

PRODUCTION OF PROPYLENE OXIDE FROM PROPYLENE GLYCOL

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ABSTRACT

The primary goal of this research was to find a renewable synthesis method for the production of propylene oxide. Significant quantities of glycerin are formed as a co-product when soybean oil is used to produce biodiesel. This glycerin can be used to produce propylene glycol, which can undergo dehydration over basic catalysts to produce propylene oxide (PO), along with eight other products: acetaldehyde, propionaldehyde, acetone, 2-propanol, 1-propanol, allyl alcohol, acetol, and dipropylene glycol. A variety of catalysts were prepared for each set of reactions, and dehydration was carried out in a plug flow reactor. For this thesis, only three main catalysts are presented, such as Na/Al₂O₃ (sodium acetate on alumina), Cs-ETS-10, and Na acac/MgO (sodium acetyl acetonate on nanocrystalline MgO). Dehydration reactions were performed with different masses of catalyst, reactor temperatures, and residence times to optimize the selectivity to PO. The highest selectivity to PO was obtained as 12.33% for Na acac/MgO catalyst at 400° C, 0.1g, and a N₂ flow rate of 20SCCM. Even though Cs-ETS-10 catalyst was active for PO production, it also produced higher amounts of dipropylene glycol (80%). Dipropylene glycol appears to act as an active intermediate in the dehydration of propylene glycol to propylene oxide over Cs-ETS-10 catalyst, which would limit PO selectivity to 50%. The Na/Al₂O₃ resulted in low selectivity of 2% to PO, although it gave an appreciable selectivity of 60% to propionaldehyde. The reaction pathway to PO over these catalysts was also studied. Dehydration of propylene glycol to propylene oxide over Na/Al₂O₃, and Na acac/MgO catalysts appears to be a direct dehydration, rather than the involvement of a dipropylene glycol active intermediate.

CHAPTER 1

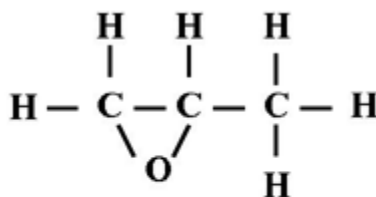
INTRODUCTION TO MANUFACTURE OF PROPYLENE OXIDE

1.1. Introduction

Propylene oxide (epoxy propane) is a significant organic chemical product used primarily as a reaction intermediate for the production of a wide range of industrial and commercial products, with a current global demand of approximately 14 billion pounds per year. It is among the top 50 chemicals produced in the world, and is classified as a high production volume (HPV) chemical. Propylene oxide (PO) is mainly used in the production of polyether polyols (poly-alcohols) for use in urethane applications such as rigid foam, flexible foam, and Coatings, Adhesives, Sealants and Elastomer (CASE) systems, and is also used in non-urethane applications such as surfactants and oil demulsifiers. The consumption in this sector accounts for over 60% of the total international output. The second major sector is the production of propylene glycol for aeroplane de-icers, fiberglass-reinforced unsaturated polyester resins, and hydraulic fluids; and the consumption in this sector accounts for 20%. Other sectors include polyglycols (6%), glycol ethers (5%) and miscellaneous applications like flame-retarding agents, synthetic lubricating agents, oil field drilling chemicals, butylene glycol, propylene carbonate, allyl alcohol, isopropanol amines, modified carbohydrates (starches), and textile surfactants which accounts for the remaining 8% [Dow Chemical Company Report,2005].

1.2. Properties of propylene oxide

Propylene oxide is a colorless, low-boiling (34.2 °C) liquid with a molecular weight of 58.08. It is also reactive and highly flammable with a wide explosive range. A propylene oxide molecule contains an asymmetrical carbon atom, so it is a chiral compound which can exist in two enantiomer forms. Industrial propylene oxide is a racemic mixture of these isomers. It is highly reactive owing to the strained three-membered oxirane ring (shown below). Oxirane structure provides easiness to addition reactions



Propylene oxide
 $\text{CH}_2\text{OCHCH}_3$

The ring C–C and C–O bond lengths have been reported as 147 and 144 pm, respectively, whereas the C–C bond for the substituted methyl group is 152 pm. Although some reactions (those with hydrogen halides or ammonia) proceed at adequate rates without a catalyst, most reactions of industrial importance utilize the use of either acidic or basic catalysts. The epoxide ring of propylene oxide may open at either of the C–O bonds depending upon the properties of catalysts used. In anionic catalysis, the bond preferentially opens at the least sterically hindered position, resulting in mostly 95% secondary alcohol products. Cationic catalysts provide a mixture of secondary and primary alcohol products [Kirk-Othmer, 4th edition]. Weak cationic catalysts, such as

zeolites, give up to 30% primary alcohol product when reacting with alcohols, while stronger cationic catalysts, such as H_2SO_4 , give up to 55% primary alcohol product. The mechanism of ring-opening reactions of epoxides takes place by nucleophilic substitution, i.e., a $\text{S}_{\text{N}}2$ mechanism, on one of the epoxide carbon atoms with displacement of the epoxide oxygen atom [March, 5th edition]. The most important reaction of propylene oxide from a commercial perspective is its violent polymerization to form poly ether polyols. PO reacts with initiators (compounds containing active hydrogen e.g. alcohols or amines) to form polyols in the presence of acidic or basic catalysts.

1.3. Reactions of propylene oxide

1.3.1. Reaction with water

Propylene oxide reacts with water to produce propylene glycol, dipropylene glycol, tripropylene glycol, and higher-molecular-weight polyglycols. This commercial process is typically run using an excess of water to maximize the production of the monopropylene glycol. Acid or base catalysts can be used to enhance reaction rates or product selectivity; however the commercial process normally uses heat and pressure without a catalyst.

1.3.2. Isomerization and Hydrogenolysis

Isomerization of propylene oxide to propionaldehyde and acetone occurs over a variety of catalysts, e.g., sodium or potassium alum, and zeolites. Stronger acid catalysts favor

acetone over propionaldehyde. Allyl alcohol yields of 90% are obtained from use of a supported lithium phosphate catalyst. Hydrogenolysis of propylene oxide yields primary and secondary alcohols as well as the isomerization products of acetone and propionaldehyde [Ullmann's, Vol A22].

1.3.3. Carbonyl Compounds

Cyclic ketals and acetals (dioxolanes) are produced from the reaction of propylene oxide with ketones and aldehydes, respectively. Suitable catalysts include stannic chloride, quaternary ammonium salts and molybdenum acetyl acetonate.

1.4. Commercial production of propylene oxide

The PO markets are expected to grow at 4% per year, in accordance with world GDP. Propylene oxide is currently produced commercially from propylene, isolated as a co-product of petroleum processing during the production of gasoline. PO is manufactured mainly by two basic processes: the traditional chlorohydrin process, and the hydroperoxide process with either tert-butanol or styrene as a co-product [Kirk-Othmer, 4th edition].

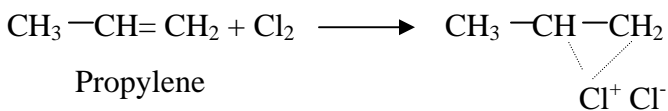
The chlorohydrin process involves reaction of propylene and chlorine in the presence of water to produce two isomers of propylene chlorohydrin, followed by dehydrochlorination with caustic or lime to propylene oxide and salt. The hydroperoxide process involves oxidation of propylene to propylene oxide by an organic hydroperoxide,

which results in alcohol as a coproduct. Two different hydroperoxides are used commercially that result in *tert*-butanol or 1-phenyl ethanol as the coproduct. The *tert*-butanol (TBA) has been used as a gasoline additive, dehydrated to isobutylene, and used as feedstock to produce methyl *tert*-butyl ether (MTBE), a gasoline additive. The 1-phenyl ethanol is dehydrated to styrene

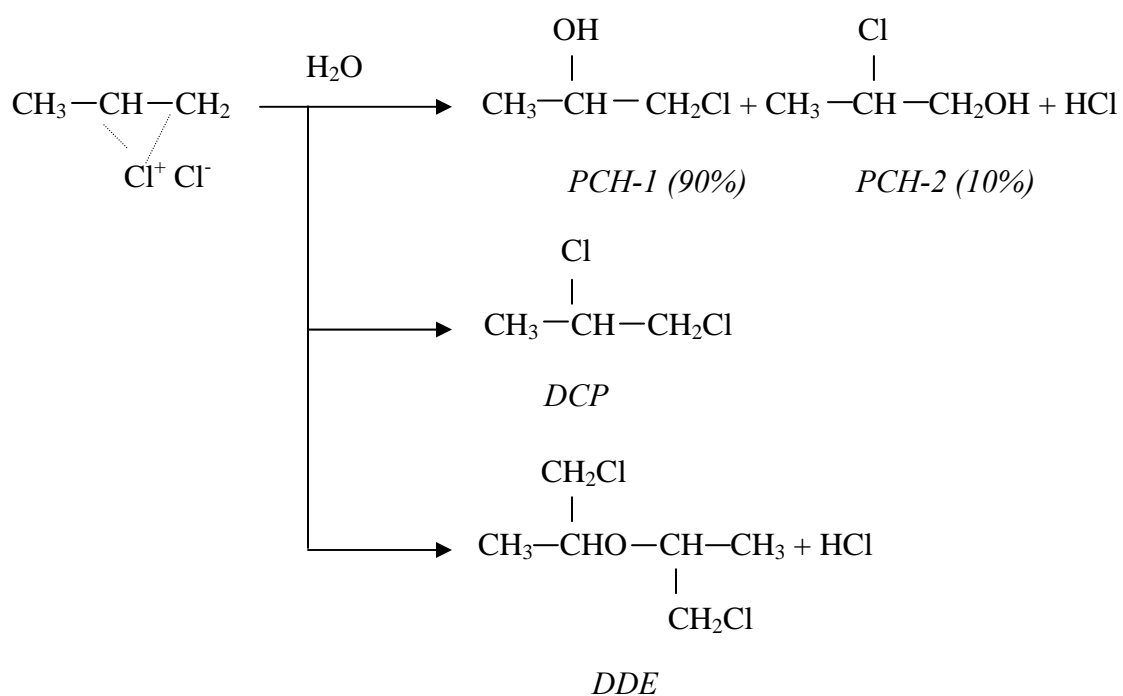
1.4.1. Chlorohydrin Process

The chlorohydrin process requires two reaction steps, chlorohydrination and epoxidation, followed by product purification. Equimolar amounts of propylene gas and chlorine are mixed with an excess of water to generate propylene chlorohydrin, and a small amount of chlorinated organic coproducts, primarily 1,2-dichloropropane. Epoxidation is accomplished by treatment of the chlorohydrin solution with caustic soda (aqueous calcium hydroxide). Propylene oxide and other organics are steam-stripped from the resulting sodium chloride or calcium chloride brine. The brine is treated, usually by biological oxidation, to reduce organic content prior to discharge. The propylene oxide is further purified to remove lights and heavies via distillation. The chemical reactions during chlorohydrin process are given below:

