron in diameter). Peak areas were measured by a Spectra-Physics Minigrator. Reactor temperatures were controlled to the nearest degree by a Leeds and Northrup Electromax III controller; the electrical power to the furnace is supplied by a Leeds and Northrup Zero-Voltage power pack. Catalyst temperatures (± 0.5 K) were measured by a Honeywell portable potentiometer.

Batch Recirculation Reactor

The reaction order studies were conducted at 548 K in a batch recirculation reactor of about 9×10^{-4} m³ volume with a recirculation rate of 0.026 m³/ks. The packing of the catalyst holder consisted of 149 to 250 micron catalyst particles diluted with ground pyrex glass inserted between layers of ground glass supported by glass wool. The catalyst holder was heated with a furnace controlled to the nearest degree by a Leeds and Northrup Electromax III controller and a Zero-Voltage power pack. The catalyst bed temperature was monitored with a Leeds and Northrup potentiometer and an iron-constantan thermocouple. The gas samples were analyzed with a Varian model 920 gas chromatograph equipped with a 1.83 m by 3.2 mm O.D. Porapak R column and a thermal conductivity detector. The sample peak areas were analyzed with a Spectra-Physics Minigrator.

B.E.T. Surface Area

Specific surface areas of the oxides were measured in a standard glass B.E.T. system using nitrogen as the adsorbate at 77 K.

Gases, Chemicals, etc.

Reactant gases for the flow experiments were used without further purification: Oxygen, extra dry grade (99.5% min.); helium, high purity (99.995%) and propylene, c.p. grade (99.0% min., liquid phase). Gases for use in the recirculation reactor were as follows: oxygen from Matheson, high purity (99.995%), helium from Matheson (99.995%), and propylene from Matheson, CP grade (99.0% in the liquid phase). The individual gases were purified as follows: O₂, a molecular sieve (5A) trap at dry ice-acetone bath temperature; He, activated charcoal trap at liquid nitrogen bath temperature; and propylene, molecular sieve trap (13X) at the ice-point temperature. Further purification of the propylene involved "freeze-pumping" at 77 K. Acrolein (obtained from Eastman Kodak) was dried over Drierite and activated charcoal before "freeze-pumping" at 77 K; water was distilled and degassed. Matheson Bone Dry carbon dioxide (99.8% min., liquid phase) was purified in an activated charcoal trap at the ice-point temperature and "freeze-pumped."

The mixed oxide catalysts were prepared using Baker's Analyzed reagent grade cuprous oxide and MCB reagent grade stannous oxide.

Pretreatment of the Catalysts

The copper-tin oxide catalysts of this study must be activated before use; nonreproducible results may be expected of these catalysts which are not pretreated. Finely divided (about 74 micron) cuprous oxide and stannous oxide were combined, mechanically, to form physical mixtures of the bulk oxide powders. The catalysts were pretreated in a flow reactor with an oxygen-helium mixture (10 mol % O₂) at 598 K for 1.8 ks. Due to agglomeration of the particles leading to excessive pressure drop, the catalysts were removed from the reactor after the oxygen treatment to be crushed, classified and returned to the flow reactor for reduction in a propylene-helium gas mixture (25 mol % propylene) at 598 K for 1.8 ks. Once pretreated these catalysts may repeatedly oxidized and reduced without agglomeration problems experienced by the "virgin" oxide powders. Thus, pretreatment of the "aged" catalysts may be accomplished in a batch reactor without the need to crush and classify after the oxygen treatment. This oxidation and reduction treatment is defined here as the "standard pretreatment" for reference in this paper.

Experimental Procedures

The kinetic data were collected using two types of reactors: a stationary-state flow system and a batch, recirculation system. For all studies other than the deactivation studies (Results-Part 3), the catalysts were pretreated between runs according to the "standard pretreatment." The flow reactor system was maintained at room pressure (about 101.3 kPa) and the temperature was varied from 548 to 603 K for the activation energy study. The steady state reactor studies involve an initial reactant concentration of helium, propylene, and oxygen in the ratio of 12/3/1 to 10/6/1. Catalyst sample weights varied from 1 to 7 g. Low conversion data for the flow reactor operated in the "differential" mode were extrapolated to zero conversion so as to obtain the initial rate of acrolein production ($dC_{\text{acrolein}}/d\tau$). The space time (τ), in units of kg catalyst-ks/m³, is the catalyst weight divided by the volumetric flow rate measured at reactor temperature and pressure. For the flow experiments the space time varied between 0.08 to 0.36 kg-ks/m³.

The orders of reaction study were conducted in the batch recirculation reactor at 548 K using from 30 to 98.6 mg of the Cu₂O/SnO (1/1) catalyst. The numbers in parenthesis following the catalyst name describe the atomic ratio of copper ions to tin ions in the mixture. A high circulation rate of reactant gases, 0.026 m³/ks, ensured the measured reaction rates were not disguised by external mass transfer effects. Data of acrolein partial pressure versus reaction time were extrapolated to zero time; a least-squares curve-fit of the data established the initial rate of acrolein production. The raw data of acrolein partial pressure in the gas phase per unit time (Pa/s) were converted to moles acrolein produced per ks per kg catalyst assuming the gases to behave ideally. For high conversion runs excess water was condensed from the gas phase using a trap immersed in ice-bath; the water partial pressure was maintained below the vapor pressure at the ice-point (610 Pa). Water was not observed to condense in the ice trap during the first hour of the reaction; all of the data used to calculate initial reaction rates were less than 900 s into each run (reactant conversions were about 10% per hour).

