

**KINETIC STUDY OF THE HYDRATION OF PROPYLENE OXIDE IN THE
PRESENCE OF HETEROGENEOUS CATALYST**

S. Akyalcin^{*}

Anadolu University, Department of Chemical Engineering, 26555, Eskisehir, Turkey

Received 3.2.2017.

Revised 16.3.2017.

Accepted 28.3.2017.

^{*} **Corresponding Author:** e-mail: sdogruel@anadolu.edu.tr; Tel: +90-222-321 35 50/6510; Fax: +90-222-323 95 01

Abstract

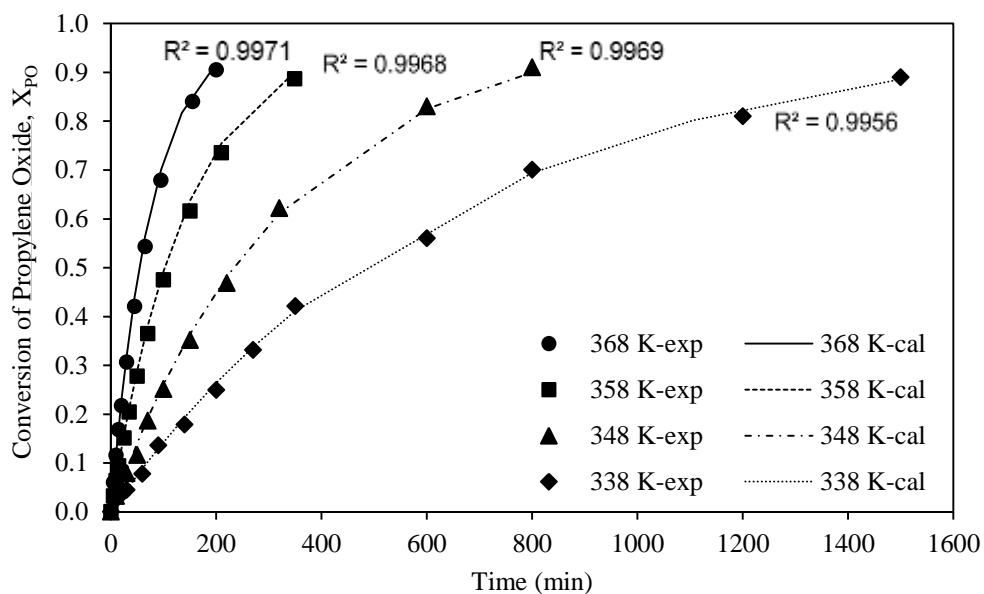
The kinetics of the hydration of propylene oxide was studied using a pressurized batch reactor for both uncatalyzed and heterogeneously catalyzed reactions. Lewatit MonoPlus M500/ HCO_3^- was used as heterogeneous catalyst, which showed better performance than Dowex Marathon A/ HCO_3^- . The effects of the parameters, namely internal and external diffusion resistances, temperature, catalyst loading and molar ratios of reactants, on the reaction rate were studied. The uncatalyzed and heterogeneously catalyzed reactions were proved to follow a series-parallel irreversible homogeneous mechanism. The temperature dependencies of the rate constants appearing in the rate expressions were determined.

Keywords: hydration reaction, propylene oxide, propylene glycol, dipropylene glycol, Lewatit MonoPlus M500/ HCO_3^- , reaction kinetics.

Highlights

- The hydration of propylene oxide was investigated detailed.
- Kinetic model was expressed in the presence of Lewatit MonoPlus M500/ HCO_3^- .
- The reactions follow a series-parallel irreversible homogeneous mechanism.
- Temperature dependencies of kinetic parameters were determined.

Graphical Abstract



Introduction

Propylene glycol (PG) is an important intermediate for numerous chemicals in the production of alkyd resins for paints and varnishes, in hydraulic fluids, and in heat transfer fluids. PG has very low toxicity, therefore it is directly used in foods, pharmaceuticals and cosmetics. Industrially, propylene glycol is produced by the hydration of propylene oxide (PO) which proceeds a series-parallel reaction. During the reaction, dipropylene glycol (DPG) and tripropylene glycol (TPG) are produced as by-products [1, 2]. DPG is a chemical intermediate in the manufacture of high-performance, unsaturated polyesters resins, polyurethanes, and plasticizers. DPG is used in hydraulic brake-fluid formulations, cutting oils, industrial soaps, and solvents [1, 3]. TPG is also used as a solvent, as textile soaps, and lubricants [1].