Chlorohydrination

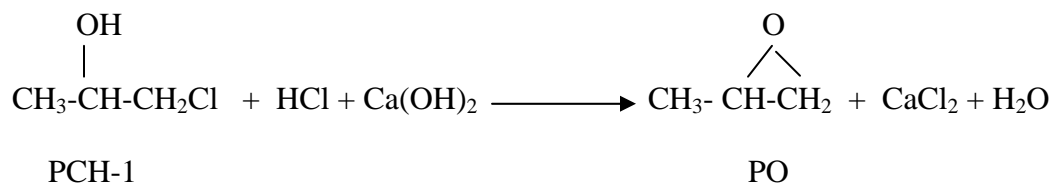


The chloronium ion intermediate can react with water to produce the desired propylene chlorohydrin (PCH), with chloride ion to produce 1,2- dichloropropane (DCP), or with propylene chlorohydrin to produce isomers of dichloro-dipropyl ether (DDE). Reactions are given below:



There are two proposed alternative processes where the chlorine is replaced in the chlorohydrin reaction by hypochlorous acid or tert-butly hypochlorite

Epoxidation



Epoxidation of propylene chlorohydrin (both isomers) to propylene oxide is accomplished using a base, usually aqueous sodium hydroxide or calcium hydroxide.

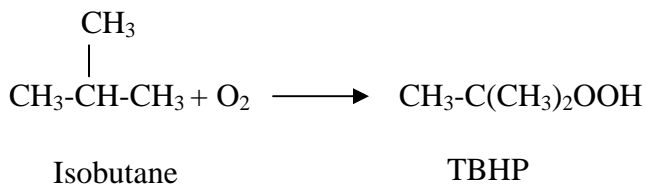
1.4.2. Hydroperoxide Process

The hydroperoxide process to produce propylene oxide involves the basic steps of oxidation of an organic to its hydroperoxide, epoxidation of propylene with the hydroperoxide, purification of the propylene oxide, and conversion of the coproduct alcohol to a useful product for sale. The coproducts are *tert*-butanol, which is converted to methyl *tert*-butyl ether and 1-phenyl ethanol, converted to styrene.

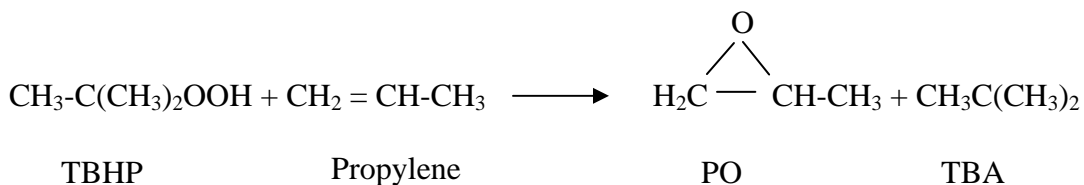
tert-Butyl Hydroperoxide Process

The first step of this process involves the liquid-phase air oxidation of isobutane to *tert*-butyl hydroperoxide (TBHP) in the presence of 10–30 wt % *tert*-butyl alcohol (TBA). This reaction occurs at a temperature of 95–150 °C and a pressure of 2075–5535 kPa (300–800 psi), resulting in a conversion of 20–30% of the isobutene, and a selectivity to TBHP of 60–80%, and to TBA of 20–40%. Unreacted isobutane, and a portion of the

TBA are separated from the product and recycled back to the hydroperoxide-forming reactor. The reaction involving isobutane and oxygen is shown below:



The *tert*-butyl hydroperoxide is then mixed with a catalyst solution to react with propylene. The catalyst is typically an organometallic that is soluble in the reaction mixture. The reaction is illustrated as:

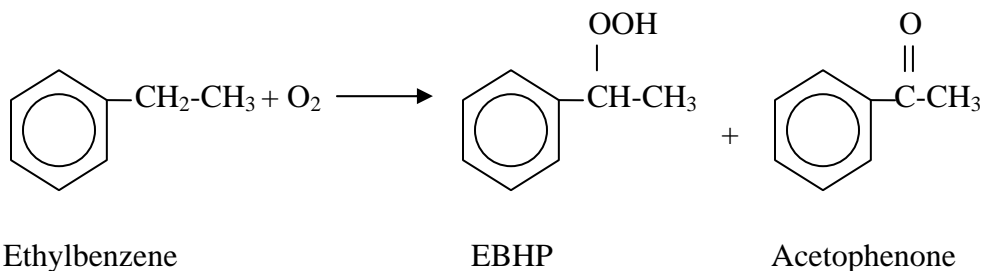


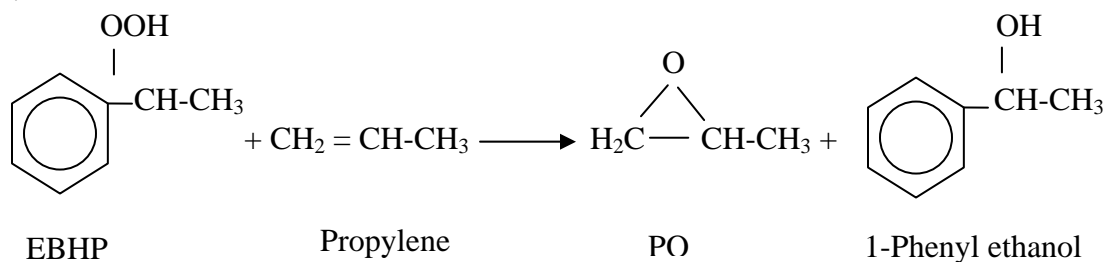
An excess of propylene is used to maximize conversion of hydroperoxide and selectivity to propylene oxide. This occurs at a temperature of 100–130 °C, the pressure is 1480–3550 kPa (215–515 psi), and the residence time is sufficient (about 2 h) for >95% conversion of the hydroperoxide. Selectivity to propylene oxide is 95–98% based on TBHP and 97–98% based on propylene. The major by-products are propylene glycol, methyl formate, and a propylene dimer. Separation of these by-products from the product propylene is difficult. Also, the presence of acids, such as carboxylic acids, results in lower product selectivity. After epoxidation, a distillation is performed to remove propylene, propylene oxide, and a portion of the TBHP and TBA overhead. TBA then

reacts with methanol to form methyl tert butyl ether (MTBE). The recovered catalyst can be treated for recycle to the epoxidation reaction. Methyl formate and propylene oxide have close boiling points, making separation by distillation difficult. Final purification of propylene oxide is accomplished by a series of conventional and extractive distillations.

Ethylbenzene Hydroperoxide Process (EBHP)

Liquid-phase oxidation of ethylbenzene with air or oxygen occurs at 206–275 kPa (30–40 psia) at 140–150 °C, and 2–2.5 hours are required for a 10–15% conversion to hydroperoxide. EBHP is concentrated to 30–35% by distillation and it is mixed with a catalyst solution and fed to a horizontally compartmentalized reactor where propylene is introduced into each compartment. The reactor operates at 95–130 °C, and 2500–4000 kPa (360–580 psi) for 1–2 hours for 92–96% selectivity to propylene oxide. The homogeneous catalyst can be molybdenum, tungsten, or titanium, and an organic acid, such as acetate, naphthenate, stearate, or heterogeneous catalysts which consist of titanium oxides on a silica support. After epoxidation, propylene oxide, excess propylene, and propane are distilled overhead. The byproducts acetophenone and 1-phenyl ethanol undergoes dehydration to form styrene. The following reactions show the formation of EBHP, and the reaction of EBHP with propylene to form PO.





1.5. Other Processes

Many other processes are in their developmental stages. Among these are the hydrogen peroxide processes, where titanium silicalite (TS-1, a porous crystalline synthetic catalyst having an average pore diameter of 0.55 nm) is used to produce PO from propylene and hydrogen peroxide [Taramasso, 1983]. Alcohol (methanol) or alcohol–water mixtures are used as solvent and carried out at a temperature of 40-60 °C in liquid phase. Yields on peroxide are quantitative, and propylene selectivity is high (95%). Propylene oxide selectivity is improved by treating the catalyst with neutral or basic salts, tin or metal cations at the expense of catalyst activity. However, the high cost of hydrogen peroxide has resulted in the non-commercialization of hydrogen peroxide process to date on a large scale.

