Research Initiation - The Yield Enhancement Effects of Mixed Metal Oxide Catalysts for Propene Oxidation

Project No: E-19-665

Project Director: M. G. White

Sponsor: National Science Foundation

Agreement Period: From 4/15/78 Until 3/31/80
(Includes 6-month flexibility period)

Type Agreement: ENG78-06209

Amount: $25,000 (NSF) 2,926 (GIT E-19-340) $27,926 TOTAL

Reports Required: Final Technical Report and Summary of Completed Project

Sponsor Contact Person(s):

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Randolph T. Hatch
Chemical Processes Program
National Science Foundation
Washington, D.C. 20550

Contractual Matters (thru OCA)
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National Science Foundation
Washington, D.C. 20550

Defense Priority Rating: N/A

Assigned to: Chemical Engineering (School/Laboratory)

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Date: 10/29/80

Project Title: Reaction Initiation - The Yield Enhancement Effects of Mixed Metal Oxide Catalysts for Propene Oxidation

Project No: E-19-665

Project Director: Dr. M. G. White

Sponsor: National Science Foundation

Effective Termination Date: 3/31/80

Clearance of Accounting Charges: 3/31/80

Grant/Contract Closeout Actions Remaining:

- Final Invoice and Closing Documents
- Final Fiscal Accounting (FCTR)
- Final Report of Inventions
- Govt. Property Inventory & Related Certificate
- Classified Material Certificate
- Other

Assigned to: Chemical Engineering (School/Division)

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CA-4 (1/79)
Dr. Huk Cheh  
Program Director  
Chemical Processes Program  
National Science Foundation  
Washington, D.C.  20550  

Dear Dr. Cheh:  

I am pleased to submit for your consideration a proposal entitled, "The Yield Enhancement Effect of Mixed-Metal Oxide Catalysts for the Selective Oxidation of Olefins." This proposal is a renewal request for the grant made to the Georgia Institute of Technology presently under my direction (NSF Grant ENG78-06209). In the Appendix to the enclosed grant proposal you will find a preliminary progress report.

Respectfully yours,

Mark G. White  
Assistant Professor  
School of Chemical Engineering  

MGW:chr  

Enclosure
APPENDIX I

Progress Report

The first six months of the project were devoted to construction and testing of two kinetic reactors: a batch recirculation reactor and a plug flow reactor. The preliminary kinetic data\(^{(23)}\) for the selective oxidation of propylene over the mixed metal oxide catalysts confirm the earlier findings of the principal investigator:\(^{(5)}\) mixtures of cuprous oxide and other metal oxides having the formula Me-0 exhibit enhanced yields for the partial oxidation of propylene to acrolein when compared to the standard cuprous oxide catalysts. (See Table I.)

While a student at Rice University, the principal investigator observed a positive catalyst-yield synergism for combining cuprous oxide with other metal oxides, such as stannous oxide or zinc oxide (see Table I). The preliminary work at the Georgia Institute of Technology (Table I) seems to reproduce and confirm the existence of the catalyst-yield synergism. The apparent effect of mixing copper (I) oxide and tin (II) oxide or zinc (II) oxide is to favor the reaction to the desired product, acrolein.

The data reported in Table I are for the selective oxidation of propylene with oxygen in a plug flow reactor using helium as a diluent. The reactor conditions were temperature equal to 275°C to 300°C, space time varying from 1 second to 5 seconds, and the concentration of the feed stream in the proportions of He:C\(_3\)O\(_2\)::12:3:1 for the data gathered at Rice while the proportions were He:C\(_3\)O\(_2\)::10:6:1 for the data obtained at Georgia Tech. Direct comparisons of the catalysts at conditions of the same reaction temperature and similar fractional oxygen conversions show the mixed oxide catalysts to have higher selectivities to acrolein than the constituent metal oxides.
alone. The magnitude of the yield enhancements for the mixed metal oxide catalysts is a 50% to 80% relative improvement over the standard Cu₂O catalyst. As expected, the yield to acrolein will be favored by increasing the propylene to oxygen ratio. Alone, stannous oxide and zinc oxide showed almost no activity for the selective oxidation of propylene at the reaction conditions considered in this study.