Individual orders of reaction were determined in the classical manner; one reactant partial pressure was varied while a diluent was employed to keep all other reactant partial pressures essentially constant. These data were extrapolated to zero conversion to minimize the effect of product partial pressures upon observed reaction rates. Specific tests for product inhibition were conducted at 548 K using an equimolar reactant mixture (9.7 kPa of O₂, C₃) and varying the initial partial pressure of each product: acrolein, water and carbon dioxide.

DEFINITION OF SELECTIVITY

As in most selective oxidation reactions, carbon dioxide is the undesired product, thus we will employ the usual definition of selectivity based upon consumption of reactant propylene:

$$\begin{aligned}\% \text{ Selectivity} &= 100 \times \frac{\text{mol propylene converted to acrolein}}{\text{mol propylene converted}} \\ &= 100 \times S/(S + 1)\end{aligned}$$

where the selectivity ratio, S , is $3 \times$ partial pressure acrolein/partial pressure of carbon dioxide. The factor 3 in the selectivity ratio makes accounting for the carbon atom stoichiometry of the reactions to form acrolein and carbon dioxide from propylene.

TABLE 1. REDUCIBILITY STUDY

Catalyst	Treatment
1. Cu/Sn (1/1)	Multiple applications of "standard pretreat"
2. Cu/Sn (1/1)	Vacuum (1.3×10^{-4} Pa) @ 598 K for 1.8 ks
3. Cu/Sn (1/1)	O ₂ @ 598 K for 1.8 ks
4. Cu/Sn (1/1)	O ₂ @ 703 K for 1.8 ks
5. Cu/Sn (1/1)	Pretreat catalyst of run 4 twice according to "standard pretreat"
6. Cu/Sn (1/1)	Reduce catalyst of run 5 in propylene-He @ 703 K
7. Cu/Sn (1/1)	Pretreat catalyst of run 6 according to "standard pretreat"
8. Cu ₂ O	"Standard pretreat"
9. Cu ₂ O	O ₂ @ 703 K followed by "standard pretreat"

^a Oxidation state of surface ions inferred by standard reaction test.

^b Oxidation state of Sn inferred from equilibrium thermodynamics.

^c Phase identified by X-ray diffraction.

^d Reactant conversions in these tests are between 5 and 10%. Reaction rates are for the production of acrolein.

Cu Oxidation State	Sn Oxidation State	Reaction Rate ^d mol/ks-kg	Selectivity ^d to Acrolein, %
+1 ^c	+2 ^c	1.02	75
+1 ^a	+2 ^b	1.00	75
+2 ^{a,c}	+2 ^{b,c}	0	0
+2 ^a	+4 ^b	0	0
+2 ^a	+4 ^b	0	0
+1 ^a	+2 ^b	0.76	80
+1 ^a	+2 ^b	0.89	80
+1 ^{a,c}	—	0.99	50
+1 ^a	—	0.99	50

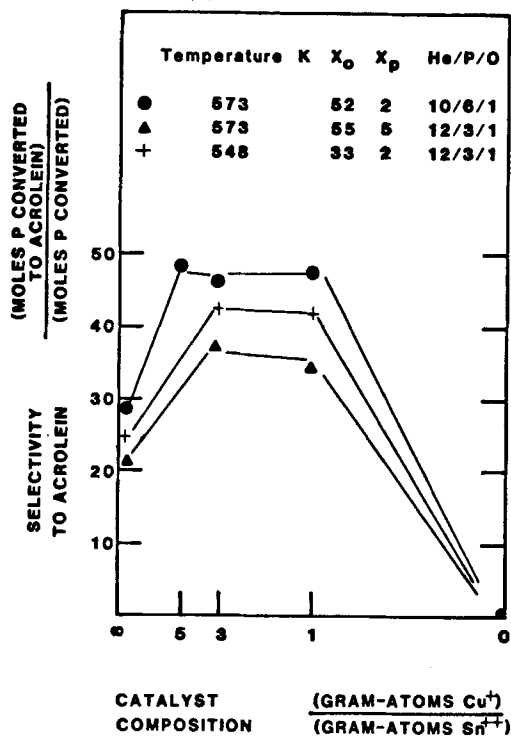


Figure 1. Propylene oxidation over mixed metal oxide catalysts.