In order to overcome the economic barrier, another process, epoxidation with in-situ hydrogen peroxide has been developed. Two different methods were employed for the formation of in-situ hydrogen peroxide. One approach is by feeding propylene and

oxygen to the oxidation stage of anthrahydroquinone by making use of the homogenous anthraquinone process. Reacting anthrahydroquinone with oxygen leads to the formation of hydrogen peroxide, which is then consumed in the oxidation of propylene to PO. The second approach is based on the oxidation of propylene by a H_2-O_2 gas mixture over a precious metal (Pd, Pt) containing titanium silicalite [Meiers et al., 1998].

The epoxidation of propylene with a H_2-O_2 mixture were also performed with a palladium impregnated TS-1 catalyst suspended in solvents such as water or methanol [Sato et al., 1996 and Mueller et al., 1996]. Developments in this field led to the usage of a highly dispersed Au/TiO₂ catalyst in a gas phase reaction which gives a propylene oxide selectivity greater than 90% [Hayashi et al., 1998]. Such gas-phase processes consume hydrogen and oxygen, yielding water as the only coproduct. Propylene conversion is typically less than 2%. Use of Pd or Pt in place of gold results in higher propylene conversion, but lower selectivity [Meiers et al., 1998].

Gas-phase oxidation of propylene using oxygen in the presence of a molten nitrate salt such as sodium nitrate, potassium nitrate, or lithium nitrate and a co-catalyst such as sodium hydroxide results in propylene oxide selectivities greater than 50% [U.S. Pat. 4,883,889]. There is ongoing research on the production of PO by electrochemical process [Otsuka et al., 1995] and photochemical oxidation [Yoshida, 1996; U.S. Pat. 4,481,092]. Applying an electrical current to a brine solution containing propylene results in oxidation of propylene to propylene oxide. All reactions take place in one reactor. Most of the reported work uses sodium or potassium bromide as the electrolyte. Bromine, generated from bromide ions at the anode, reacts with propylene and water to form propylene bromohydrin and the hydroxide generated at the cathode then reacts with the

bromohydrin to yield propylene oxide. PO can be produced by the photochemical oxidation of propylene over SiO₂ based catalysts, and also by reacting with oxygen in the presence of α -diketone sensitizers and an aprotic solvent.

1.6. Motivation of this project

As discussed in the previous sections, the commercial production of PO by both the chlorohydrin, and hydroperoxide processes produce large amounts of by-products which needs to be further processed, either to meet the sale specifications or for the proper discharge to the environment. In addition to the construction and operation expenditure, the processing and disposal costs will only increase the manufacturing costs of the product. Moreover, these processes are energy intensive, involve multiple steps and have low selectivity. Due to the high pressure and large volume of recycle streams involved in the hydroperoxide processes, the capital required for these processes is considerably higher than for the chlorohydrin process. However, the raw material cost for chlorohydrin is higher than for the hydroperoxide routes. Also, many developing processes incorporate catalysts which contain precious metals like gold, palladium etc. In addition to these disadvantages, both commercial and developing processes utilize propylene as the feed stock. This indicates that both economic and environmental benefits for the production of propylene oxide could be achieved by finding an alternative production route than using propylene as the feedstock.

Significant quantities of glycerin were produced as a co-product when soybean oil was used to produce biodiesel. Dr. Suppes and his colleagues at the University of Missouri-

Columbia have shown that this glycerin can be used to produce propylene glycol with 100 % selectivity [Suppes et al., 2005]. The cost of propylene has increased per pound in comparison with the cost of propylene glycol and therefore, replacing the propylene with propylene glycol as feedstock will be an advantageous process. Higher oil prices also contribute to the attractiveness of this synthesis route since propylene is produced when oil is cracked to produce gasoline.

French patent [FR 2345440, 1976] reports that the dehydration of 1,2-diols like propane 1,2-diols, butane 1,2-diols leads to a preferential epoxy formation without the disadvantages of other commercial process like chlorohydrin process and hydrogen peroxide process. According to the patent, the dehydration of diols should take place either in liquid or vapor phase at a temperature range of 250-550 °C, and in contact with a catalyst of basic matter. The selectivity of propylene oxide was reported as 36%. The raw material used here is 1,2 propane diol (propylene glycol) to achieve our primary goal of investigating a renewable synthesis route for the production of propylene oxide from the coproduct of biodiesel. The substances in the basic matter settings consists of compounds such as the carboxylates, acetates, salts like borates, aluminates, silicates, or the hydroxides of metals of group I, II and III A of periodic classification, in particular, sodium, potassium, lithium, calcium and barium.

A variety of catalysts were investigated for this project, but only three main catalysts are described here: Na/Al₂O₃, Cs-ETS-10 and Na acac/MgO. The work in this thesis is organized in the following manner: Chapter 2 discusses the dehydration of PG over these catalysts for different mass of catalysts, reactor temperatures, and residence times to optimize the selectivity to PO formed. The reaction pathway of propylene glycol to

propylene oxide over these catalysts is discussed in chapter 3 and the final chapter summarizes the contributions from this research, and outlines the potential opportunities for future work.

CHAPTER 2

DEHYDRATION OF PROPYLENE GLYCOL

2.1 Introduction

Propylene oxide (PO) is currently produced commercially from propylene which is isolated as a co-product of refinery catalytic cracking process during the production of gasoline. PO is manufactured mainly by two basic processes: the traditional chlorohydrin process and the hydroperoxide process with either tert-butanol or styrene the co-product. These processes are energy intensive and involve multiple steps; low selectivity, accompanied by huge volumes of effluent waste water and by products. As mentioned in section 1.6, significant quantities of glycerin were formed as a co-product, when soybean oil was used to produce biodiesel. Dr. Suppes and his co-workers at the University of Missouri-Columbia have shown that glycerin could be used to produce propylene glycol (PG) with almost 100% selectivity [Suppes et al., 2005]. Hence, our research was focused on whether an alternate route for the production of PO could be obtained from the co-product, propylene glycol.

The French patent [FR 2345440, 1976] reports that the dehydration of propylene glycol leads to the formation of propylene oxide without the disadvantages of other commercial process like chlorohydrin and hydrogen peroxide process. The selectivity of propylene oxide was reported as 36% with the formation of eight other additional products like acetaldehyde, propionaldehyde, acetone, alcohols like 1-propanol, 2-propanol, allyl alcohol, acetol (intermediate product) and dipropylene glycol. The catalysts discussed in

the patent are mainly basic in nature and the catalyst used here is sodium acetate supported on different types of alumina.

This chapter has five major sections, Section 2.2 discusses primarily about the catalyst preparations of three main catalysts: sodium loaded on alkali modified alumina (Na/Al₂O₃), cesium chloride ETS-10 (Cs-ETS-10) and sodium acetyl acetonate supported on magnesium oxide (Na acac/MgO). Section 2.3 consists of the experimental set up of the reaction process and its calculations. Section 2.4 includes the results and discussion, followed by Section 2.5, reactive distillation and finally the concluding section.

2.2 Catalyst preparation

2.2.1. Preparation of Na/Al₂O₃ catalyst

The research was mainly focused on three different types of alumina: acidic, basic and adsorption alumina. The catalysts were prepared according to the procedure given in patent [FR 2345440, 1976]. A definite amount (corresponding to the wt %) of sodium acetate was dissolved in an appropriate quantity of distilled de-ionized water (sufficient to wet the surface of alumina) and heated to 60 °C on a hot plate. To this 15 g of alumina was added and heated for a few more minutes. The beaker was kept on a hot stirrer plate and the agitation was maintained until all the water was evaporated. Finally, the beaker with the catalyst contents were placed in an oven and dried in air overnight at 90 °C.

2.2.2. Preparation of Cs-ETS-10 catalyst

Cs-ETS-10 catalyst was prepared for an earlier study by the partial ion exchange of ETS-10 with cesium chloride solution [Dorskocil, 2004].

2.2.3. Preparation of Na acac/MgO catalyst

About 6 g of MgO was transferred to a 250 ml Erlenmeyer flask to which 300 ml of tetrahydrofuran (THF) was previously added. The flask was continuously purged with argon to remove moisture and other impurities. To this 8.4 g of sodium acetyl acetonate (Na acac) was added. An intimate mixture of acac and MgO was prepared by stirring them for almost 24 hours. The solution was then transferred to 15 ml centrifuge tubes, and the excess acac was removed by washing it with chloroform. After washing the mixture with chloroform, the catalyst was recovered by centrifugation. This process was continued until all the excess acac was removed. The catalyst was then placed in an oven and dried in air overnight, and heat treated under vacuum at 500 °C.

2.3. Experimental Section

2.3.1. Reactor set up

The dehydration reaction was conducted using a plug flow reactor system. The main components of the system include a plug flow reactor, a 4-port valve (Valco, Valve I), a gas chromatograph (Thermoquest Trace GC) and an air actuated 6-port GC gas sampling valve (Valco, UW-type- Valve II) which contains a 0.5 ml sample loop.