A significant amount of effort was required to convert the laboratory space into a functioning catalysis research laboratory which includes a plug flow reactor and associated parts and a batch recirculation reactor. The kinetic data reported in Table I were gathered in the differential plug plug flow reactor. The temperature of the reactor was controlled by a Leeds and Northrup Electromax III controller while the Hoskin's electric furnace was energized by a Leeds and Northrup 11906 Zero-Voltage-Firing Power Supply. The catalyst temperature was sensed by an iron-constantan thermocouple connected to a Leeds and Northrup Model 8686 millivolt potentiometer. The reactor effluent was analyzed by a Hewlett-Packard HP 5722 Gas Chromatograph coupled to a Spectra-Physics Minigrator and a Linear Recorder, Model 361.

Part of the proposed work will require the batch recirculation reactor, which is near completion. The all-glass reaction system features a double-action, positive displacement pump also fabricated in pyrex by the Georgia Tech Glass Shop. The Hoskin's electric furnace is controlled by a Leeds and Northrup Electromax III controller and a Leeds and Northrup Zero-Voltage-Firing Power Supply. The gas analysis equipment is as follows: Varian Aerograph Model 920 Gas Chromatograph, Spectra-Physics Minigrator, and a Linear Recorder, Model 361.
Table I
Selective Oxidation of Propylene Over Metal Oxides

<table>
<thead>
<tr>
<th>Catalyst Sample</th>
<th>Initial Concentrations He:C(_3)H(_2):O(_2)</th>
<th>Reactor Temperature</th>
<th>Oxygen Conversion, Percent</th>
<th>Selectivity* to Acrolein, Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(_2)O</td>
<td>12:3:1</td>
<td>275°C</td>
<td>34.3</td>
<td>24.9</td>
</tr>
<tr>
<td>SnO</td>
<td>12:3:1</td>
<td>275°C</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>ZnO</td>
<td>12:3:1</td>
<td>275°C</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu(_2)O/SnO(1:1)</td>
<td>12:3:1</td>
<td>275°C</td>
<td>32.6</td>
<td>42.5</td>
</tr>
<tr>
<td>Cu(_2)O/SnO(3:1)</td>
<td>12:3:1</td>
<td>275°C</td>
<td>32.4</td>
<td>42.3</td>
</tr>
<tr>
<td>Cu(_2)O/ZnO(1:1)</td>
<td>12:3:1</td>
<td>275°C</td>
<td>25.4</td>
<td>40.6</td>
</tr>
<tr>
<td>Cu(_2)O</td>
<td>12:3:1</td>
<td>300°C</td>
<td>58.8</td>
<td>23.1</td>
</tr>
<tr>
<td>Cu(_2)O/SnO(1:1)</td>
<td>12:3:1</td>
<td>300°C</td>
<td>55.3</td>
<td>33.8</td>
</tr>
<tr>
<td>Cu(_2)O/SnO(3:1)</td>
<td>12:3:1</td>
<td>300°C</td>
<td>55.9</td>
<td>35.7</td>
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<tr>
<td>Cu(_2)O/ZnO(1:1)</td>
<td>12:3:1</td>
<td>300°C</td>
<td>43.3</td>
<td>45.2</td>
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<td>Cu(_2)O</td>
<td>12:3:1</td>
<td>300°C</td>
<td>60.7</td>
<td>20.3</td>
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<tr>
<td>Cu(_2)O/SnO(1:1)</td>
<td>12:3:1</td>
<td>300°C</td>
<td>60.4</td>
<td>34.0</td>
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<tr>
<td>Cu(_2)O/SnO(3:1)</td>
<td>12:3:1</td>
<td>300°C</td>
<td>58.2</td>
<td>38.9</td>
</tr>
<tr>
<td>Cu(_2)O</td>
<td>10:6:1</td>
<td>300°C</td>
<td>54.7</td>
<td>23.0</td>
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<tr>
<td>Cu(_2)O/SnO(1:1)</td>
<td>10:6:1</td>
<td>300°C</td>
<td>62.3</td>
<td>47.6</td>
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<tr>
<td>Cu(_2)O/SnO(1:1)</td>
<td>10:6:1</td>
<td>300°C</td>
<td>36.0</td>
<td>61.7</td>
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<tr>
<td>Cu(_2)O/SnO(1:1)</td>
<td>10:6:1</td>
<td>300°C</td>
<td>42.6</td>
<td>66.6</td>
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<tr>
<td>Cu(_2)O/SnO(1:1)</td>
<td>10:6:1</td>
<td>300°C</td>
<td>47.3</td>
<td>64.2</td>
</tr>
</tbody>
</table>