The hydration of PO can occur either non-catalytically or catalytically. Noncatalytic hydration of PO is carried out at high temperature with a large amount of water (12 to 20 mol water (W)/mol PO) [4]. This process causes high energy consumption and also increases the cost contributed by the purification of the product. Acid or base catalysts can be used to enhance reaction rates or PG selectivity. Both homogenous and heterogeneous catalysts can be used for the hydration of PO. While sulfuric acid [5] and salts of some acids [6, 7] are used as homogeneous catalysts, ion-exchange resins [8, 9], solid base [10] and solid acid [11] catalysts can serve as heterogeneous catalysts. Compared to homogeneous catalysts, heterogeneous catalysts are noncorrosive and can be easily removed from the reaction mixture by decantation and filtration. Additionally, heterogeneous catalyst suppresses side reactions, leading to higher purity of product [12].

Liu et al. synthesized PG and DPG by the hydration of PO over solid base catalysts. They reported that sol-gel derived $\text{Na}_2\text{O-ZrO}_2$ showed the excellent performance among the others and under the optimal reaction conditions, PO conversion, PG selectivity and DPG selectivity reached 99.9 %, 46.2 %, and 41.3 %, respectively [10]. Shaikhutdinov et al. reported the kinetics of propylene oxide hydration in the presence of bis(ethane-1,2-diol)molybdate. They suggested a mathematical description of PO disappearance and PG formation [13]. Kozlovsky et al. studied the kinetics of hydration of ethylene and propylene oxides in concentrated aqueous solutions and proposed the first-order kinetics of ethylene or propylene oxide consumption. They reported that 96 % PG yield was obtained in the presence of 0.25 mol/L sodium bicarbonate at 94 °C when the W/PO molar ratio was 33.7/1 [7]. The same reaction was also studied in a batch reactor by Reman and Van Kruchten using Amberlite 400/ HCO_3^- , immobilized anions of salts on heterogeneous carrier. They reported that the selectivity of PG and DPG was 95.5 % and 3.9 %, respectively when the conversion of PO was 99 % at 120 °C. They compare catalytic and non-catalytic PO hydration reaction data. Analysis of the product which is obtained from non-catalytic reaction at 160 °C showed that the selectivity of PG and DPG was found as 81.5 % and 17.8 %, respectively when more than 99 % of PO had been converted [9]. Horbatenko et al. investigated stepwise and concerted mechanisms for the formation of PG and DPG over ZSM-5 zeolite. They report that although the formation of the PG is faster, the formation of DPG as a byproduct cannot be avoided using ZSM-5 zeolite [14].

In the present work, the kinetic model was established for representing the hydration of PO in the presence of Lewatit MonoPlus M500/HCO₃⁻ which showed better performance than Dowex Marathon A/HCO₃⁻. The kinetic model was rearranged for the formation of PG and DPG.

Materials and methods

Materials

Propylene oxide (99.0%) was purchased from Acros. Deionized water (18.2 MΩ) was used in all experiments. Lewatit MonoPlus M500 and Dowex Marathon A in chloride forms were converted in the bicarbonate form and used as catalysts [9, 15]. The properties of the ion-exchange resins reported by manufacturer are given in Table 1.

Insert Table 1.

Apparatus

The experiments were performed in a 450 mL stainless steel, high-pressurized batch reactor (Parr 4562), equipped with a heating jacket, a cooling coil, a sampling line, two oblong windows, and a catalyst basket with uniflow stirrer. A controller (Parr 4843) was used to control temperature and stirrer speeds in the reactor and to monitor the reactor pressure.

Procedure

A known amount of the fresh catalyst in a catalyst basket and a predetermined amount of water, providing the desired W/PO molar ratio, were loaded into the reactor. A nitrogen line to the stainless steel feeding vessel and the reactor were connected to the system. The reactor content was heated to the reaction temperature, and it was kept constant during the reaction. Meanwhile, the amount of the PO, providing the desired W/PO molar ratio, was introduced into the reactor after heating to the reaction temperature in a stainless steel vessel. The total volume was kept constant at 150 mL in all experiments. Then, the sample was collected in a cold trap and analyzed to determine the initial composition of the reaction mixture. Thereafter, a 1 mL liquid sample was periodically withdrawn from the reactor for analysis.

Analysis

A HP 7890 gas chromatograph equipped with flame ionization detector (GC-FID) was used to determine PG, DPG and TPG concentrations in all samples and a high polarity HP-INNOWax capillary column was used to separate the compounds in the samples. The FID and injector temperatures were set to 250 °C. The column temperature was programmed to be increased from 100°C to 220 °C at a rate of 8 °C·min⁻¹. 1,3- butanediol (≥99.0%) was used as an internal standard. Mass balance calculations based on the stoichiometric equations given in Eqs. 1a-1c were used to determine the concentration of PO and W. The initial concentration of PO was also determined by the concentration of the products obtained when the reaction was completed.

