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Hayden Fowler

University of Alabama in Huntsville

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An Investigation of Copper Catalysts for Propylene Epoxidation

Hayden Fowler

Department of Chemical and Materials Engineering

Abstract – The industry for propylene oxide (PO) is in need of a more efficient, environmentally-friendly method of PO production. This study is focused on optimizing conditions for the gas-phase epoxidation of propylene with molecular oxygen in a single step over Cu catalysts for use in future research involving Au-Cu bimetallic catalysts. To do this, a 5 wt% Cu/SiO₂ catalyst was prepared using incipient wetness impregnation and tested over a temperature range of 220-300 °C, varying the flow rate and ratio of reactants. Lower total flow rates led to higher conversions, and using excess oxygen favors complete combustion of propylene to CO₂. As temperature was increased, conversion and CO₂ selectivity were increased, and PO selectivity was decreased. These conditions will be used to design future Au-Cu bimetallic catalyst testing parameters.

I. Introduction

Propylene oxide (PO) is a very highly-valued chemical intermediate, produced at a rate of 8 million tons per year with a price of \$2,500 per ton, making PO production a \$20 billion industry [1]. PO is used to synthesize other chemicals and polymers, such as propylene glycols, polyurethane, and polyether polyols [2]. These products are in turn used for a variety of applications, including the automobile, construction, pharmaceutical, and cosmetics industries. Products like polyurethane foams and polyester resins are largely made possible by PO [2].

All current industrial methods for producing PO occur in multiple steps in the liquid phase. This requires separation processes for retrieving PO from other reaction products. Because of this, the cost and energy requirements of production plants is greatly increased. Furthermore, the most popular industrial methods of PO production are the chlorohydrin and hydroperoxide coproduct processes, accounting for 91% of commercial PO production in total [3]. Both methods produce an excessive amount of unwanted

byproducts. The chlorohydrin process produces 2.2 tons of CaCl₂ salts per ton of PO, along with toxic, chlorinated, organic compounds at a much smaller amount, making this method overwhelmingly wasteful and environmentally harmful [3]. The hydroperoxide coproduct process produces useful byproducts; however, their production is much greater than demand, being produced at two to three times the amount of PO [3].

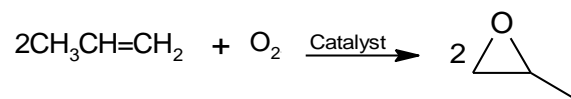


Figure 1: Propylene reacts with molecular oxygen over a catalyst to give propylene oxide. This method would be a beneficial alternative to current industrial methods.

Industrial production of PO has major downfalls, including being wasteful, expensive, inefficient, and environmentally harmful. The PO industry and the environment would greatly benefit from a more efficient, environmentally-friendly method of PO production. One possible alternative is the gas-phase epoxidation of propylene by molecular oxygen in the presence of a catalyst, as shown in **Figure 1** [3]. This method, occurring in a single step, would greatly lessen the amount of equipment needed in plants, resulting in lower costs and energy usage. Due to the greater efficiency, PO could be produced in larger amounts at lower prices, allowing for more PO production plants to open and for more jobs to be created. When the gas-phase reaction is optimized, the only byproduct is water, making this method non-wasteful and environmentally friendly. Therefore, optimizing this method for industrial use would improve, if not eliminate, all current problems seen in current industrial methods.

Au-Cu bimetallic catalysts could be the answer to this alternative method of production. Bimetallic catalysts offer a promising method for combining the best qualities of two metal catalysts.

Many investigations have been done using coinage metals, i.e. Au, Ag, and Cu, as the catalyst for this reaction [1,4]. The current benchmark catalyst for this reaction is Au, reaching selectivity for PO near 100% [1]. However, the conversion of propylene to PO is low, and Au is expensive. Evidence exists to suggest that Cu may provide better conversion than Au and a better selectivity than Ag [1,5]. Compared with Au, non-precious metal Cu offers an inexpensive, earth-abundant alternative. However, the selectivity of the reaction for PO from Au is still superior. Therefore, it is of great interest to produce a bimetallic Au-Cu catalyst to increase the conversion of propylene while maintaining the high selectivity offered by Au alone.

Before beginning this research, it would be beneficial to fully understand the performance and behavior of Cu catalysts for the reaction. While Au catalysts are mostly understood, Cu catalysts may operate optimally at completely different conditions for this reaction. This may include a different temperature range, amount of copper present, flow rate of reactants, or even ratio of reactants present. A better understanding of how monometallic Cu catalysts work will provide greater insight when designing bimetallic Au-Cu catalysts later, especially when considering reaction conditions and relative amounts of each metal present.