Selectivity = moles of propylene converted to acrolein / moles of propylene converted

NOTE: The last five table entries were obtained at Georgia Tech.
The aged cuprous oxide/stannous oxide catalysts (Cu/Sn atomic ratio equals 3/1) were analyzed at Georgia Tech for bulk crystal structure by x-ray diffraction. The G.E. diffractometer with copper Kα radiation was used on the samples of fine powder suspended on clear plastic tape. The data of d-spacing and relative intensities are reported in Table II. All of the reflections except two (d = 2.351 \AA, I/I₀ = 15.6 and d = 2.0910 \AA, I/I₀ = 14.1) may be explained from the x-ray spectra of the constituent metal oxides or a different oxidation state of the constituent metal oxide, i.e., SnO₂. These two additional reflections which appear in the x-ray diffraction pattern of the aged catalysts may be new crystalline phases of the bulk metal oxides. Further study may shed light on any connection between this observed change in crystal structure and the enhanced yields of acrolein over these mixed-metal oxide catalysts.
<table>
<thead>
<tr>
<th>Cu$_2$O-SnO (3:1) aged</th>
<th>SnO$_2$ literature</th>
<th>Cu$_2$O literature</th>
<th>Sn literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>d, Å</td>
<td>I/Îo</td>
<td>d, Å</td>
<td>I/Îo</td>
</tr>
<tr>
<td>3.3606</td>
<td>82.9</td>
<td>3.351</td>
<td>100</td>
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<td>3.0304</td>
<td>18</td>
<td>3.02</td>
<td>9</td>
</tr>
<tr>
<td>2.6496</td>
<td>70.7</td>
<td>2.644</td>
<td>81</td>
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<tr>
<td>2.4694</td>
<td>100</td>
<td>2.465</td>
<td>100</td>
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<tr>
<td>2.3749</td>
<td>27.3</td>
<td>2.369</td>
<td>24</td>
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<td>2.3510</td>
<td>15.6</td>
<td>2.309</td>
<td>5</td>
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<td>2.3161</td>
<td>11.7</td>
<td>2.3161</td>
<td>15.6</td>
</tr>
<tr>
<td>2.1401</td>
<td>36.6</td>
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<td>2.0910</td>
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<td>1.765</td>
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<td>1.765</td>
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<td>1.6757</td>
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<td>1.498</td>
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<td>1.439</td>
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<td>1.415</td>
<td>15</td>
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<td>1.3227</td>
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<td>1.322</td>
<td>7</td>
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<td>17.1</td>
<td>1.287</td>
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<td>1.233</td>
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<td>1.2149</td>
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<td>1.1849</td>
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<td>1.1546</td>
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<td>1.1170</td>
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<td>1.092</td>
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<td>1.0815</td>
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<tr>
<td>1.0363</td>
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<td>1.036</td>
<td>4</td>
</tr>
<tr>
<td>0.97874</td>
<td>4.9</td>
<td>0.9795</td>
<td>4</td>
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<tr>
<td>0.94939</td>
<td>8.5</td>
<td>0.9505</td>
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<tr>
<td>0.92937</td>
<td>4.3</td>
<td>0.9291</td>
<td>3</td>
</tr>
<tr>
<td>0.91435</td>
<td>4.6</td>
<td>0.914</td>
<td>3</td>
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<tr>
<td>0.90832</td>
<td>7.1</td>
<td>0.9081</td>
<td>8</td>
</tr>
<tr>
<td>0.90654</td>
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<td>0.9091</td>
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</tr>
<tr>
<td>0.88174</td>
<td>7.1</td>
<td>0.8819</td>
<td>7</td>
</tr>
</tbody>
</table>
November 7, 1979