To determine the equivalent concentration of bicarbonate in the catalysts, the catalysts were treated with 10 % NaCl solution [16], and then the solution was titrated with 0.1 N HCl solution [17].

Results and discussion

Reaction mechanism and kinetic modeling

The experiments were performed in a high-pressurized batch reactor to observe the effects of the parameters on the reaction rate. For each experiment, the parameter under investigation was varied while keeping the others constant.

The experimental data show that the formation of TPG is negligible in the presence of the catalyst while it is significant in the uncatalyzed reaction. Therefore, the hydration of PO can be considered to proceed in a three step series-parallel reactions for uncatalyzed reactions and in a two-step series-parallel reactions for the catalyzed reactions [3, 4]:



If each step given in Eqs. 1a-1c is assumed as an irreversible, bimolecular and constant density reaction, the reaction rate expressions can be written as follows:

$$-\frac{dC_{PO}}{dt} = k_1 C_W C_{PO} + k_2 C_{PG} C_{PO} + k_3 C_{DPG} C_{PO} \quad (2a)$$

$$\frac{dC_{PG}}{dt} = k_1 C_W C_{PO} - k_2 C_{PG} C_{PO} \quad (2b)$$

$$\frac{dC_{DPG}}{dt} = k_2 C_{PG} C_{PO} - k_3 C_{DPG} C_{PO} \quad (2c)$$

$$\frac{dC_{TPG}}{dt} = k_3 C_{DPG} C_{PO} \quad (2d)$$

where k_1 , k_2 , and k_3 are the reaction rate constants. Eqs. 2a-2d were tested with the experimental data by using the nonlinear regression analysis with Polymath 6.10 software. The aim of the data fitting procedure is to minimize the mean square differences between the calculated values of the reaction rate (r_{calc}) with values obtained from the experimental data (r_{exp}) as shown below:

$$\min \phi = \sum_{alldatasamples} (r_{calc} - r_{exp})^2 \quad (3)$$

Using the experimental data for each temperature, reaction rate constants were calculated.

Uncatalyzed reaction

The uncatalyzed reactions were carried out at 358, 373, and 388 K with W/PO molar ratio of 7.5/1. The calculated values of k_1 , k_2 , and k_3 with 95 % confidential interval are shown in Table 2.

Insert Table 2.

Applying the Arrhenius equation using the values given in Table 2, the reaction rate constants as a function of temperature were determined as follows:

$$k_1 = \exp(11.52 - 7713 / T) \text{ L/mol}\cdot\text{min} \quad (4)$$

$$k_2 = \exp(16.87 - 9421/T) \text{ L/mol}\cdot\text{min} \quad (5)$$

$$k_3 = \exp(43.45 - 19086/T) \text{ L/mol}\cdot\text{min} \quad (6)$$

Catalyzed reaction

The effects of the parameters, namely catalyst type, external and internal diffusion resistances, temperature, catalyst loading, and molar ratio of reactants on the reaction rate were observed for catalyzed hydration reaction.

Effect of catalyst type

The reaction was conducted at 358 K with W/PO molar ratio of 7.5/1 in the presence of two types of catalyst, namely Lewatit MonoPlus M500/HCO₃⁻ and Dowex Marathon A/HCO₃⁻. Each catalyst containing the same amount of HCO₃⁻, which are corresponding to 0.15 mol HCO₃⁻/L in equivalent, was used in the experiment. For the prescribed conditions, the average reaction rates can be calculated using Eq. 7:

$$-r_{A,ave} = \frac{\int_{C_0}^C -r_A dC}{C - C_0} \quad (7)$$

where $-r_A = -\frac{dC_A}{dt}$ was obtained from the slope of concentration-time curve [18]. The average reaction rate calculated using the conversion range from 0% to 90% and PG selectivity based on the percentage of PO converted into PG for the conversion of 90 % are given in Table 3.

Insert Table 3.

Table 3 shows that, as expected, the average reaction rate and PG selectivity for the reactions with the catalyst are much higher than those of the reactions without catalyst. Additionally, Lewatit MonoPlus M500/HCO₃⁻ showed better performance than Dowex Marathon A/HCO₃⁻. Therefore, Lewatit MonoPlus M500/HCO₃⁻ was used as a catalyst for the hydration of PO and the kinetic model was developed in the presence of this catalyst. •

External and internal diffusion significance

Prior to the kinetic study, it is important to study the influence of external and internal mass transfer resistances. The effect of the external mass transfer resistance on the reaction rate is directly

related to the stirring speed [19]. To observe the effect of external diffusion on the reaction rate, the experiments were performed at 358 K, with the catalyst loading of 0.15 mol HCO₃⁻/L in equivalent (Lewatit MonoPlus M500/ HCO₃⁻) and the W/PO molar ratio of 7.5/1, under 350 rpm and 600 rpm. The results are shown in Figure 1.