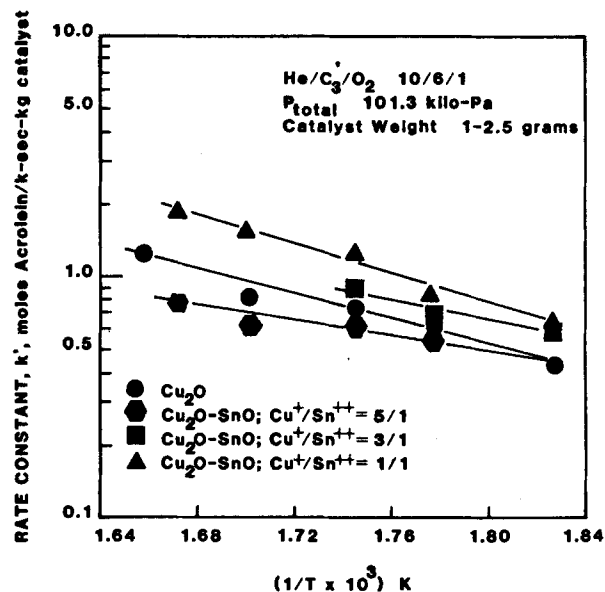


Figure 2. Arrhenius plot for the selective propylene oxidation over mixed metal oxide catalysts.

vacuum (1.3×10^{-4} Pa) treatment at 598 K for 1.8 ks (Table 1, entries 1 and 2). When oxidized in oxygen at 598 K for 1.8 ks and evacuated at 598 K for 1.8 ks, this catalyst showed no activity (Table 1, entry 3). The same catalyst particles when oxidized in oxygen for 1.8 ks at 703 K and evacuated at the same temperature for 1.8 ks were completely inactive to the acrolein reaction; only a small amount of carbon dioxide and water were the reaction products of the "standard test" (Table 1, entry 4). Two successive "standard pretreatments" failed to restore any of the catalyst activity; reducing the catalysts in a propylene-helium mixture (25 mol % propylene) at 703 K restored 74% of the original activity (0.757 mol acrolein/ks-kg). This catalyst, subsequently pretreated according to the "standard pretreat," showed an additional activity increase to 88.2% of the original activity (Table 1, entry 7). The regenerated catalysts of the high temperature oxidation treatment showed higher selectivities to acrolein (80% at propylene conversion of 9%) compared to the base run catalysts (75% selectivity at propylene conversion of 9%). In all of these tests reported in Table I the propylene conversions were between 5 and 10%. The performance of the Cu₂O catalysts were unaffected by any of the oxidation-reduction treatments (Table 1, entries 8 and 9).

Effect of Catalyst Composition on Acrolein Yields and Energetics

Although stannous oxide is inert to the reactants at reaction conditions (Figure 1), the mixed oxide catalysts show acrolein yields 1½ times those obtained over unsupported cuprous oxide under similar reaction conditions. These yield enhancements are observed

RESULTS

Reducibility Study

The reducibility of the mixed oxides and Cu₂O were examined by oxidizing the catalyst in low oxygen partial pressures at 598 and 703 K followed by reduction in propylene at 598 and 703 K, Table 1. Under these conditions the reducibility of the copper ion in the Cu₂O and mixed oxide catalysts may be determined as a function (if any) of the tin oxidation state. Only the cuprous ion is active for the acrolein reaction; thus, the oxidation state of the copper ion may be inferred from the activity of the catalyst to the propylene oxidation reaction at the following conditions (standard reaction test): temperature, 548 K; propylene partial pressure = oxygen partial pressure, 9.7 kPa; total pressure, 101.5 kPa; weight of catalysts, 98.6 mg. These studies were conducted in the batch recirculation reactor apparatus; prior to running the "standard reaction test" the catalysts were evacuated to 1.3×10^{-4} Pa at the temperature of the reduction to remove some of the sorbed species. For the catalyst subjected to the "standard pretreatment," the reaction rate over the Cu₂O/SnO (1/1) oxide is 1.02 mol acrolein/ks-kg with a selectivity to acrolein of 75%. The activity and selectivity of this catalyst is stable to successive applications of the "standard pretreatment" and to

TABLE 2. DEACTIVATION STUDY FOR SELECTIVE OXIDATION OF AN EQUIMOLAR MIXTURE OF PROPYLENE AND OXYGEN OVER A COPPER/TIN OXIDE (1/1) CATALYST

Run Number	Initial Rate of Propylene Consumption r_p	Initial Rate of Acrolein Production r_{ai}	Final Rate of Acrolein Production r_{af}	Selectivity to Acrolein	$\frac{r_{af}}{r_{ai}}$	% Recovered by Evacuation
1	1.36	1.02	0.412	75	0.404	—
2	0.816	0.561	0.276	69	0.493	26.5
3	0.724	0.449	0.215	62	0.480	34.8
4	0.707	0.367	0.163	52	0.444	41.4
5	1.68	1.22	0.412	73	0.338	—

Rates of reaction are reported in units of mol/ks-kg catalysts.

Weight of copper-tin (1/1) catalyst = 98.6 mg.

Temperature = 548 K.

Propylene partial pressure = oxygen partial pressure = 9.7 kPa.

Surface area of catalyst = 30 m²/g catalyst.

Between each run the catalyst is evacuated to 1.3×10^{-4} Pa for 1.8 ks.