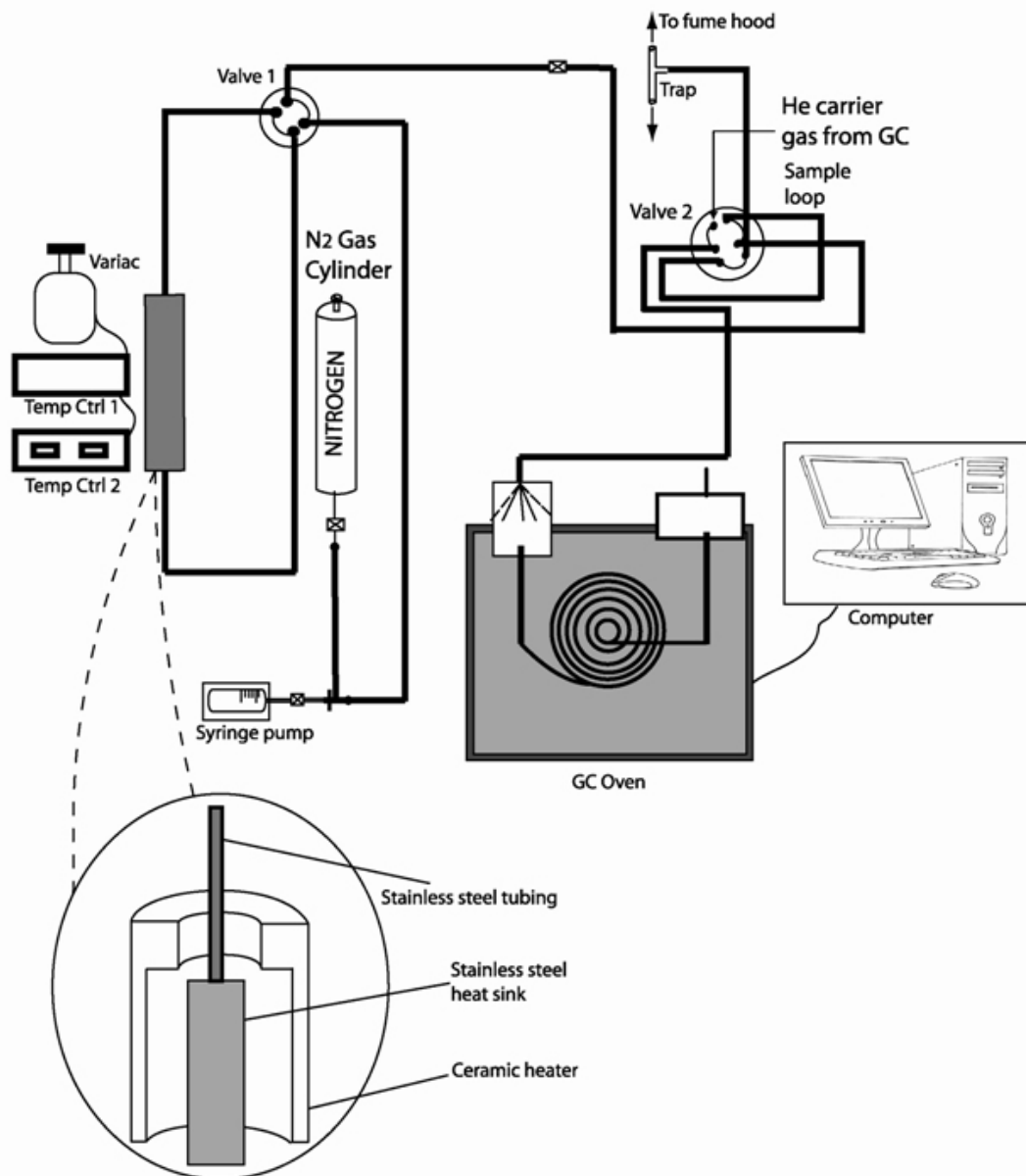


Figure 2.1: Experimental set up of a plug flow reactor

The plug flow reactor consists of a long piece of stainless steel tubing with an OD of 0.25 inches and a length of 19.5 inches. This stainless steel tubing was sheathed by a 0.7 inches OD and 12 inches long cylindrical brass rod, which acts as a heat sink and create more uniform temperatures throughout the length of the reactor. A type K thermocouple was inserted in the middle of the reactor to detect the temperature of the reactor during the entire process. (See Figure 2.1)

Some glass wool was placed inside the stainless steel reactor to support the catalyst bed in the middle of the reactor. The catalyst was pelletized to 30-40 mesh size and was loaded into the reactor carefully to obtain maximum uniformity of the catalyst bed. Once the catalyst was properly loaded, the reactor was placed inside an Omega ceramic cylindrical heater (870 W and 120 V) and connected to the temperature controller I (Cole-Parmer, Series 6890010).

The Valve I was used to control whether the reactants bypassed or passed through the reactor i.e. with or without reacting with the catalyst. Initially, the reactants: propylene glycol and nitrogen (carrier gas) were bypassed through the reactor until the flow of reactants became steady, which was determined by sampling the reactant stream to the GC to find the relative concentration of propylene glycol. This was done by analyzing the trace of propylene glycol in the GC. Once the concentration of propylene glycol remained stable, Valve I was turned clockwise to start the flow of reactants through the catalyst bed of the reactor. The reactants continuously flowed through the catalyst bed for 8-9 hours and sampling to the GC was performed simultaneously. Analysis of the GC trace from the product stream of the plug flow reactor provided the data for the formation of PO and

other products like acetaldehyde, propionaldehyde, acetone, 2-propanol, 1-propanol, allyl alcohol, acetol and dipropylene glycol.

2.3.2. Catalyst pre-treatment

The pelletized catalyst was loaded into the reactor and the treatment process involved ramping the catalyst from room temperature to 500 °C in 8 hours with a N₂ flow rate of 20 SCCM. Then, the catalyst was heated for a period of 4 hrs at 500 °C, after which it was cooled to the appropriate temperature at which the dehydration reaction was investigated.

2.3.3 Dehydration reaction

The dehydration reaction was conducted with a pre-treated catalyst at a specific reactor temperature. The feed, propylene glycol was loaded into a 10 ml gas tight syringe and was injected to the feed stream using a syringe pump (Cole-Parmer Instrument Company, 74900 series). Here, the flow rate of propylene glycol was 1 ml/hr. The flow rate of nitrogen (carrier gas) was maintained at 20 SCCM using a mass flow controller (Sierra Instruments, 110 VAC). The stainless steel tubing in the plug flow reactor system was heated using flexible electric heating tapes (Thermolyne), while the valves (Valve I and Valve II) were encased in heated enclosures and temperature of both heating tapes and the valve enclosures were controlled by temperature controller II (Love Controls Division, 16A series). The temperature of the heat traced tubing was kept constant at 220 °C and that of the heated valve enclosures was maintained at 225 °C. These temperatures ensured that the propylene glycol remained in the vapor phase (boiling point of propylene glycol

is 189 °C) throughout the entire process and to the point where it is injected to the GC. The bold lines in Figure 1 represent the heat traced tubing. When Valve I was in the bypass position, propylene glycol vapors were injected to the GC through a sample loop for the trace to be analyzed and when the sample was not injected to the GC, the effluents were collected in a trap and nitrogen was vented to a fume hood.

The gas chromatograph (GC) was operated with a capillary column and flame ionization (FID) detector to separate and analyze the components injected to the GC. For analyzing a sample inside the GC, a trace method was developed beforehand, because no two peaks could be seen overlapped in the GC trace i.e. all species entering the sample loop should have a different retention time. So, before the reaction, the standards of all the products: acetaldehyde, propylene oxide, propionaldehyde, acetone, 2-propanol, 1-propanol, allyl alcohol, acetol, dipropylene glycol and the reactant: propylene glycol was injected into the GC and the retention times were noted. The GC parameters chosen for the experiments were : oven temperature of 35 °C, right inlet temperature of 225 °C, split flow of 15 ml/min, split ratio of 30, carrier gas (He) flow rate of 0.5 ml/min, detector base temperature of 225 °C and the flow rates of air, H₂ and make up He were 350,35,50 ml/min respectively.

The sample was injected to the GC automatically using a 6-port valve (Valve II). This valve consisted of a 0.5 ml sample loop to ensure that the sample volume injected to the GC remained constant for every injection. Once the sample was introduced in to the heated injector, it was carried through the capillary column of the GC by helium and separated into its respective components. These components then came into contact with the FID, which registered a voltage signal corresponding to a relative concentration. The

voltage signals appear as peaks, and these data were recorded using the GC software and saved in the designated folder. A representation of a typical GC trace is shown in Figure 2.2