Insert Figure 1.

Figure 1 shows that the reaction rate does not change with the stirring speed, which indicates that the external diffusion is not the rate-controlling step. Therefore, all experiments were carried out at constant stirring speed of 350 rpm.

To observe the effect of internal diffusion on the reaction rate, the reaction can be performed in the presence of different particle sizes of the catalyst. However, Lewatit MonoPlus M500 has uniform size (monodisperse) of 0.62 mm. Therefore, the temperature criteria applied to investigate the effect of the internal diffusion. Since internal diffusion step is less temperature dependency than reaction step [20, 21]. In this respect, Figure 2 shows that the average reaction rate calculated using the conversion range from 0% to 90% doubles for every 10 K increase in temperature. Thus, it is reasonable to neglect the effect of internal pore diffusion, considered as a physical step.

Insert Figure 2.

These results confirm the literature findings claiming that the influence of external and internal diffusion can be neglected for most of the hydration reactions catalyzed by ion exchange resins [18, 22, 23].

Effect of catalyst loading

The experiments were performed at different Lewatit MonoPlus M 500/HCO₃⁻ loadings of 0-0.15 mol HCO₃⁻/L in equivalent in the mixture with W/PO molar ratio 7.5/1 at 358 K. The effect of catalyst loading on the conversion of PO is given in Figure 3a. The average reaction rates can be calculated from the experimental data given in Figure 3a by using Eq. 7. A plot of the average reaction rate versus catalyst loading is given in Figure 3b.

Insert Figures 3a and 3b.

As seen from Figure 3b, the average reaction rates, $(-r_{PO})_{ave}$, is increasing linearly with the catalyst loading under expressed conditions. This is the expected result, since the active surface area is proportional to the amount of catalyst. It also confirms that the effects of the internal and external diffusions are negligible [24]. From Figure 3b, the mathematical expression between the average reaction rate and the catalyst loading can be given by

$$(-r_{PO})_{ave} = 0.0907 * C_{cat} \left(\frac{molHCO_3^-}{L} \right) + 0.0043 \quad (8)$$

where 0.0043 corresponds to the average uncatalyzed reaction rate. This result clearly confirmed the experimental result given in Table 3.

Effect of reactants mole ratio

Hydration reactions were realized at W/PO molar ratios of 1.9/1, 4.7/1, 7.5/1, 11.8/1, while maintaining a catalyst loading of 0.13 mol of HCO_3^-/L in equivalent and a temperature of 358 K. The results are shown in Figure 4.

Insert Figure 4.

As seen from Figure 4, the conversion of PO increases with an increase in the molar ratio of W/PO. The PG selectivity at 90 % conversion and the values of average reaction rates calculated using the conversion range from 0 % to 90% for the prescribed conditions are given in Figure 5.

Insert Figure 5.

Figure 5 shows that PG selectivity increases by increasing W/PO molar ratio. This is an expected result, since the reaction given in Eq. 1b will be suppressed due to the low concentration of PO, and PG in dilute solution. Similarly, the average reaction rate of PO will not increase with high W/PO molar ratio since the concentration of PO decreases as the reaction proceeds. As an intercept of the two curves given in Figure 5 will give the optimum W/PO molar ratio of 6/1.

Effect of temperature

The experiments were realized at different temperatures of 338, 348, 358 and 368 K under the constant reaction conditions, with W/PO molar ratio of 7.5/1 and catalyst loading of 0.15 mol HCO_3^-/L in equivalent. The calculated reaction rate constants with the confidence limits for each temperature are given in Table 4. In the prescribed conditions, the formation of tripropylene glycol is negligible.

Insert Table 4.

Applying the Arrhenius equation using the values given in Table 4, the reaction rate constants as a function of temperature were determined to be:

$$k_1 = \exp(15.72 - 8705/T) \text{ L/mol}\cdot\text{min} \quad (9)$$

$$k_2 = \exp(20.53 - 10777/T) \text{ L/mol}\cdot\text{min} \quad (10)$$

To compare the activation energies for uncatalyzed and catalyzed reactions, uncatalyzed reaction rate constants given in Eqs. 4 and 5 were rearranged by equalizing the corresponding frequency factors given in Eqs. 9 and 10.

$$k_1 = \exp(15.72 - 9277/T) \text{ L/mol}\cdot\text{min} \quad (11)$$

$$k_2 = \exp(20.53 - 10782/T) \text{ L/mol}\cdot\text{min} \quad (12)$$

When Eqs. 9 and 10 were compared with Eqs. 11 and 12, the activation energies for k_1 and k_2 decrease by 4.76 and 0.04 kJ/mol, respectively with a catalyst loading of 0.15 mol HCO_3^- /L in equivalent. Consequently, the reaction rate and PG selectivity increase in the presence of Lewatit MonoPlus M500/ HCO_3^- . It also indicates that PG selectivity decreases with temperature in the presence of the same amount of catalyst.