% Recovered by evacuation is: $(r_{ai} \text{ of run } i + 1 - r_{af} \text{ of run } i) / (r_{ai} \text{ of run } i + 1)$.

for reactant partial pressures between 6:1 (propylene rich) to equimolar, and for reaction temperatures between 548 and 573 K in the range of oxygen conversions to 55%. At constant reaction conditions, the acrolein yields are relatively insensitive to changes in catalyst composition between 16 to 50 atom % tin.

Pseudorate constants for the production of acrolein (mol acrolein/ks-kg catalyst) over several mixed oxide catalysts (Figure 2) were obtained by extrapolating the data of the differential flow reactor to zero conversion. Activation energies for the copper-tin oxide catalysts change with tin concentration between 29.7 kJ/mol (16 atom % Sn) to 60.0 kJ/mol (50 atom % Sn); apparently these variations in E_A are compensated by changes in the preexponential factor.

Effect of Propylene/Oxygen Ratio on Yields and Catalysts Activity

High conversion data obtained in the batch recirculation reactor show acrolein yields for the copper-tin oxide catalysts similar to the yield data obtained in the plug flow reactor for the same catalyst composition at the same conditions. The selectivity to acrolein for a Cu₂O/SnO (1/1) catalyst at 548 K and oxygen conversions to 70% varied between 45% for an equimolar starting mixture to

about 75% for a 4/1 propylene-rich reactant mix.

The composition of the reacting atmosphere affects the deactivation of the mixed oxide catalysts; the Cu₂O/SnO (1/1) catalysts is quickly deactivated (40% decrease in the initial, propylene conversion rate after 2.5 ks) for an equimolar reactant mixture whereas a propylene-rich gas mixture (3/1) will deactivate the catalyst at a relatively slow rate (12% decrease in the initial, propylene conversion rate after 2.5 ks). Studies to quantify the activity of the Cu₂O/SnO (1/1) catalyst (Figure 3) in the batch recirculation reactor for an equimolar reactant mixture at 548 K show a reversible and irreversible deactivation. After 0.75 to 1.50 ks into each run, the instantaneous rate of acrolein production is 1/2 of the initial rate; 30 to 40% of this deactivation is recovered upon evacuation to 1.3×10^{-4} Pa for 1.8 ks at room temperature. The initial acrolein production rates for each run decrease with total exposure time to the reactants; the average selectivity to acrolein per run decreases monotonically with exposure time from 75% to 52% (Table 2). A positive intercept (about 30 Pa) is indicated for data extrapolated to zero time on runs 2 to 4 (the numbers beside the lines of Figure 3 drawn through the data indicate the run number). Reduction of the deactivated catalysts in a propylene-helium mixture (20 mol % propylene) for 11.7 ks at 598 K restores the catalyst activity and selectivity (Run 5). Small amounts of carbon dioxide (1.5×10^{-5} mol) and water (not measured) are evolved during the propylene reduction of the catalysts.

Order of Reaction Tests over Cu₂O/SnO (1/1) Catalysts

Oxygen order of reaction tests at 548 K, studied over the widest pressure range of interest: 1.33 to 13.3 kPa, show the acrolein production rate to be first order in oxygen partial pressure; the conversion rate of oxygen is unchanged with the partial pressure of oxygen (Oakes, 1981). At the same temperature, the acrolein rate

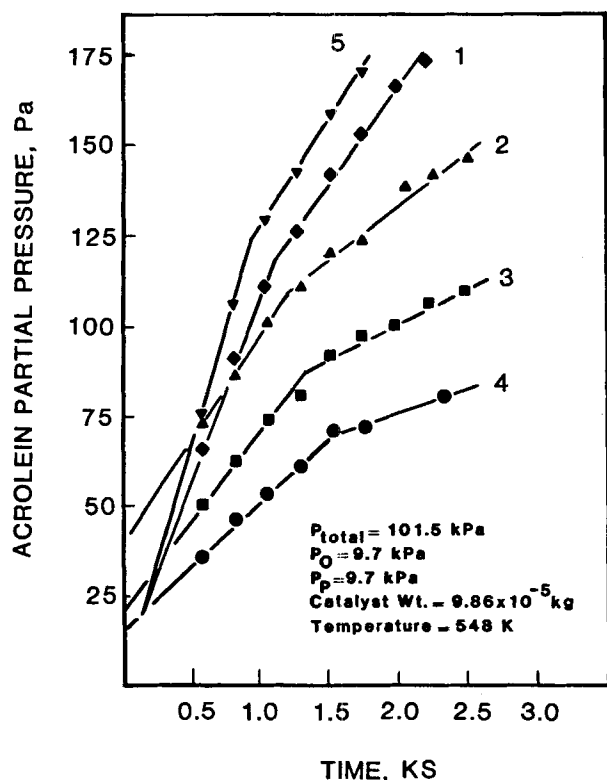


Figure 3. Deactivation of a copper-tin oxide catalyst: Run 1 (fresh catalyst), ◆; run 2, ▲; run 3, ■; run 4, ●; run 5 (reduced in propylene at 598K), ▼.