National Science Foundation
Division of Grants and Contracts
Post-Award Projects Branch
1800 G. Street, N.W.
Washington, D.C. 20550

Dear Sirs:

Please find in the enclosures the Final Project Report for the
NSF Grant ENG78-06209.

Respectfully yours,

M.C. White
Chemical Engineering
PART I—PROJECT IDENTIFICATION INFORMATION

1. Institution and Address
Georgia Institute of Technology
Atlanta, Georgia 30332

2. NSF Program
Chemical Process

3. NSF Award Number
ENG78-06209

4. Award Period
From 4/15/78 To 3/31/80

5. Cumulative Award Amount
$25,000

6. Project Title
Research Initiation -- The Yield Enhancement Effects of Mixed Metal Oxide Catalysts for Propene Oxidation to Acrolein

PART II—SUMMARY OF COMPLETED PROJECT (FOR PUBLIC USE)

The reaction of hydrocarbons over multi-component catalysts will be studied. Selected metal oxides will be combined with cuprous oxide to provide a catalyst system for study of synergism. The catalyst system is sufficiently uncomplicated to be well suited for an in-depth study. This should lead to a better understanding of multi-component catalyst interactions and provide the basis for developing new multi-component catalyst systems.

Mixtures of cuprous oxide and stannous oxide were pre-treated to yield a selective and active agent for the selective oxidation of propene to acrolein. These mixed oxide catalysts exhibited an 80% relative increase in the yield of acrolein when compared to the standard cuprous oxide catalysts. X-ray diffraction data together with surface area measurements were used to partially characterize the mixed oxide catalysts.

PART III—TECHNICAL INFORMATION (FOR PROGRAM MANAGEMENT USES)

1. ITEM (Check appropriate blocks)
   NONE ATTACHED PREVIOUSLY FURNISHED TO BE FURNISHED SEPARATELY TO PROGRAM
   Check (✓) Approx. Date

a. Abstracts of Theses X
b. Publication Citations X
c. Data on Scientific Collaborators X
d. Information on Inventions X
e. Technical Description of Project and Results X
f. Other (specify)

2. Principal Investigator/Project Director Name (Typed)
Mark G. White

3. Principal Investigator/Project Director Signature

4. Date
11/6/79

Introduction

During the first year we sought to (1) prepare the mixed oxide catalysts in a reproducible manner; (2) to characterize the enhanced yields of the selective oxidation product, acrolein; and (3) to characterize the catalysts by BET surface area measurements and by x-ray diffraction techniques. Since this grant was a research initiation grant, there was much effort expended to building a viable catalysis laboratory (described in Part I of this report). Mr. David E. Self received a M.S. degree in Chemical Engineering as a result of his completion of an M.S. thesis (summarized in Part II).
Part I. Description of the Catalysis Laboratory

Two chemical reactors were constructed in the catalysis laboratory: a differential flow reactor and a batch, recirculation reactor. The support structure and utilities for the laboratory were installed by the principal investigator prior to the start of this grant and hence will not be described here.