Comparison of experimental data with model results

When the reaction rate expression given in Eq. 2a is rewritten in terms of PO conversion, the following equation can be obtained:

$$-r_{PO} = C_{PO_0} \frac{dx_{PO}}{dt} = C_{PO_0}^2 (1 - x_{PO}) [k_1(S - x_{PO}) + k_2(P + x_{PO}) + k_3(D + x_{PO})] \quad (13)$$

The predicted PO conversion based on the model was calculated by numerical integration of Eq. 13.

The results obtained at temperatures of 338-368 K under the condition of $S = \frac{C_{W_0}}{C_{PO_0}} = 7.5$,

$P = \frac{C_{PG_0}}{C_{PO_0}} = 0$, $D = \frac{C_{DPG_0}}{C_{PO_0}} = 0$, $C_{PO_0} = 4.89$ mol/L, in the presence of 0.15 mol HCO_3^- /L in equivalent

are given in Figure 6. As seen in Figure 6, there is a good agreement between the calculated curves and the experimental points.

Insert Figure 6.

Conclusion

Two types of catalysts, Dowex Marathon A/ HCO_3^- and Lewatit MonoPlus M500/ HCO_3^- , have been tested in the hydration of propylene oxide. Preliminary investigation showed that Lewatit MonoPlus M500/ HCO_3^- has better performance than the other. Consequently, the kinetic model was developed in the presence of Lewatit MonoPlus M500/ HCO_3^- . The hydration of propylene oxide was found to follow the series-parallel irreversible reaction mechanism in which the reaction rate expression, based on the consumption of propylene oxide, can be given by Eq. 2a. The conversion of propylene oxide increases with the increase of temperature and catalyst loading. It is also observed that the average reaction rate increases linearly with catalyst loading in accordance with Eq. 8. Lewatit MonoPlus M500/ HCO_3^- reduces the activation energy of PG production by 4.76 kJ/mol with catalyst loading of 0.15 mol HCO_3^- /L in equivalent. The selectivity of PG obtained at W/PO molar ratios of 1.9/1 and 11.8/1 is about 78 % and 96%, respectively while keeping the catalyst loading of 0.13 mol of HCO_3^- /L in equivalent at temperature of 358 K. The kinetics of hydration of propylene oxide was also studied in the literature in the presence of bis(ethane-1,2-diol) molybdate. It is reported that the selectivity of PG in the presence of molybdenum glycolates is about 97-99 % at W/PO molar ratio of 34/1 and 128/1 [13]. Although this result seems to be better than that of present study, that is an expected result since the PG selectivity increases by increasing W/PO molar ratio. Therefore, Lewatit MonoPlus M500/ HCO_3^- can be recommended for the hydration of propylene oxide.

Acknowledgements

This work is supported by Scientific Research Project Commission of Anadolu University (Project No: 1605F453).

Nomenclature

$$D = C_{DPG_0} / C_{PO_0}$$

DPG=dipropylene glycol

k = rate constant

$$P = C_{PG_0} / C_{PO_0}$$

PG=propylene glycol

PO=propylene oxide

$$S = C_{W_0} / C_{PO_0}$$

T = temperature (K)

TPG=tripropylene glycol

x_i = mole fraction of component i

Subscripts

ave=average

0 = at initial condition

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Figure captions

Figure 1. Effect of stirring speed on the conversion of PO at 358 K, W/PO=7.5/1 and catalyst loading of 0.15 mol HCO_3^-/L in equivalent

Figure 2. Effect of temperature on the average reaction rate at 358 K with W/PO molar ratio of 7.5/1 and a catalyst loading of 0.15 mol of HCO_3^-/L in equivalent.

Figure 3. a) Effect of the catalyst loading on conversion of PO **b)** Effect of the catalyst loading on the average reaction rate (358 K with W/PO molar ratio of 7.5/1).