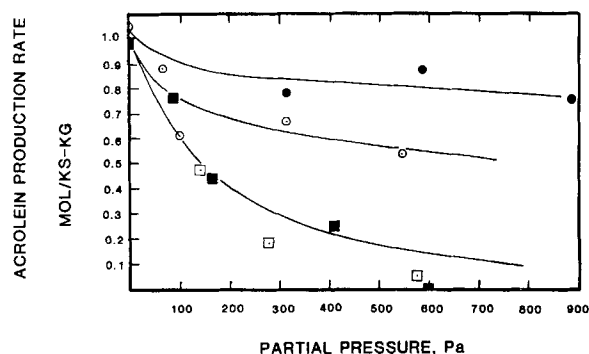


Figure 4. Inhibition of the reaction rate by products over a copper-tin oxide (1/1) catalyst and a copper oxide catalyst. List of symbols: water inhibition data over copper oxide, ●; water inhibition data over copper-tin oxide, ○; acrolein inhibition data over copper oxide, ■; acrolein data over copper-tin oxide data, □. Solid lines are predicted rate of reaction using Eq. 1. Reaction temperature is 548 K.

depends upon the propylene partial pressure to a fractional power, 0.19, in the pressure range of 9.33 to 22.7 kPa; the conversion rate of oxygen is unchanged with propylene partial pressure (Oakes, 1981). Acrolein production rate at 548 K is virtually zero when the gas phase acrolein concentration exceeds (Figure 4) 0.006 mol fraction (acrolein partial pressure = 600 Pa); for these conditions the production rate of carbon dioxide shows a very small increase (about 14%) with increasing acrolein partial pressure. Gaseous water concentrations to 0.006 mol fraction (600 Pa) will inhibit the acrolein production rate at 548 K to one half the value for no water present, initially. The carbon dioxide yields are not significantly altered with changes in the water partial pressure. Carbon dioxide initial concentrations as high as 0.02 mol fraction do not significantly affect the rate of acrolein production.

Product Inhibition Tests over a Bulk Cu_2O Catalyst

Literature data for product inhibition of the cuprous oxide catalysts are vague; Margolis (1973) and others report the catalysts are inhibited by an increase in product partial pressures without quantifying the reduction in reaction rates nor specifying which products are the most serious inhibitors. Our tests for inhibition of water and acrolein show the cuprous oxide is inhibited by acrolein in the same manner as the copper-tin oxide catalyst whereas the acrolein production rate over Cu_2O is inhibited by only 20% of the original value with water partial pressures to 879 Pa (Figure 4).

Specific Surface Area

All of the catalyst samples were of the same specific surface area: $30 \pm 3 \text{ m}^2/\text{g}$ catalysts. The pretreatment at 598 K and aging processes did not affect the surface area.

DISCUSSION

In the study of these copper-tin oxide catalysts we have endeavored to compare the mixed oxide system and the single oxide Cu_2O system with regard to the reducibility of the copper ion, number and type of active sites, and reaction kinetics. Clearly, these phenomena are interrelated in so far as the nature of the reactive site is dependent upon the oxidation state of the metal ion(s) comprising the site and the yields over the catalyst are dependent upon the number and types of reactive sites.

In determining the reducibility of the copper ions we inferred the oxidation state of the copper ion from the results of the "standard reaction test" for the formation of acrolein. The cuprous ion is active for this reaction whereas copper metal and the cupric ion are not active (Wood et al., 1969; Inui et al., 1980); at the low oxidation temperatures of this study (548 to 598 K) stannous and stannic ions are inactive to the reactants (Self, 1979). Thus, the yields of acrolein obtained from the "standard test reaction" over the treated catalyst allowed a qualitative determination of the copper ion oxidation state.

The cuprous ion in both the Cu_2O and the copper-tin oxide catalysts is converted to the cupric ion when exposed to an oxygen atmosphere at 598 and 703 K. The bulk oxidation state of the copper ion in catalysts so equilibrated with an oxygen atmosphere may be confirmed by thermodynamic data; the CuO decomposition pressure at 703 K is 1.0 fPa and the phase diagram for the Cu, Cu_2O , CuO , O_2 system show CuO is the stable bulk phase at 703 K for oxygen partial pressures greater than 0.1 μPa (Bloem, 1958). At 598 K the decomposition pressure of CuO is lower than 1.0 fPa. The kinetic data for the copper redox reactions show the reduction of CuO occurs readily at 538 K in hydrogen (Keely, 1965) and the air oxidation of Cu_2O and the $\text{Cu}_2\text{O}/\text{SnO}$ (1/1) catalysts is rapid at 553 K (White, 1982).