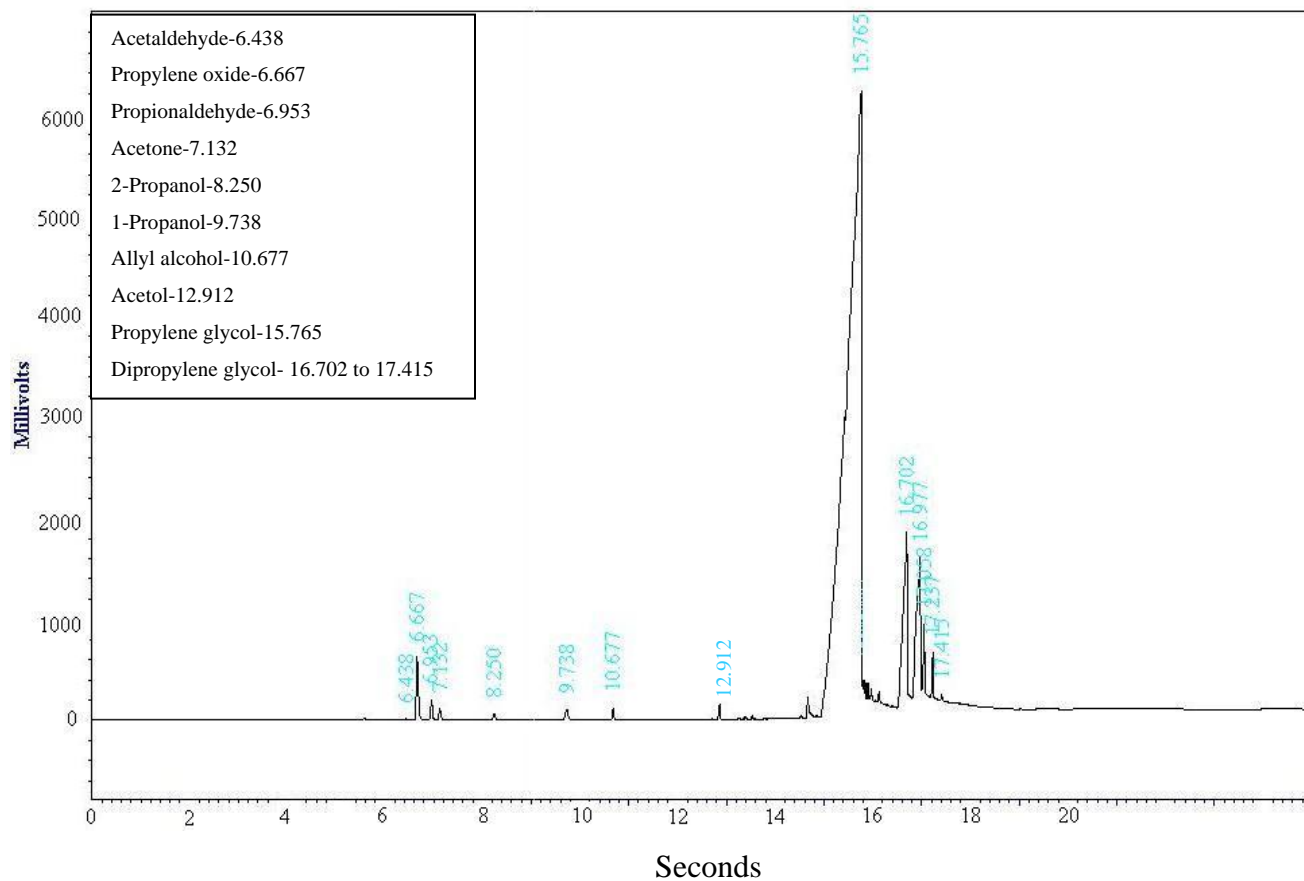


Figure 2.2: GC trace of a sample performing the dehydration of propylene glycol over Cs-ETS-10 catalyst

2.3.4. Analysis and calculation

After developing a method for a particular reaction, the response factors (RF) for each component were determined. For obtaining the response factors, decane (whose response factor was already known) was injected into the GC with all the other compounds whose RF needs to be determined. The response factors were calculated by analyzing the area under each peak which can be expressed as:

$$\frac{(\text{Area of Decane/ RF of Decane})}{(\text{Area of the compound/ RF of the compound})} = \frac{\text{Mass of Decane}}{\text{Mass of the compound}} \quad (1)$$

After obtaining the RF for all components, the mass of the compound were converted to moles to calculate the selectivity to a product.

$$\text{Selectivity} = \frac{\text{Number of moles of the product}}{\text{Total number of moles formed}} \quad (2)$$

2.4 Results and Discussions

2.4.1. Dehydration reaction with Na/Al₂O₃ as catalyst

The French patent [FR 2345440, 1976] reports that the dehydration of propylene glycol over sodium supported on alumina produces PO with 36% selectivity. So as a first step, our focus was to investigate on the importance of support alumina on the selectivity of

products. Three types of alumina such as adsorption, basic and acidic alumina were studied during the investigation (See Figure 3)

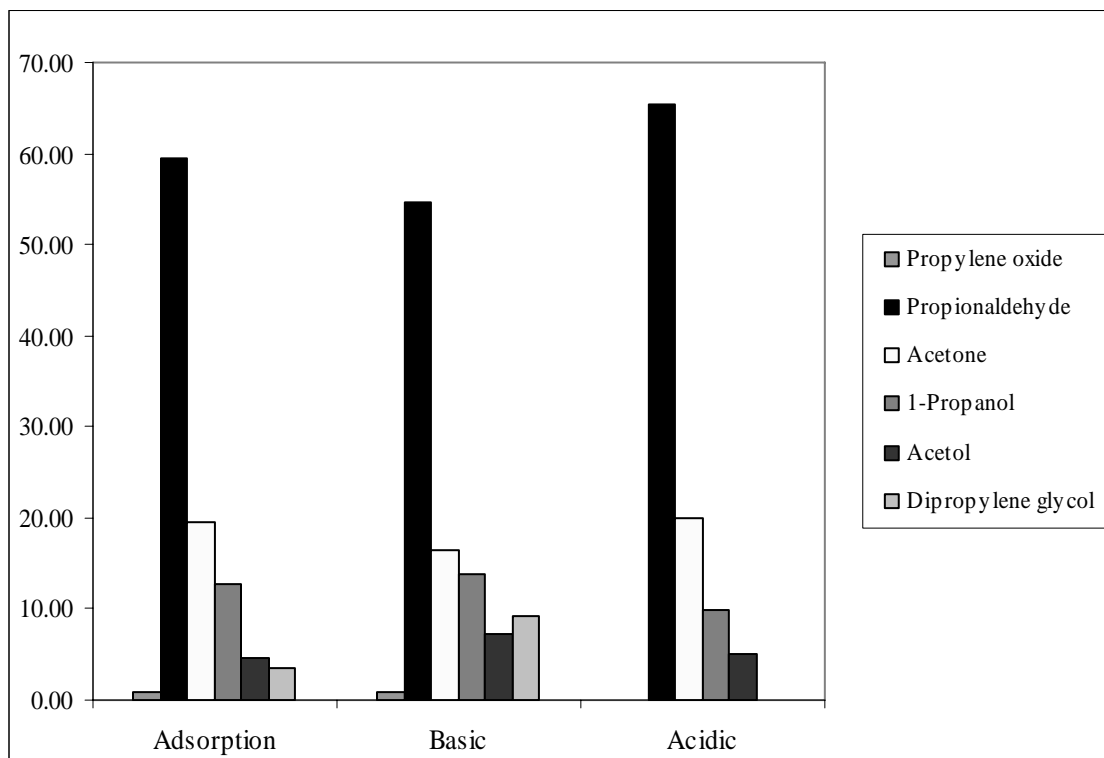
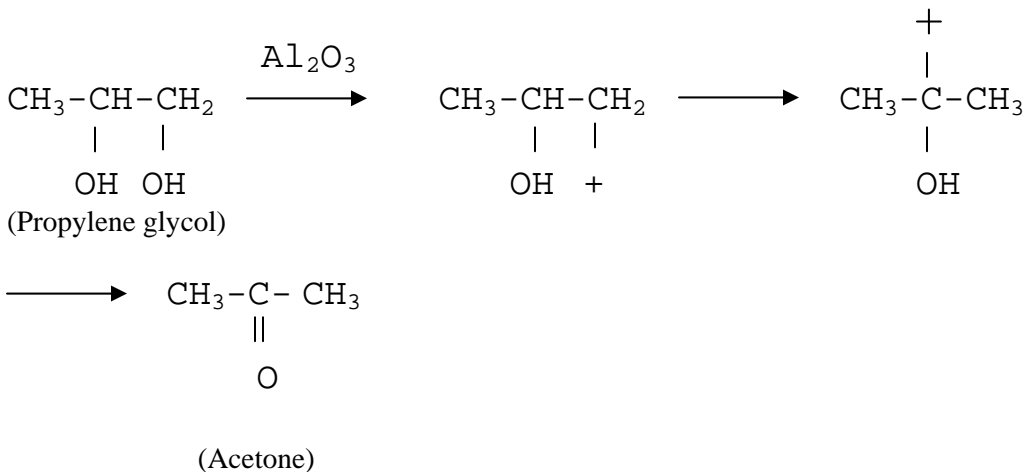
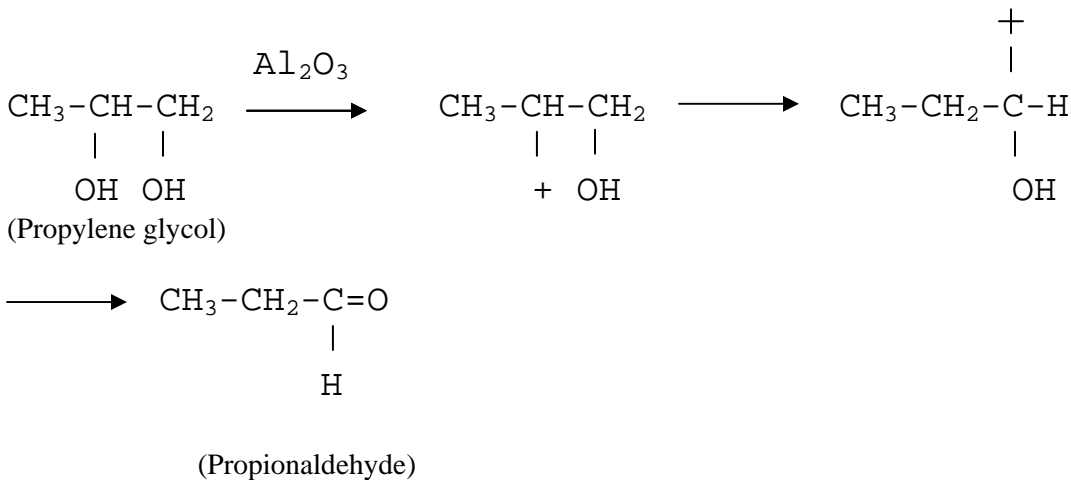


Figure 2.3: Selectivity to major products formed over 0.1 g of adsorption, basic and acidic alumina at 400 °C and N₂ flow rate of 20 SCCM

From Figure 2.3, one could observe that, although the adsorption and basic alumina gave a low selectivity to propylene oxide (1%), the adsorption, basic and acidic alumina presented a high selectivity of 60%, 55% and 65%, respectively, to propionaldehyde. They also gave a selectivity of 18% to acetone. This is because when glycols are treated with acid types, they can be rearranged to give aldehydes or ketones, although elimination without rearrangement can also be accomplished. This reaction is called the pinacol rearrangement [March, 5th edition, Tagaya et al., 2004]. Depending upon which

OH group migrates, the glycol can give rise to different products. Here, PG can give rise to propionaldehyde or propanone.