Figure 4. Effect of W/PO molar ratio on conversion of PO at 358 K and a catalyst loading of 0.13 mol of HCO_3^-/L in equivalent

Figure 5. Effect of the W/PO molar ratio on the average reaction rate and PG selectivity at 358 K and a catalyst loading of 0.13 mol of HCO_3^-/L in equivalent

Figure 6. Experimental points and calculated curves from kinetic model at different temperatures

Table 1. Properties of Ion-Exchange Resins

Resin	Lewatit MonoPlus M500	Dowex Marathon A
Manufacturer	LANXESS Deutschland GmbH.	Dow Chemical Co.
Functional group	$-\text{[Ph-CH}_2\text{-N(CH}_3\text{)}_3\text{]}^+$	$-\text{[Ph-CH}_2\text{-N(CH}_3\text{)}_3\text{]}^+$
% Moisture	48-55	50-60
Total exchange capacity(equiv./l)	>1.3	1.2
Particle size(mm)	0.62	0.525-0.625
Polymer type	Gelular	Gelular

Table 2. Calculated values of k_1 , k_2 and k_3 for the uncatalyzed reaction with 95 % confidential interval

Temperature (K)	$k_1 \times 10^4$ (L/(mol·min))	$k_2 \times 10^4$ (L/(mol·min))	$k_3 \times 10^4$ (L/(mol·min))
358	0.439±0.051	0.768±0.075	0.356±0.048
373	1.08±0.11	2.411±0.172	9.855±1.891
388	2.319±0.066	5.865±0.738	21.265±2.32

Table 3. Average reaction rate and PG selectivity at 358 K with W/PO mol ratio of 7.5/1

Catalyst type	Conversion range	$-r_{PO,ave}$, (mol/(L·min))	PG Selectivity (%)
Uncatalyzed	0-0.90	0.00443	82.1
Dowex Marathon A/ HCO_3^-	0-0.90	0.0157	92.7
Lewatit MonoPlus M500/ HCO_3^-	0-0.90	0.0182	95.0

Table 4. Calculated reaction rate constants with 95 % confidence interval

Temperature (K)	$k_1 \times 10^4$ (L/(mol·min))	$k_2 \times 10^4$ (L/(mol·min))
338	0.449±0.096	0.109±0.037
348	0.886±0.200	0.303±0.195
358	1.905±0.312	0.786±0.347
368	3.584±0.249	1.655±0.581

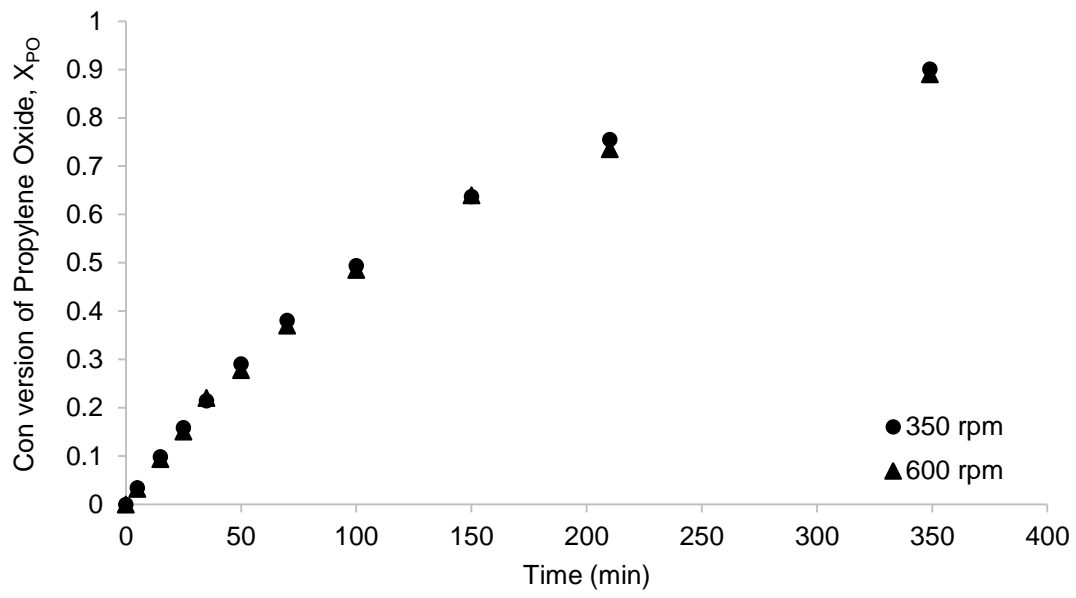


Figure 1.