Below 703 K the tin bulk oxidation state in the mixed oxide is stannous at the conditions of this study. X-ray analysis of SnO and the copper-tin catalysts showed no conversion of SnO to higher oxidation states upon pretreatment of the samples at 598 K in oxygen-helium mixtures (Self, 1979). Spinedi and Gauzzi (1957)

show the SnO powders subjected to air oxidation will convert to SnO_2 at 703 K. Mossbauer data of the $\text{Cu}_2\text{O}/\text{SnO}$ (1/1) catalyst oxidized at 598 K in an oxygen-helium mixture for 1.8 ks show only 4% conversion of the SnO to SnO_2 (Oakes, 1981). Thus the bulk and surface region, as measured by the Mossbauer technique, is stable to oxygen atmospheres between 10^{-5} Pa and 1.01×10^5 Pa for temperatures below 703 K. Other surface sensitive tools, such as XPS, may show the top layers of tin are in the +4 oxidation state whereas the tin layers removed from the surface are in the stannous state. Above 703 K in the presence of O_2 there is rapid conversion of SnO to SnO_2 ; equilibrium thermodynamics show the decomposition pressure of cassiterite at 703 K is 10^{-37} kPa. Once formed the stannic phase is obviously very stable.

The yields of the "standard test reaction" observed over the treated catalyst plus the Mossbauer data and the XRD data allow us to conclude the reducibility of the copper ion in the mixed oxide is influenced by the oxidation state of the tin ion; for the conditions where the stannous ion is stable the copper ion in the mixture is oxidized and reduced with approximately the same ease that copper in "pure" copper oxide may be oxidized and reduced. However, the copper ion in a mixture containing predominantly stannic ions apparently resists reduction at mild conditions (propylene at 598 K for 1.8 ks). Once the tin ions are reduced to the stannous state by reduction in propylene at 703 K, the copper ions will respond to the reduction treatment at 598 K. The high temperature oxidation and reduction treatment causes a 13% decline in the activity and a 5% increase in the selectivity; since the BET specific surface area and the pore volume of these samples were not measured (insufficient sample size) sintering of the catalysts at 703 K cannot be ruled out as an explanation to the activity decline and the selectivity improvement.

In examining the results of the selective poisoning studies, it is necessary to discuss the catalyst deactivation with exposure time observed for equimolar feed mixtures (Figure 3 and Table 2). We attribute this decline in activity (as measured by propylene disappearance) and loss of acrolein selectivity to: 1. coverage of the surface sites by products (an effect reversed by evacuation at room temperature); and 2. to a change in the gross oxidation state of the catalysts (an effect which may be reversed by reduction of the catalysts). The kinetic data in the batch recirculation reactor for cuprous oxide and the $\text{Cu}_2\text{O}/\text{SnO}$ (1/1) catalysts show a break in the acrolein partial pressure versus time curve as shown in Figure 3; the decrease in the slope (about 50%) may be the result of site blockage by products as the reactant conversion level (about 3–5%) is too low to affect the reaction rate by a factor of 2. The partial pressure of acrolein necessary to inhibit the reaction rate decreases with exposure time between runs 1–4 (denoted as 1–4 on Figure 3); there may be an accumulation of products on the surface which are not removed by the room temperature evacuation step between runs. At the reaction temperature of this study, 548 K, acrolein and water are sorbed to the copper oxide surface (Mikhal'chenko et al., 1973-a, 1973-b; Inui et al., 1980). Thus a part of the deactivation with exposure time may be explained by strong product sorption.

In addition to strong product sorption, the active sites for acrolein production over the mixed oxides and single oxides may be destroyed upon oxidation of the cuprous ions to cupric ions in the slightly oxidizing atmosphere of the reaction mixture. Since the activity and selectivity of the mixed oxide were restored by the propylene reduction treatment at 598 K, it is possible that the part of the catalyst deactivation that remained upon evacuation at room temperature is due to overoxidation of the cuprous ions to cupric ions. At the conclusion of run 4, we estimate the stoichiometry of the mixed oxide is $\text{Cu}_2\text{O}_{1.13}\text{SnO}$ assuming only the copper ions are oxidized. X-ray analysis of the mixed oxides strongly suggest the tin phase does not experience oxidation-reduction cycles when the reaction temperatures are below 598 K (Self, 1979). This change in the bulk oxidation state of the copper ions, estimated from the gram-atoms of oxygen in the products of the reduction at 598 K (run 5), corresponds to a penetration depth of 300 oxide layers into the copper oxide crystal (assuming a layer is 10^{19} O atoms/ m^2). Such a surface layer rich in cupric ions has been shown by Mi-

khal'chenko et al. (1973b) to sorb the acrolein molecules very strongly such that overoxidation of the unsaturated aldehyde to carbon dioxide is favored.

Thus, the catalyst deactivation with exposure time is attributed to two mechanisms: a short term, reversible-to-evacuation process in which acrolein active sites are covered by products and a long term process in which the gross oxidation state of the copper ions is changed. These two processes are reversed by the standard pretreatment at 598 K; the oxidation step cleans the surface of hydrocarbon products whereas the reduction step adjusts the oxidation state of the copper ions to the proper value for the selective olefin oxidation. We believe the product retarding effect to stabilize the copper oxidation state reported by Inui et al. (1980) is not operative in our studies since water is not present in the *initial* reactant mixture as is the case for the Japanese studies (2% by volume).