One significant observation to be noted from Figure 2.3 is that there is no trace of PO formed with acidic alumina. Also, after the reaction with acidic alumina, the exit stream line from the reactor got clogged up completely. This might be due to the fact that the acidic alumina polymerized propylene glycol to form other additional products which

blocked the tubing of the reactor. More reactions with acid alumina as support catalyst were abandoned due to the possibility of polymerization and clogging of the tubing of the reactor. Reactions were continued with modified basic and adsorption alumina catalysts.

Since, there was no appreciable difference in the selectivity to products using adsorption and basic alumina as support, the next step was to investigate the effect of alkali loading on the production of propylene oxide. The patent [FR 2345440, 1976] reported that 2-wt% Na acetate on alumina would give maximum selectivity of 36% to PO. Therefore, initially a 2-wt% Na/Al₂O₃ catalyst was used to perform the dehydration reaction. Figures 2.4 and 2.5 graphically represents the selectivity to major products formed with 2-wt% Na/Al₂O₃ and basic alumina at 400 °C, with a N₂ flow rate of 20 SCCM.

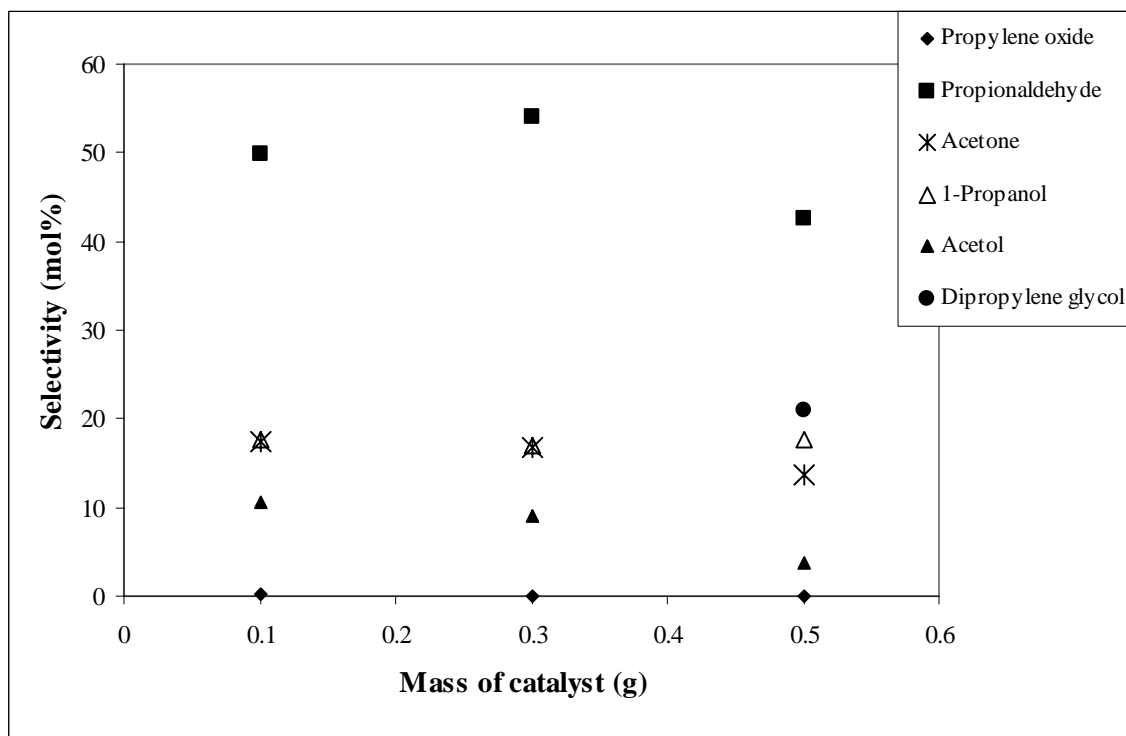


Figure 2.4: Selectivity to major products formed with 2-wt% Na acetate adsorption alumina at 400 °C, N₂ flow rate of 20 SCCM

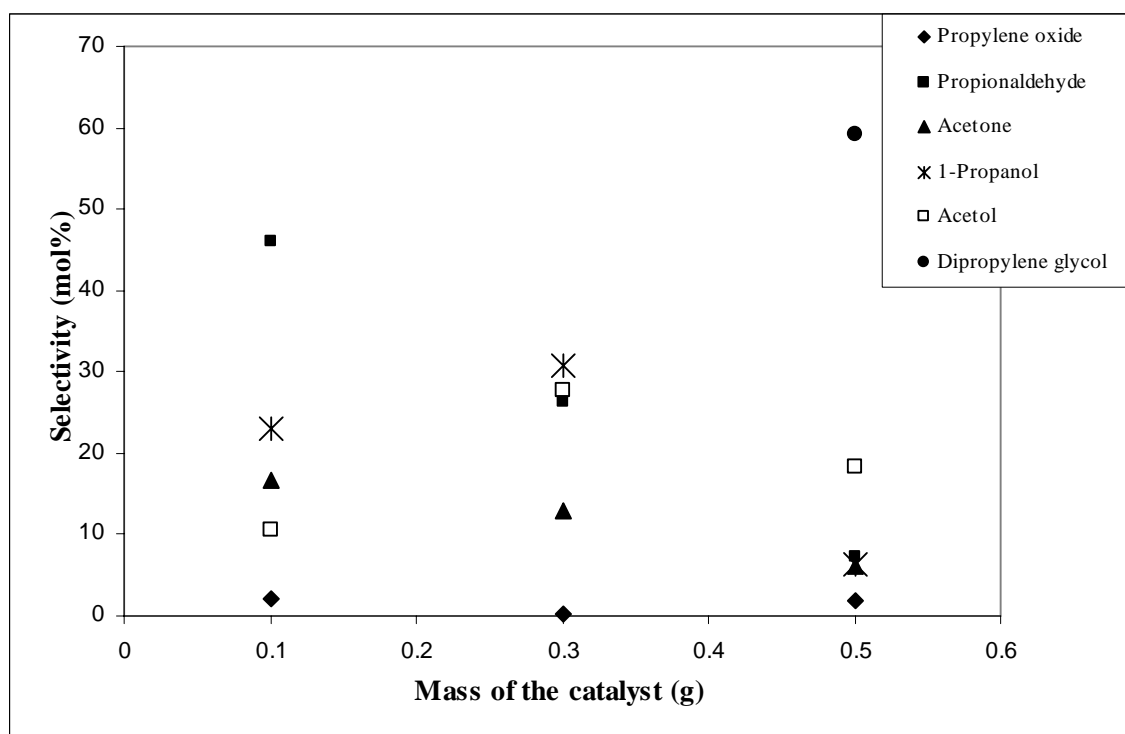


Figure 2.5: Selectivity to major products formed with 2-wt% Na acetate basic alumina at 400 °C, N₂ flow rate of 20 SCCM

Adsorption and basic alumina modified with sodium loading of 2-wt% were tested under the same reactor conditions with 0.1, 0.3, and 0.5 g of each catalyst. From Figures 2.4 and 2.5, it can be noted that increasing the amount of 2-wt% sodium modified adsorption and basic alumina did not show any increase in the selectivity of PO. However, the increase in the amount of 2-wt% sodium modified adsorption alumina showed a relatively stable selectivity of 50%, 16% and 18% to propionaldehyde, acetone and 1-propanol, respectively. On the contrary, the increase in the amount of 2-wt% sodium modified basic alumina showed a decrease in the selectivity to propionaldehyde from 46% to 7%. This could be due to the difference in the chemical properties of adsorption and basic alumina (pinacol rearrangement) depending on the migratory aptitudes of OH group. Moreover, for both 2-wt% basic and adsorption alumina, there is an increase in the production of dipropylene glycol at higher amounts of catalysts. Since the residence time

for the reaction increases as the amount of catalyst increases, condensation reactions between propionaldehyde and acetol might have led to the higher production of DPG for 2-wt% adsorption alumina. But, for 2-wt% basic alumina, there is a decrease in selectivity to propionaldehyde, 1-propanol and acetone and an increase in the selectivity to acetol and DPG at higher amounts of catalyst; which could have also been occurred due to the condensation reactions of the three products formed during dehydration with smaller amounts of catalyst.

Since these reactions did not show any considerable increase in the selectivity of propylene oxide, a series of reactions were conducted with changes in the loading of sodium on adsorption alumina. The graphical representation of the selectivity to various products over different alkali loadings on adsorption alumina is shown in Figure 2.6.