The purpose of this study was to optimize the conditions for the reaction of propylene with molecular oxygen over Cu catalysts. This work was based on Lambert's research on Cu catalysts for propylene epoxidation, and a comparison was done with Lambert's work accordingly [7]. The conditions to be optimized were total flow rate of reactants, ratio of propylene to oxygen, and temperature. Furthermore, characterization was done on the catalyst in order to understand the function of Cu catalysts for the reaction. The data and conclusions obtained from this study will be used when designing future experiments involving the testing of Au-Cu bimetallic catalysts.

II. Experimental

Catalyst Preparation

A 5 wt% Cu/SiO₂ catalyst was prepared using incipient wetness impregnation (IWI). 100 mL of a Cu(NO₃)₂ precursor solution was created by dissolving Cu(NO₃)₂·3H₂O (Sigma Aldrich, 61197) in deionized water to give a 0.118 g Cu(NO₃)₂·3H₂O/mL solution.

4.845 mL of precursor solution was deposited onto 2.85 g of SiO₂ via pipette. The catalyst was dried in static air at atmospheric pressure for 10 hours at 120 °C. The catalyst was then calcined in flowing air (50 mL/min) at 300 °C for 4 hours. The catalyst was pressed and sieved to a grain size of 180-250 μm. Prior to testing, the catalyst was reduced in 5% H₂ in Ar (total flow: 25 mL/min) for 1 hour and at 300 °C. The reduction of the Cu species in the catalyst is done to remove oxygen from the surface of the catalyst prior to reaction of propylene with oxygen. The reduction yields water from combining hydrogen and oxygen at the surface.

Catalytic Reaction

100 mg of catalyst was diluted by 1 g of quartz and loaded into a glass tube to create a packed bed reactor. The reactor was placed into a furnace to allow for temperature control. The flow rates of reactant and carrier gases were varied to determine the effects of flow rates and ratios on the catalytic performance.

The catalyst was tested at the following conditions on a temperature range of 220-300 °C:

- 5% O₂, 5% C₃H₆, balanced in Ar at a flow rate of 50 mL/min
- 5% O₂, 5% C₃H₆, balanced in Ar at a flow rate of 20 mL/min
- 5% O₂, 10% C₃H₆, balanced in Ar at a flow rate of 20 mL/min

The catalyst testing system is shown in **Figure 2**. The products of reaction were identified and the relative amounts measured using gas chromatography via HP 5890 Series II gas chromatograph. Using these relative amounts, the conversion of propylene and the selectivity for each product were calculated via equations 1 and 2.

$$(1) \text{ Conversion} = 1 - \frac{\left(\frac{\text{Amount of propylene}}{\text{present after reaction}} \right)}{\left(\frac{\text{Amount of propylene}}{\text{present before reaction}} \right)}$$

$$(2) \text{ Selectivity} = \frac{\left(\frac{\text{Amount of PO}}{\text{present}} \right)}{\left(\frac{\text{Amount of total}}{\text{products present}} \right)}$$

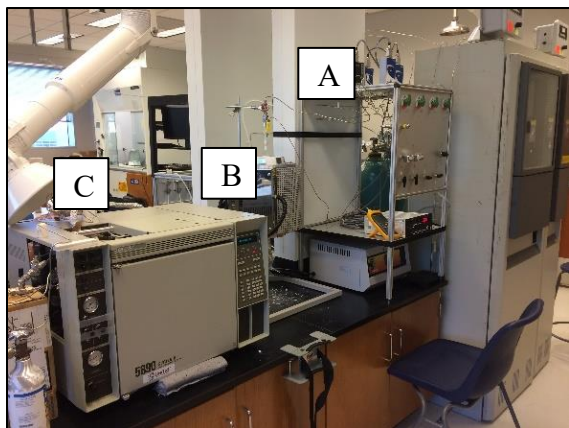


Figure 2: The catalyst testing system consists of mass flow controllers (A), reactor and furnace (B), and gas chromatograph (C).

Catalytic Characterization

X-Ray diffraction (XRD) analysis was performed on the catalyst before and after reaction using a Rigaku MiniFlex 600 X-ray diffractometer.