Differential Flow Reactor

The differential flow reactor was a 12mm x 30cm long quartz tube with a 5mm O.D. thermowell inserted axially (See Fig. 1). The catalysts were supported in the annular space by plugs of quartz wool. The catalyst temperature was sensed by an iron-constantan thermocouple connected to a Leeds and Northrup millivolt potentiometer. The reactor was immersed in a Hoskins electric furnace which was controlled by a Leeds and Northrup Electromax controller. The reactant gases (oxygen, propylene, and helium) were independently metered by three Fisher-Porter rotameters with downstream needle valves. Analyses of the products were determined by a Hewlett-Packard chromatograph (HP 5722), a Spectra-Physics Minigrator, and a Linear Recorder. This reactor is ideal for "screening" catalysts for selectivity and activity as well as for obtaining preliminary kinetic data.

Batch Recirculation Reactor and Vacuum System

The batch recirculation reactor and the attached vacuum system are shown in Figure 2. The vacuum system and storage bulbs plus the BET system all connect to the batch recirculation system. This all-pyrex system features a variable frequency, double-acting, positive displacement pump. The catalysts may be easily inserted into the quartz catalyst holder which is heated by a Höskins electric furnace.
The furnace temperature is controlled by a Leeds and Northrup Electromax controller and the catalyst temperature is sensed by an iron-constant thermocouple connected to a Leeds and Northrup millivolt potentiometer. Product concentrations are determined by a Varian model 920 Gas Chromatograph, a Spectra-Physics Minigrator, and Linear Recorder. This batch reactor will be devoted to the determination of the reaction kinetics and mechanisms.
Part II. Results of the First Year's Work

The first objective was the development of a preparation and pretreatment method to render reproducible catalysts. Mechanical mixtures of the constituent metal oxides were pretreated according to the following method:

1. Oxidation of the mixture in a helium-oxygen stream at 325°C for thirty minutes.
2. Reduction of the catalyst in a stream of helium-propylene at 325°C for thirty minutes.

Omission of either step would result in a catalyst that was either unselective or inactive. Initially, we chose this simple procedure for catalyst preparation in lieu of a co-precipitation method because the mechanical mixture catalysts worked! The future work on this project will attempt to develop better catalysts by the co-precipitation method.

Having perfected a manner to prepare the catalysts, we sought to characterize the yields over these oxides for the selective oxidation of propylene to acrolein. The performance of the mixed oxides as compared to the constituent metal oxides were measured at a standard set of conditions: temperature = 300°C, oxygen conversion = 52%, He/C3H6/O2 initial concentrations = 10/6/1. These "high" oxygen conversion results are summarized in Figure 3 as percent selectivity to acrolein (defined as moles of propylene converted to acrolein divided by moles of propylene converted) versus virgin catalyst composition, expressed as moles Cu⁺/mole Sn++. Clearly, the mixed oxide catalysts are more selective (49% vs. 29%) than the cuprous oxide, and stannous oxide is an inert to the reactant mixture. These few data suggest the enhanced yield to acrolein is somewhat unaffected by the relative concentration of cuprous oxide to stannous oxide in the virgin, mixed oxide catalysts.
Energies of activation for the selective oxidation were determined from differential reactor data of rate constants (based on the rate of production of acrolein reported in Figure 4) for the reaction over cuprous oxide and several mixed oxide catalysts. For these low O₂ conversion data (less than 10%) at temperatures of 548 °K to 603 °K, the selectivity to acrolein was in excess of 90%. The initial reactant concentrations were in the proportions of He: C₃H₈: O₂:: 10: 6:1. These data of rate constants vs. reciprocal absolute temperature may be fit to the Arrhenius expression with values of the pre-exponential factor k₀, and activation energy as given in Table I. The Arrhenius constants for the reaction over these catalysts vary with catalysts composition in a manner similar to the findings of previous investigators on other reaction and catalysts systems; that is, low values of the pre-exponential factor are "compensated" by low values of the activation energy.