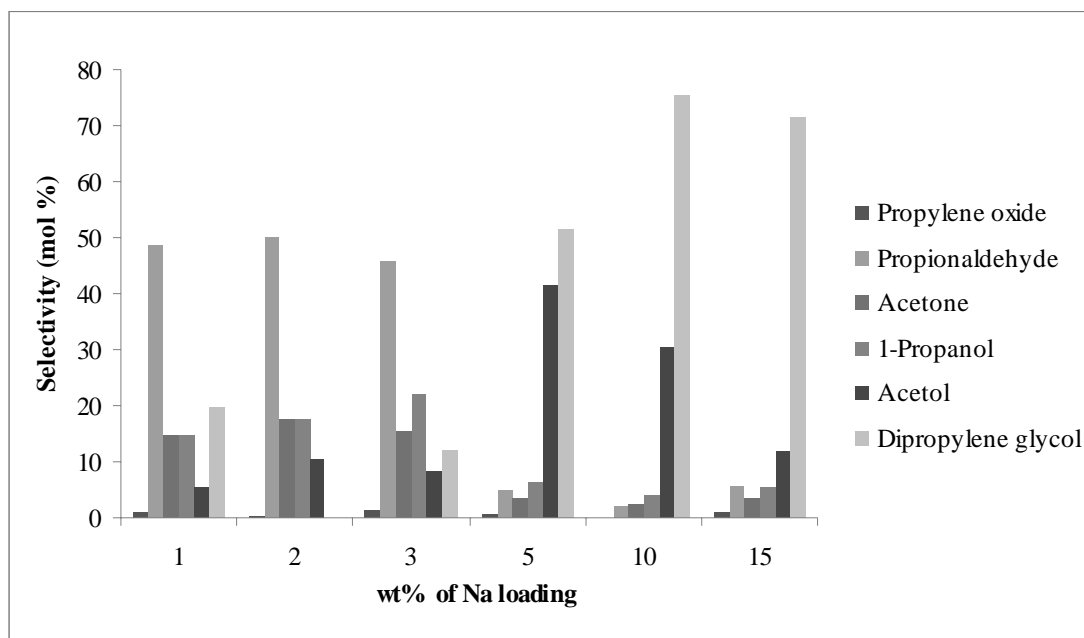


Figure 2.6: Selectivity to products formed over 0.1 g of varied sodium loadings on adsorption alumina at 400 °C and N_2 flow rate of 20 SCCM

Varying the sodium loading on adsorption alumina did not have much effect on the selectivity to PO as studied from Figure 2.6. Moreover, the increased sodium loading led to the decrease in the selectivity to propionaldehyde, acetone and 1-propanol but increased the selectivity to DPG and acetol. The reason for this could also be explained from the fact that the propionaldehyde, acetone and alcohol formed over low Na/Al₂O₃ (1-3 %) catalysts might have reacted with other products, which were formed over high Na/Al₂O₃ (5-15 %) during dehydration, which contributed to the higher production of DPG and acetol. Alumina, in general, gave very low selectivity to acetaldehyde, 2-propanol and allyl alcohol. (Note that the selectivity to these three products are not shown in Figures 2.3-2.6 and Table 2.1)

Dehydration reaction of PG was also conducted at 360 °C to investigate the effect of temperature on the selectivity to products. Selectivity to PO did not have an appreciable increase by reducing the reaction temperature. Also, the selectivity remained fairly constant for all the major products (See Table 2.1).

Table 2.1: Selectivity to products formed over 2-wt% Na/Al₂O₃ at different temperatures and N₂ flow rate of 20 SCCM

<i>Catalyst</i>	<i>PO</i>	<i>Propionaldehyde</i>	<i>Acetone</i>	<i>1-Propanol</i>	<i>Acetol</i>	<i>DPG</i>
2% Na Acetate adsorption Al₂O₃ (0.1g) at 360 °C	1.32	36.27	18.96	20.40	14.86	6.69
2% Na Acetate adsorption Al₂O₃ (0.1g) at 400 °C	0.20	49.86	17.42	17.63	10.48	0

Although the patent [FR 2345440, 1976] described the selectivity to propylene oxide as 36 %, the set of experiments conducted following the procedure of the patent only gave selectivity to propylene oxide as 2%. This could be explained by the fact that the

experiments described in the patent were conducted in the late 70's and hence, the lack of advanced technology and sophisticated equipments like Gas Chromatograph (FID) could have led the researchers to misidentify the peak of PO with the peaks of propionaldehyde or acetone, its isomers, whose retention time is 6.9 and 7.1 seconds as compared to the retention time of PO which is 6.6 seconds.

2.4.2. Dehydration reaction with Cs-ETS-10 catalyst

According to the patent [FR 2345440, 1976], dehydration of propylene glycol over Na/Al₂O₃ was conducted and the results were studied. Since the selectivity to propylene oxide was only 2% with Na/Al₂O₃ catalyst, we decided to focus our attention on a more basic catalyst. Cs-ETS-10 is a highly basic zeolite catalyst [Suppes et al., 2003]. This section mainly discusses about the various reactions conducted using Cs-ETS-10 catalyst to investigate the production of propylene oxide. Figures 2.7 and 2.8 shows the graphical representation of the selectivity to various products over Cs-ETS-10 catalyst at 400 °C and N₂ flow rate of 20 SCCM.

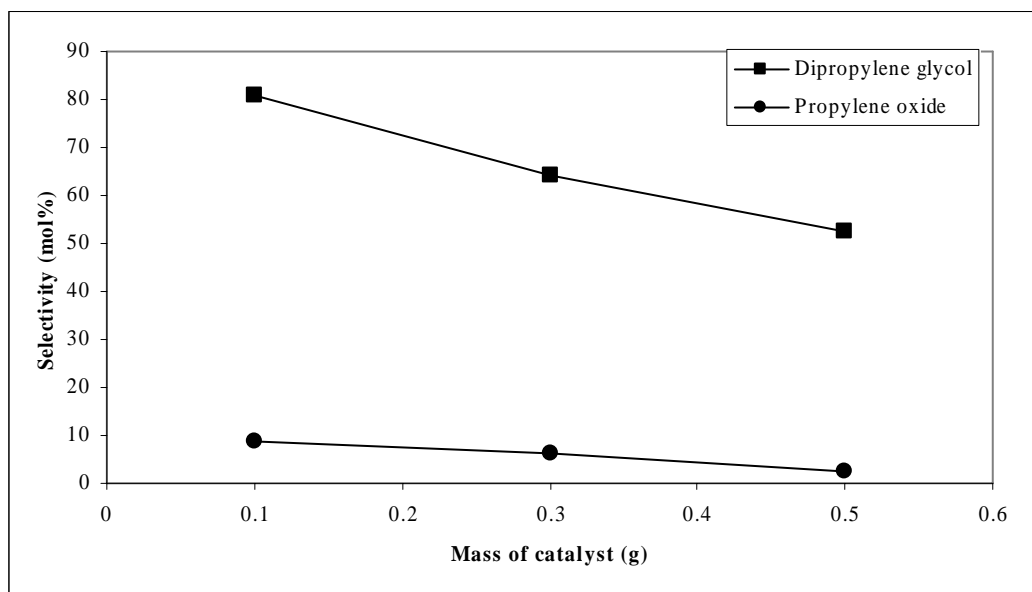


Figure 2.7: Selectivity to PO and DPG over Cs-ETS-10 catalyst at 400 °C and at N₂ flow rate of 20 SCCM

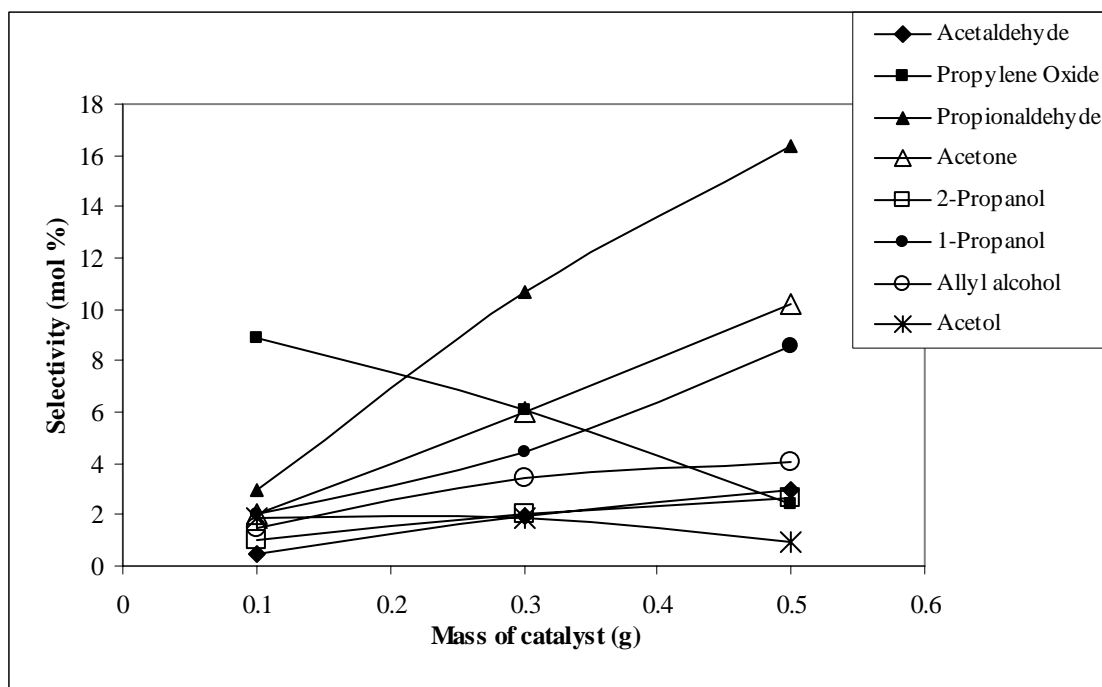


Figure 2.8: Selectivity to various products (except for DPG) over Cs-ETS-10 catalyst at 400 °C and at N₂ flow rate of 20 SCCM