The data of product inhibition by water and acrolein over Cu₂O and copper-tin oxide catalysts show both catalysts are poisoned "equally" by acrolein, but the copper oxide catalyst is less sensitive to water poisoning than the mixed oxide catalysts (Figure 4). The rate data for acrolein inhibition over each catalysts are correlated, for acrolein partial pressures less than 300 Pa and water partial pressures to 900 Pa, by the following equation.

$$r_{\text{acrolein}} = \frac{kP_{O_2}}{[1 + K_a P_a + (K_w P_w)^{0.5}]} \cdot \frac{1}{[1 + K_a P_a]} \quad (1)$$

At 598 K the correlated constants are as follows for the copper oxide and the copper-tin oxide catalysts:

Constant Units	Copper Oxide	Copper-Tin Oxide
kP_{O_2} [mol acrolein/ ks·kg]	1.01	1.01
K_w [Pa^{-1}]	1.55×10^{-4}	1.23×10^{-3}
K_a [Pa^{-1}]	2.48×10^{-3}	2.48×10^{-3}

At acrolein partial pressures greater than 300 Pa this correlation (Eq. 1) will not predict the slightly "negative" acrolein production rate (at 600 Pa) observed for the reaction over cuprous oxide. The equilibrium adsorption coefficient for the water in contact with the Cu₂O catalysts is roughly 12.6% of the water adsorption coefficient for the copper-tin oxide catalysts. Since the "inhibition" data are obtained over freshly regenerated catalysts, the long term exposure effects due to change in gross oxidation state are minimized; thus, only the "reversible" deactivation effects due to product sorption on reactive sites are represented by these data. The correlated water equilibrium coefficients show the copper-tin oxide catalysts are very sensitive to water sorption.

The difference in reaction orders between the water inhibition rate data and the acrolein inhibition rate data over each of the catalysts may be explained by a two-site model in which acrolein and carbon dioxide are produced on each site; one site is more selective to the acrolein reaction than the other site. A dual-site model for copper oxide catalysts was reported by Mikhail'chenko et al., (1973a,b); these Russian investigators show the active copper surface to sorb propylene and acrolein in a weak, reversible manner by pi-electron bonding on one type of site and to sorb on another type of site in a strong, "irreversible" manner. Water was reported to be strongly sorbed on the surface. In the Russian model, however, the nonselective reactions occur on one site (the strong, irreversible sorbing sites) and the selective reactions occur on the weakly-sorbing, reversible sites. The type A site of our model is poisoned by sorption of polar molecules such as water whereas the type B site is poisoned by sorption of molecules having pi-electrons. From a consideration of the correlated rate and adsorption equilibrium constants for the acrolein inhibition data over the copper-tin oxide and Cu₂O catalysts, both have nearly the same total number of acrolein producing sites per unit mass of catalyst assuming the acrolein molecule is sorbed to both types A and B sites. The water inhibition data suggest the copper oxide catalysts have only 12–13% of the type A sites as the copper-tin oxide catalysts. We speculate the type A sites are more selective to the acrolein reaction than the type B sites since the catalyst having the greater number of the A sites, the mixed oxide, is the more selective catalyst. With these few

data it would be premature to characterize these sites completely; however, we may speculate the type B site may sorb acrolein and propylene via the pi-electron system whereas the type A site may sorb species by some other mechanism in addition to pi-bonding, possibly the mechanism of ionosorption as described by Hauffe (1955). Such sorption by electron withdrawing groups (H₂O, OH⁻, O⁻, etc.) is favored on Cu₂O and p-type semiconductors in preference to electron donating groups (pi-bonding; e.g., White and Hightower, 1981). Water, having no pi electrons, will not sorb to the type B site; thus, the rate of acrolein production will not be completely inhibited by the sorption of water. On the other hand, acrolein may sorb to both types of sites to completely inhibit the production of acrolein. On the A sites, the very polar acrolein molecule (dipole moment = 2.90 Debye at 298 K; J. A. Dean, 1979) may sorb by ionosorption whereas on the type B site it will sorb via the conjugated pi-electron system.

The data of reaction orders for propylene and oxygen over the mixed oxides, first order in oxygen and nearly zero order in olefin, are in substantial agreement with the reaction orders reported by Margolis (1963). From these data we conclude the mixed oxides and Cu₂O catalysts "utilize" the reactants for the acrolein reaction in the same manner. It does not appear that the selectivity improvement associated with the mixed oxides is explained by a change in the established reaction mechanism for Cu₂O (Keulks et al., 1978).

The energetics of the selective oxidation reaction appear to vary with catalyst composition in such a way as to suggest the reaction is compensated over these catalysts. There is good agreement between the observed activation energy (55 kJ/mol) over unsupported Cu₂O and the data of Margolis (1963) for Cu₂O/SiO₂ and Cu₂O/pumice ($E_A = 50$ –59 kJ/mol). A sensitivity analysis of the mixed oxide activation energy data (after Satterfield, 1980) shows an uncertainty of ± 10.8 kJ/mol assuming a relative error in the rates constants of $\pm 10\%$. This uncertainty in the activation energy data may not falsify the apparent compensation of the data.

The specific surface areas of the catalysts are nearly equal and unchanged by the standard pretreatment, thus no error is incurred for comparing the reaction rates on a per unit mass basis rather than a per unit surface area basis. The reaction is not hindered by pore diffusion; the Arrhenius plots are linear and the Weisz-Prater criterion is satisfied (Self, 1979).