The catalysts were analyzed for specific surface area by the B.E.T. method using nitrogen as the adsorbate at a catalyst sample temperature of 77 °K. The specific surface areas for all the catalysts are between 25 x 10⁴ and 30 x 10⁴ m²/kg and these surface areas do not change appreciably with the pretreatment.

The oxide catalysts were analyzed for crystal structure by x-ray diffraction; the virgin, constituent metal oxides were identified as cuprous oxide (cuprite) and stannous oxide (SnO)₄ T. See Figure 5. After the constituent metal oxides were pretreated separately, the diffraction patterns were interpreted as follows: the pretreated cuprous oxide sample contained cuprite and large amounts of zero-valent copper; no evidence of cupric oxide in the sample. The pretreated stannous oxide sample contained cassiterite (SnO₂), Sn₂O₃, Sn₃O₄ and Sn₅O₈ (Figure 5). One sample of the mixed metal oxide catalysts (equal molar mixture of Cu₂O and SnO) was analyzed by XRD prior to the oxygen treatment (i.e. virgin catalysts), subsequent to the oxygen treatment, and after the reduction treatment (Figure 6).
The oxygen treatment caused radical changes in the crystal structure of the mixed metal oxide; some of the very strong reflections characteristic to cuprous oxide dissipated, or were severely reduced in magnitude, but the reflections characteristic to stannous oxide were changed only slightly by the oxygen treatment. The reduction treatment with propylene partially restored the x-ray diffraction pattern observed for the virgin catalysts with small shifts towards the lower angles (0.2° in 2θ) and small changes in the relative intensities (I/I₀) for some of the reflections. The pretreated catalysts showed the evidence of the formation of a new crystalline phase; small peaks not observed in the virgin material are present in the pretreated catalysts at values of 2θ equal to 33.9°, 43.25°, 51.7°, 52.4°, 62.6°, 69°, 89.8°, 92.2°, 105.5°. The XRD spectrum of the aged mixed metal oxide after pretreatment cannot be explained in terms of a combination of the XRD spectra of the aged constituent metal oxides which have been pretreated in the same manner.

Two other mixture compositions of the copper-tin catalysts (Cu⁺/Sn⁴⁺ = 3/1 and 5/1) were analyzed by the x-ray diffraction technique (see Figure 7). The aged catalysts are observed to have somewhat different x-ray diffraction patterns from the virgin materials; both of these catalysts exhibit a reflection at 2θ = 26.5° whereas the 1:1 Cu⁺/Sn⁴⁺ catalyst did not have such a reflection. These three catalysts have very similar selectivity-activity characteristics, very similar specific surface areas, but vastly different crystal structures. We are presently at a loss to explain the implications of these data. Obviously, the surface characteristics of these oxides must be investigated as a next step to understanding these catalysts systems.
**TABLE I - Arrhenius Constants for Selective Oxidation Catalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$k_0 \text{ ml/gm-sec}$</th>
<th>$E_A \text{ kcal/gmole}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$O</td>
<td>1558.7</td>
<td>13.1</td>
</tr>
<tr>
<td>Cu$_2$O:SnO(1:1)</td>
<td>9338.5</td>
<td>14.5</td>
</tr>
<tr>
<td>Cu$_2$O:SnO(3:1)</td>
<td>408.7</td>
<td>11.3</td>
</tr>
<tr>
<td>Cu$_2$O:SnO(5:1)</td>
<td>6.89</td>
<td>7.1</td>
</tr>
</tbody>
</table>
FIGURE 1. REACTOR SCHEME, STEADY STATE FLOW OR PULSE OPERATIONAL MODES
FIGURE 2. RECIRCULATION REACTOR