III. Results and Discussion

XRD Characterization

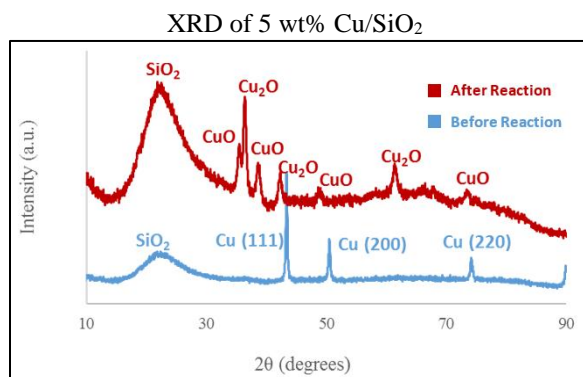


Figure 3: The XRD spectra of the catalyst were taken before (blue) and after (red) reaction. Before reaction, the peaks are consistent with unoxidized Cu, while after reaction, peaks indicate the presence of Cu^+ and Cu^{2+} .

The XRD spectra taken before reaction of propylene and oxygen to PO, shown in Figure 3, are consistent with SiO_2 and Cu^0 . This indicates that Cu^0 is the only present oxidation state of Cu prior to reaction and that the copper species in the catalyst were completely reduced by H_2 .

After the reaction, as shown in Figure 3, the spectrum changes significantly, indicating a change in present species. Upon further analysis, it was determined that the new peaks are consistent with the Cu^+ and Cu^{2+} oxidation states. Copper is oxidized easily, and given that molecular oxygen was used as a reactant, these results were consistent with the literature [6,7].

Catalytic Performance

The observable products of reaction were PO, CO_2 , acrolein, ethanal, and acetone. Of these, CO_2 and acrolein were major, and PO was of interest. These were the major products noted in the literature as well [5]. Due to the minimal amounts of ethanal and acetone being produced, these byproducts will not be discussed further in this report.