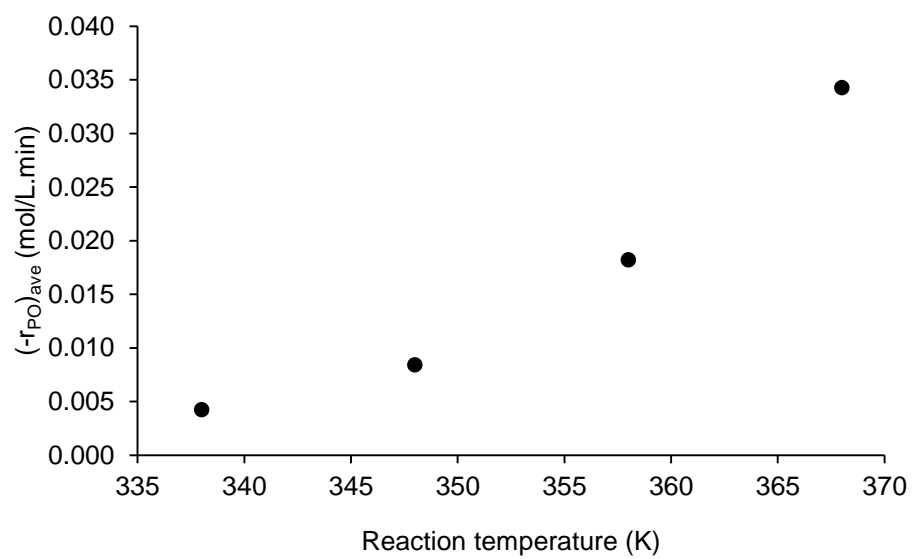
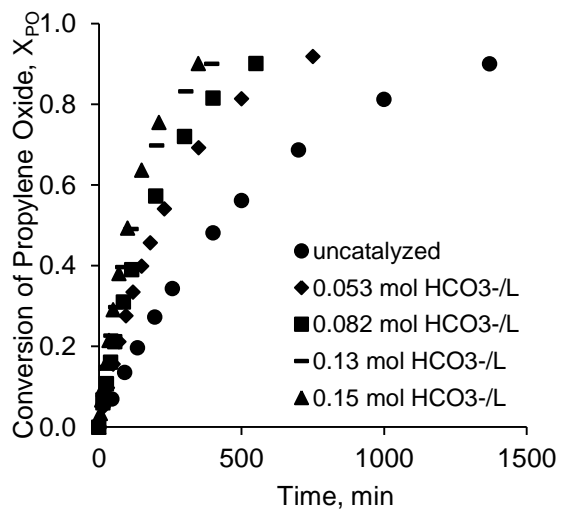
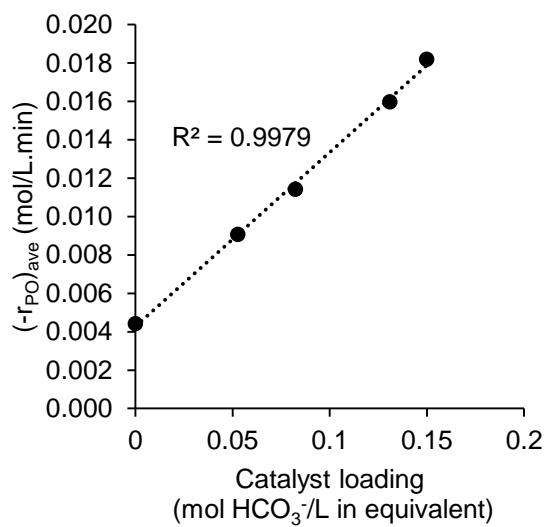


Figure 2.



(a)



(b)

Figure 3.

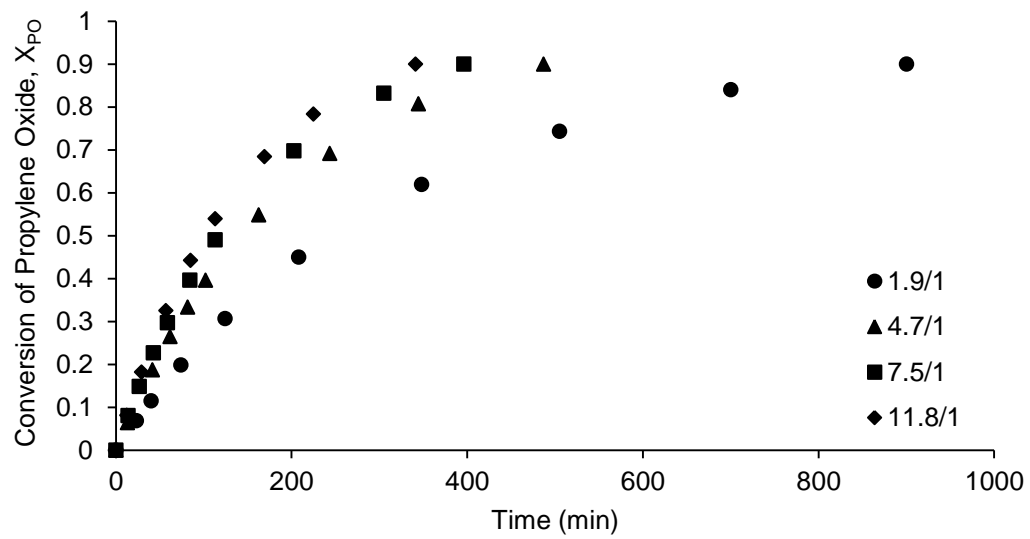


Figure 4.