- STORAGE BULBS
- POSITIVE DISPLACEMENT PUMP
- OIL DIFFUSION PUMP
- MECHANICAL PUMP
- McLEOD GUAGE TO EXHAUST
- GAS SAMPLING VALVE TO VACUUM TO GAS CHROMATOGRAPH
- CATALYST SAMPLE FOR BET SYSTEM
- CATALYST HOLDER
- GAS MIXING VOLUME
- BYPASS
- U-TUBE MANOMETER
FIGURE 3. SELECTIVITY TO ACROLEIN FOR PROPYLENE OXIDATION
OVER MIXED METAL OXIDE CATALYSTS

TEMPERATURE = 573°K
He/C₃H₆/O = 10/6/1
OXYGEN CONVERSION = 52%
FIGURE 4. ARRHENIUS PLOT FOR SELECTIVE OXIDATION OVER MIXED METAL OXIDE CATALYSTS

He/C₃H/O = 10/6/1
P Total = 101.3 kPa

- Cu₂O
- Cu₂O-SnO; Cu⁺/Sn⁴⁺ = 5/1
- Cu₂O-SnO; Cu⁺/Sn⁴⁺ = 3/1
- Cu₂O-SnO; Cu⁺/Sn⁴⁺ = 1/1
FIGURE 5. X-RAY DIFFRACTION PATTERN FOR CUPROUS OXIDE AND STANNOUS OXIDE

Cu₂O (VIRGIN)

Cu₂O (PRETREATED)

SnO (VIRGIN)

SnO (PRETREATED)

2θ

20° 30° 40° 50° 60° 70° 80° 90° 100° 110° 120°
FIGURE 6. X-RAY DIFFRACTION PATTERN FOR Cu$_2$O/SnO = 1/1 MIXTURE

(VIRGIN)

AFTER O$_2$ TREATMENT

AFTER OXIDATION AND REDUCTION TREATMENT

2θ

20° 30° 40° 50° 60° 70° 80° 90° 100° 110° 120°
FIGURE 7. X-RAY DIFFRACTION PATTERN FOR Cu₂O/SnO 5/1 AND 3/1 MIXTURE

5/1, VIRGIN

5/1, PRETREATED

3/1, VIRGIN

3/1, PRETREATED

2θ

20° 30° 40° 50° 60° 70° 80° 90° 100° 110° 120°
Catalysts for the partial oxidation of propylene to acrolein were studied to determine if a catalyst-yield synergism was produced by mixing stannous oxide (SnO) with cuprous oxide (Cu$_2$O), a known catalyst for this reaction. Catalysts with cation atomic ratios (Cu/Sn) of 1:1, 3:1, and 5:1 were used and their performance for the selective oxidation reaction were compared to cuprous oxide catalyst.

Differential reactor data were obtained for each catalyst and used to construct zero order plots of acrolein mole fraction vs. space-time at several reaction temperatures. The limiting slopes of these zero order plots which are proportional to the rate constants, were used to construct Arrhenius plots for each catalyst. Energies of activation for the formation of acrolein were obtained from the slopes of these Arrhenius plots for each of the mixed oxide (8-14 kcal/mole) catalysts and compared to that of the cuprous oxide (13 kcal/mole). A plot of selectivity to acrolein at high oxygen conversion (~55%) vs. catalyst tin concentration showed the mixed oxide catalysts to be slightly more active.
(-50 relative %) and much more selective to the product acrolein (49% selectivity vs. 29% selectivity) than the cuprous oxide catalyst. Stannous oxide when used alone as catalyst did not show significant activity for the oxidation of propylene.

X-Ray diffraction data for the virgin and aged states of the catalysts used in this study indicated that some of the stannous oxide in the mixed oxide catalysts was oxidized to stannic oxide (SnO$_2$) during the aging process. Stannous oxide alone was not converted to stannic oxide when aged under the same reaction conditions.

Surface area analysis of the virgin and aged states of all the catalysts yielded data which could not, by itself, explain the increases in activity and selectivity of the mixed metal oxide catalysts. This indicated that the catalyst-yield synergism was due to something other than a change in pore size or surface area.