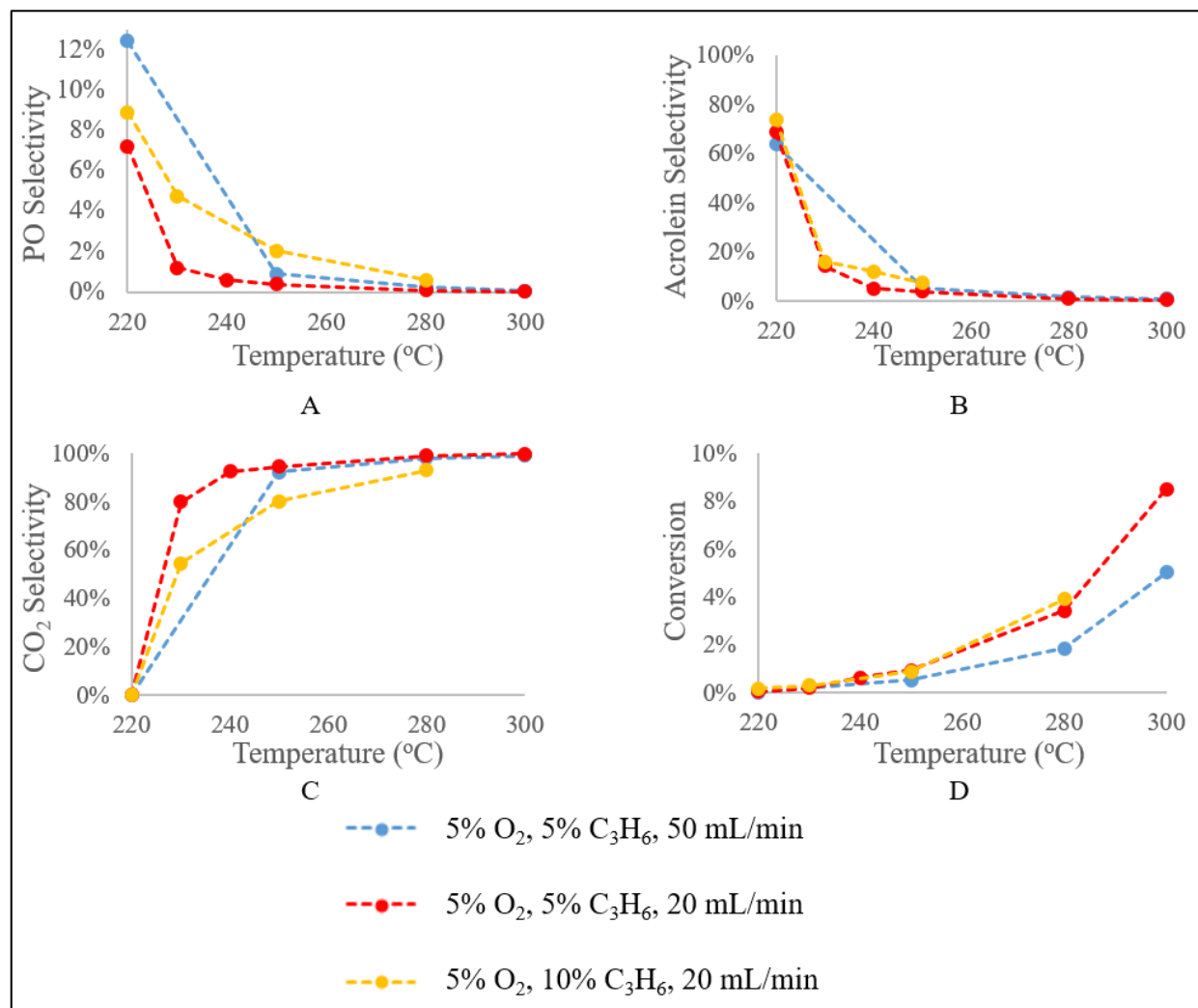
Performance of 5 wt% Cu/SiO₂

Figure 4: The data are presented from the tested scenarios: 5% O₂/5% C₃H₆/ 90% Ar at 50 mL/min (●), 5% O₂/5% C₃H₆/ 90% Ar at 20 mL/min (●), and 5% O₂/10% C₃H₆/ 90% Ar at 20 mL/min (●). (A) The selectivity of the reaction for PO decreases significantly as temperature increases. A greater flow rate for a 1:1 ratio of propylene to oxygen gives a higher selectivity. However, a 2:1 ratio of propylene to oxygen at a lower flow rate performs better for PO selectivity over the entire temperature range. (B) Acrolein is a major product for the lowest temperature in the range for each scenario. As temperature increases, selectivity for acrolein decreases similarly for each scenario. (C) Above temperatures of 220 °C, CO₂ becomes the dominant product of reaction, reaching selectivity of around 90% for higher temperatures. Decreasing the flow rate and providing a more stoichiometric 2:1 ratio of propylene to oxygen significantly hinders CO₂ production for lower temperatures. (D) Conversion of propylene increases as temperature increases but does not light off within this temperature range. Lower flow rates give better conversions, but changing the ratio of propylene to oxygen has a small effect.

Effect of Temperature

For each case tested, temperature has a major effect on the conversion of propylene and the selectivity for certain products of reaction. As shown in **Figure 4A and 4B**, as temperature is increased, the selectivity of the reaction for PO and acrolein is decreased significantly. The opposite is true for selectivity of the reaction for CO₂, as it increases with

increasing temperature, as shown in **Figure 4C**. Conversion also increases with increasing temperature, as shown in **Figure 4D**. However, the conversion curves for each case do not light off within this temperature range. This is in good agreement with Lambert's work, in which conversion curves also do not light off within this temperature range [7].

From this data, it appears that at lower temperatures where PO selectivity is higher, conversion is very small, and vice versa. Higher temperatures drive the reaction towards combustion of propylene to generate more CO₂. This effect is also present in the literature [7,8,9]. Therefore, this catalyst alone would not be suitable for propylene epoxidation. However, combining Cu with Au and operating at a higher temperature could potentially increase the conversion of reaction while maintaining high selectivity. Since the reaction with Au will differ, an optimal temperature range for the bimetallic catalyst will need to be found. This temperature range can serve as the maximum consideration of temperatures, assuming Au follows the same pattern of decreasing PO selectivity with increasing temperature.

Effect of Flow Rate

From **Figure 4A**, it is shown that PO selectivity decreases when the total flow rate is decreased from 50 mL/min to 20 mL/min while maintaining a 1:1 ratio of propylene to oxygen. However, the selectivity for CO₂ and acrolein do not appear to be affected by the decrease in flow rate. Conversion behaves opposite of PO selectivity, increasing when the total flow rate is decreased from 50 mL/min to 20 mL/min maintaining a 1:1 propylene to oxygen ratio.

These trends can be explained by the residence time of reactants in the catalyst bed. A higher flow rate should give a lower residence time. Lower residence times may also mean less time for the reactants to be converted into products. Therefore, by this logic, an increase in flow rate, resulting in a decrease in residence time, should result in a lower conversion, and vice versa for a decrease in flow rate. This is shown by the data in **Figure 4**.