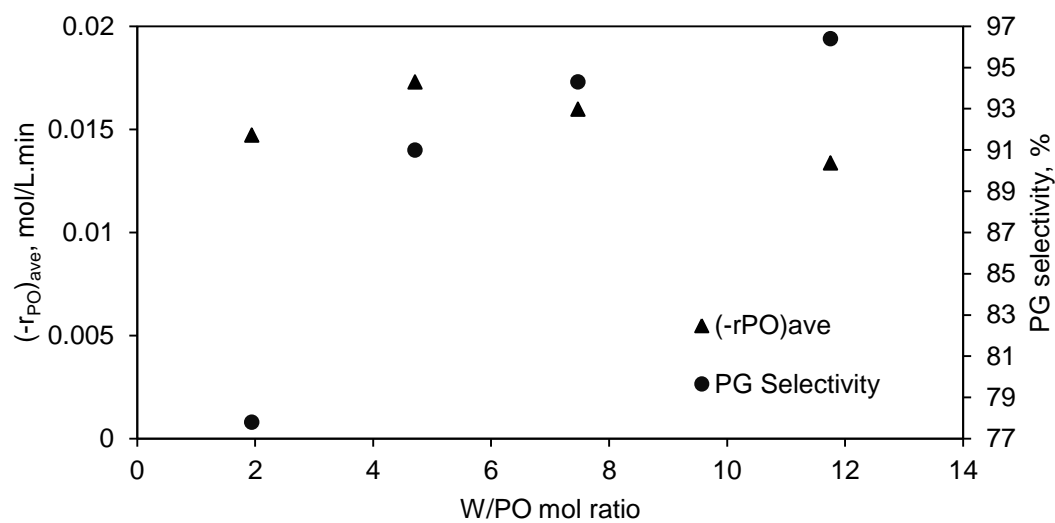


Figure 5.

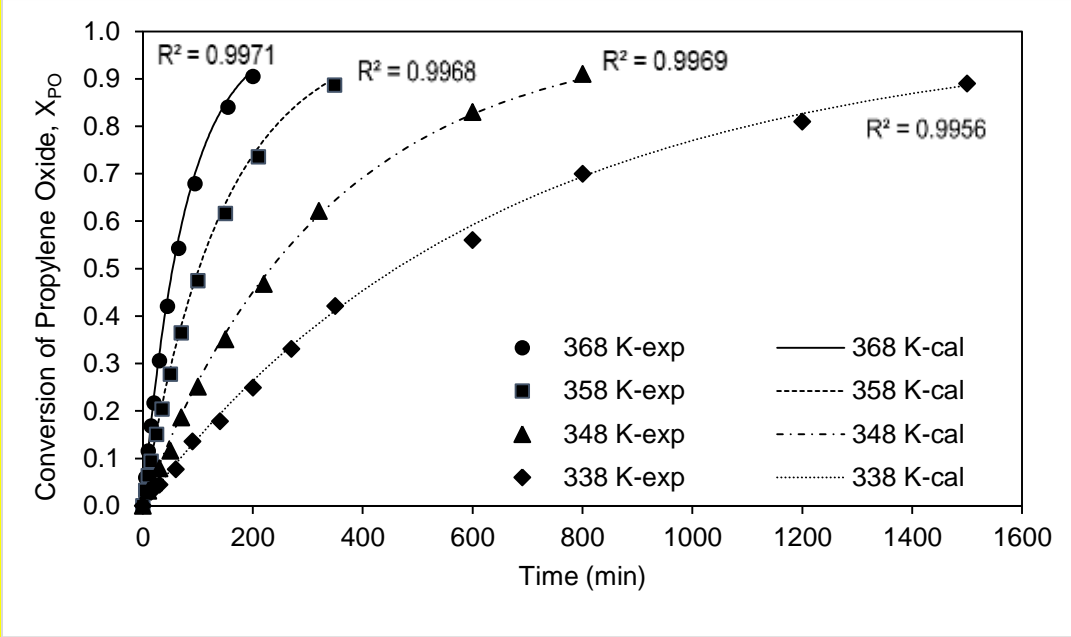


Figure 6.