The preexponential factors specific to the weight of copper ion (Table 3) show an increase as the copper ion is diluted in the inert SnO from 16 to 50 atom % tin; however, only the most dilute catalysts shows a preexponential factor greater than pure Cu₂O. While Cimino et al. (1973) reported a similar increased activity of transition metal ions (t.m.i.) in dilute *solid solutions* of an inert matrix as compared to concentrated solid solutions, it would be imprudent to relate our results to the results of the Italian workers for the following reasons: the copper-tin oxides may not be solid solutions, the t.m.i. concentration in the matrix is one order of magnitude higher in our samples than the samples of the Cimino study, and the E_A changes appreciably with catalysts composition unlike the results of the Italians. It is possible that a small number of copper ions are "dissolved" into the SnO lattice during the activation of the catalysts. A compensation plot of our data over four catalysts compositions (Figure 5) are in good agreement to the correlated data of Moro-oka et al. (1966, 1968) for propylene oxidation over several mixed oxides; the compensation parameters of this work ($e = 0.1017$, $B = 15.7$) are close to the Moro-oka data ($e = 0.1017$, $B = 15.5$). One interpretation of these data is a surface

TABLE 3. ARRHENIUS CONSTANTS FOR MIXED OXIDE SELECTIVE OXIDATION CATALYSTS

Catalyst	Atom % Tin	Wt. % Tin	E_A , kJ/mol	k_o	k'_o
Cu ₂ O	0	0	54.8	4.3×10^{28}	4.3×10^{28}
Cu ₂ O/SnO (5/1)	16	25	29.7	1.9×10^{26}	2.5×10^{26}
Cu ₂ O/SnO (3/1)	33	39	47.2	1.1×10^{28}	1.8×10^{28}
Cu ₂ O/SnO (1/1)	50	66	60.6	2.5×10^{29}	7.4×10^{29}

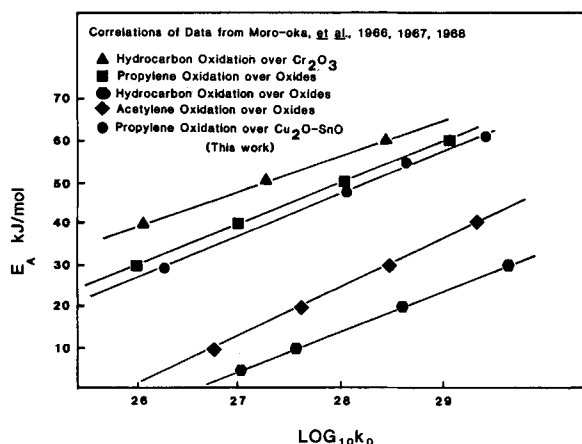


Figure 5. Compensation plot for hydrocarbon oxidation catalysis.

heterogeneous to sorption and/or reaction (Laidler, 1954; Galwey, 1977). In light of the previous discussion of the dual-site model, the compensation due to product sorption is a reasonable explanation of the rate constant data with temperature.

We propose the enhanced selectivity of the mixed oxides results from the formation of highly selective sites at the expense of somewhat less selective sites; the total number of acrolein active sites is speculated to remain constant during the genesis of the more selective, type A sites. The reducibility of the mixed oxides is influenced by the tin ion oxidation state such that the copper ions in the mixture may be stabilized to reduction.

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NOTATION

- B = constant in the compensation equation, $\log_{10} k_o = B + eE_A$. The constant B is the $\log_{10} k_o$ when $E_A = 0$
- E_A = activation energy for the production of acrolein [=] kJ/mol
- e = constant of proportionality in the compensation equation, $\log_{10} k_o = B + eE_A$
- k = rate constant for the dual-site model [=] moles acrolein/ks-kg
- k_o = preexponential factor of Arrhenius Law, specific to weight of copper in the catalysts [=] molecules acrolein/ks-g Cu
- k_o = preexponential factor of Arrhenius Law, specific to weight of catalyst [=] molecules of acrolein/ks-g catalyst
- k' = pseudorate constant for the production of acrolein [=] mol acrolein/ks-kg catalysts
- K_w = equilibrium adsorption constant for water in dual-site model [=] Pa⁻¹
- K_a = equilibrium adsorption constant for acrolein in the dual-site model [=] Pa⁻¹
- P_w = partial pressure of water in the gas phase [=] Pa
- P_a = partial pressure of acrolein in the gas phase [=] Pa
- P_O = partial pressure of propylene in the gas phase [=] kPa
- P_p = partial pressure of propylene in the gas phase [=] kPa
- P_{total} = reactor pressure [=] kPa
- r_{acrolein} = rate of acrolein formation [=] moles acrolein/ks-kg catalyst

- S = selectivity ratio, calculated from the yields of carbon dioxide and acrolein
- S_A = specific surface area [=] m²/g catalyst
- T = reactor temperature [=] K
- X_O = fractional conversion of oxygen
- X_p = fractional conversion of propylene

Greek Letters

- τ = spacetime, at reaction conditions [=] kg catalyst-ks/m³

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