Effect of Reactant Ratios

Figure 4A shows that changing the ratio of propylene to oxygen from 1:1 to 2:1 has a significant effect on the selectivity of the reaction to PO while maintaining a constant total flow rate of 20 mL/min. This is true for the entire temperature range. Likewise, from **Figure 4C**, the selectivity of the reaction to CO₂ is decreased with this change in ratio. **Figure 4D** does not indicate a major change in conversion with this ratio change within this temperature range. **Figure 4B** could show a slight increase in acrolein selectivity with this ratio change, but the effect does not appear to be major.

This phenomenon is best explained by the stoichiometry of the reaction, shown in **Figure 1**. This reaction shows a 2:1 ratio of propylene to oxygen to give PO. **Figure 4A and 4C** show that the change in

ratio from 1:1 to 2:1 leads to an increase in PO and decrease in CO₂. This indicates that a more stoichiometric ratio of reactants favors partial oxidation of propylene to PO, while an excess of oxygen favors complete combustion of propylene to CO₂.

A similar effect can be seen in literature; a decrease in the partial pressure of oxygen led to a decrease in CO₂ production [10]. However, in the case of this work, it resulted in more acrolein production, which was the reaction of interest. In this study, the selectivity towards acrolein is also increased when the ratio of propylene to oxygen is increased. Therefore, it can be concluded that partial oxidation to either acrolein or propylene is favored over complete combustion to CO₂ with more stoichiometric feeds.

Comparison with Lambert

Comparison of 5 wt% Cu/SiO₂ with Lambert's Catalyst

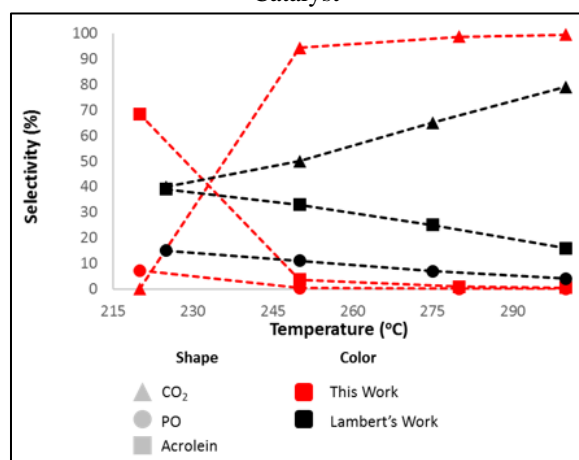


Figure 5: A comparison of the data from this work and Lambert's work is given for the selectivity of major observed products. Both catalysts were prepared similarly and tested under similar conditions. The general trends for selectivity are the same for both works. However, this work's catalyst has a greater selectivity for CO₂, especially as higher temperatures.

The preparation of the 5 wt% Cu/SiO₂ catalyst by IWI was largely inspired by a similar catalyst prepared in Lambert's work [7]. A comparison between the two catalyst performances with regards to the production of major products is shown in **Figure 5**. The trends of major product selectivity vs. temperature were similar for both catalysts. However, the amount of product formed in each case was drastically different, especially in the case of Acrolein and CO₂. The catalyst of this work produced significantly more CO₂, and CO₂ production increased much more rapidly earlier in the temperature

range. Lambert's catalyst produced much less CO₂ at a more linear relationship to temperature.

Furthermore, at 220 °C, no CO₂ was detectable, and the selectivity for Acrolein was higher than that of Lambert's. One possible explanation for this is the limits of the GC used in this experiment. CO₂ may have been present but not able to be detected. Otherwise, CO₂ production for this catalyst has a very strong dependence on temperature.

Overall, Lambert's catalyst performs better for PO selectivity, while the catalyst of this work largely favors combustion to CO₂. Changing the ratio of propylene to oxygen helped to decrease this effect. However, more solutions could be attempted from here, including adding a promoter or changing the support.

IV. Conclusion

The results of this study will provide a guideline for testing the conditions of future Cu-

containing catalysts, particularly Au-Cu bimetallic catalysts. The goal is to use Cu to increase propylene conversion while maintaining high selectivity for PO offered by Au. Therefore, from these results, decreasing flow rate and providing a stoichiometric ratio of reactants will be considered for future Cu catalyst testing. Using higher temperature will also be considered for increasing conversion. However, the reaction temperature will also be largely dependent on the reaction conditions needed for Au catalysts. In general, trends have been established for temperature, flow rate, and reactant ratios with respect to selectivity and conversion. Therefore, a baseline for adjustments for future catalyst testing has been established.

V. Acknowledgments

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