Initially, 0.1g of CsCl-ETS-10 catalyst was tested at 400 °C and N₂ flow rate of 20 SCCM. Dehydration reaction over CsCl-ETS-10 catalyst gave a higher production of PO compared to Na/Al₂O₃ catalyst for the same reaction parameters. However, while this catalyst was active for propylene oxide production, it also produced higher quantities of dipropylene glycol. From Figure 2.7, one could observe the maximum selectivity to PO is 9% and the selectivity to dipropylene glycol is 80% for 0.1g of the catalyst. In order to have a better understanding about the selectivity to propylene oxide, several series of reaction runs were carried out by changing the reaction parameters such as the reaction temperature, the amount of catalyst and the flow rate of N₂. First, the reaction was carried out by increasing the amount of catalyst. In particular, 0.3 and 0.5 g of Cs-ETS-10 catalyst were reacted by maintaining the reaction temperature at 400° C and a N₂ flow

rate of 20 SCCM. From Figures 2.7 and 2.8, one could observe that, while the selectivity to propylene oxide and dipropylene glycol decreases as the amount of catalyst increases, the selectivity to aldehydes, acetone and alcohols increases as the amount of catalyst increases. The reason could be that the PO and DPG formed with smaller amounts of catalysts might have reacted further with other products formed, to contribute to the increased production of aldehydes, ketone and alcohols. PO could also isomerize to form propionaldehyde [Ai et al., 2003]. A significant observation to note from this reaction is that as the selectivity to PO decreased to 6% and 3%, the selectivity to dipropylene glycol also dropped to 64% and 53% for 0.3 and 0.5 grams respectively, while the selectivity to all the other products increased as the amount of catalyst was increased. These results could lead one to interpret that the production of propylene oxide may depend on the production of dipropylene glycol, i.e. for dehydration of propylene glycol with Cs-ETS-10 as catalyst, the reaction pathway to propylene oxide may occur through dipropylene glycol as the reaction intermediate. More about the reaction pathway for the dehydration of PG will be discussed in the next chapter. The conversion of propylene glycol for these reactions ranges from 76- 98%.

Since, an increase in the amount of catalyst did not favor an increase in the selectivity to propylene oxide; the next step was to vary the reaction temperature. The graphical representation shown in Figures 2.9 and 2.10 illustrates the effect of temperature on the selectivity of products over Cs-ETS-10 catalyst.

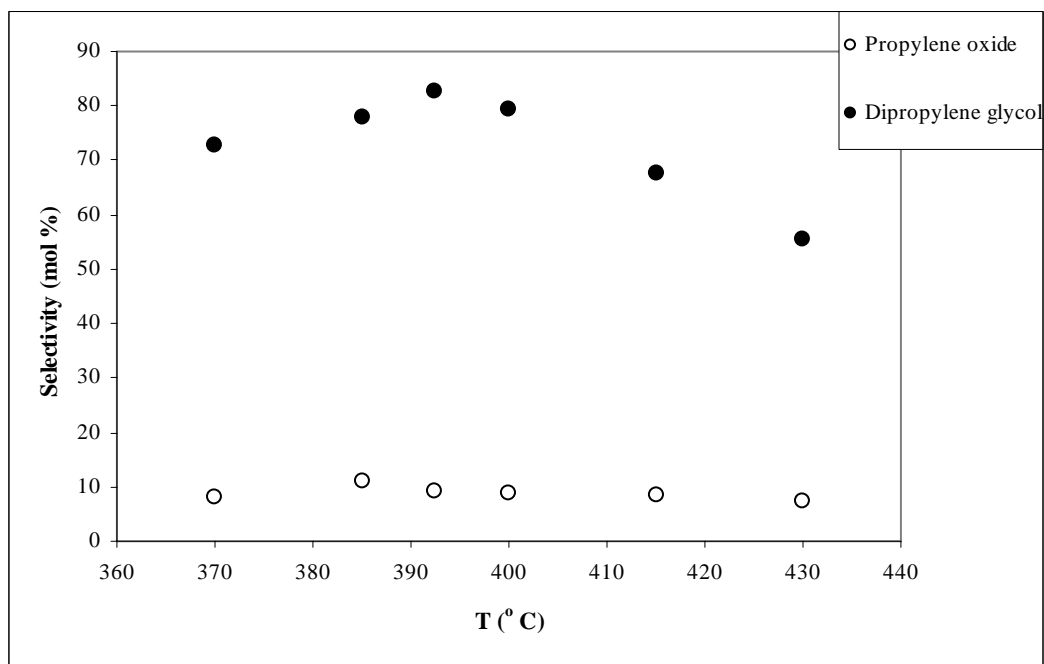


Figure 2.9: Selectivity to PO and DPG over 0.1 g of Cs-ETS-10 catalyst at various temperatures and N_2 flow rate of 20 SCCM

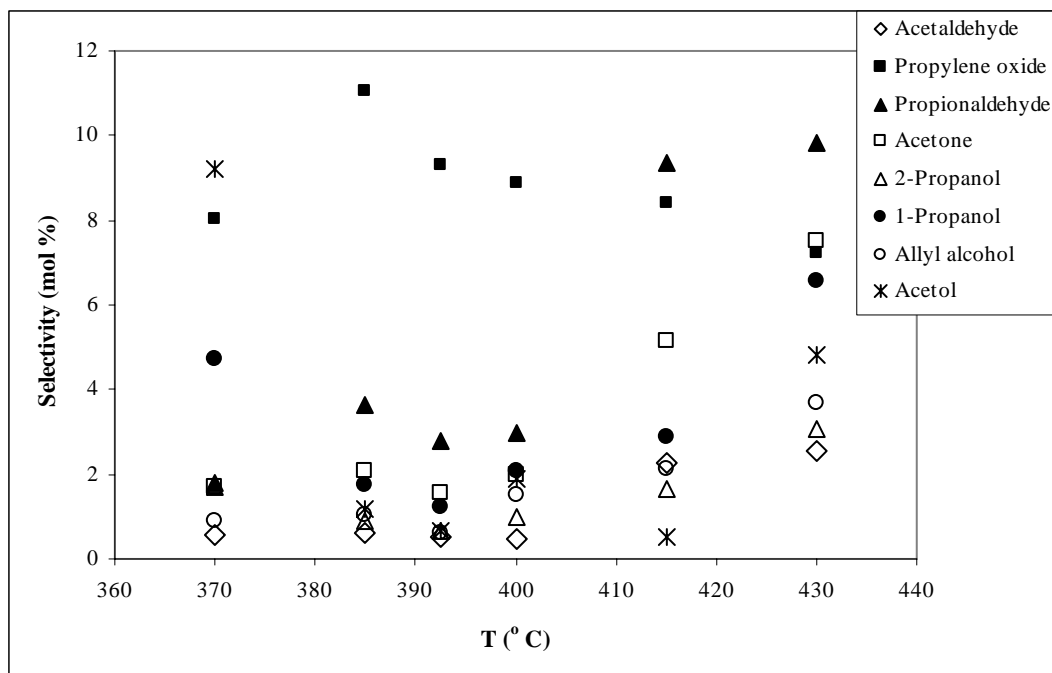


Figure 2.10: Selectivity to various products (except for DPG) over 0.1 g of Cs-ETS-10 catalyst at 400 °C and at N_2 flow rate of 20 SCCM

A series of reaction runs were performed by varying the reaction temperature from 370° C to 430° C with 0.1g of catalyst and N₂ flow rate of 20 SCCM. Reducing the reaction temperature to 370° C led to low rate of production and hence, decreasing the temperature did not increase the selectivity to PO. At 385° C, the selectivity to propylene oxide increased to 11%. To further study the effect of temperature on the selectivity, the reaction temperature was again increased to 392.5 °C, 415 °C and 430 °C, respectively. From Figure 2.9, the optimum temperature for the highest selectivity to propylene oxide is 385 °C. Dipropylene glycol gave a high selectivity of 50-80% at all temperatures. All the other products gave a selectivity lower than 12% over Cs-ETS-10 catalyst. When comparing the Cs-ETS-10 with Na/Al₂O₃ catalyst, the latter proved to be a better catalyst for the higher production of propionaldehyde, acetone and alcohols but provided a low selectivity to PO and DPG. On the other hand, Cs-ETS-10 gave a high selectivity to DPG (50-70%) and a selectivity of 11% to PO. This might be mainly due to the structure of ETS-10 i.e. its higher basicity and large pore structure might have aided in the production of DPG, which in turn led to the production of PO (detailed explanation is given in Chapter 3, Section 3.4.2).

The next step was to investigate whether the residence time had any effect on the selectivity to propylene oxide. Reactions were also carried out at different temperatures to observe the production of PO. Table 2.2 summarizes the selectivity to various products at different flow rates and temperatures (X represents the % conversion)

Table 2.2: Selectivity to products over 0.1 g of Cs-ETS-10 catalyst at different flow rates and temperatures

Products	N₂ – 20, 370 ° C X = 76	N₂ – 30, 370 ° C X = 81	N₂ – 20, 400 ° C X = 80	N₂ – 30, 400 ° C X = 85
Acetaldehyde	0.56	0	0.47	0.96
Propylene oxide	8.02	10.85	8.89	6.94
Propionaldehyde	1.79	2.31	2.98	3.91
Acetone	1.71	1.71	2.00	2.94
2-Propanol	1.71	0.92	1.00	1.67
1-Propanol	4.73	2.95	2.06	3.86
Allyl alcohol	0.92	0.90	1.49	1.46
Acetol	9.22	4.99	1.87	3.41
Dipropylene glycol	72.69	75.36	80.75	75.16

As observed from Table 2.2, the change in the flow rates did not have much effect on the selectivity to PO and other major products. However, one could notice a possible trend in the selectivity to products regarding the flow rates. When the flow rate was increased from 20 to 30 SCCM at 400°C, all products except for PO and DPG showed an increasing tendency to selectivity over the Cs-ETS-10 catalyst. Also, when the residence time was reduced at 370°C, all products except PO and DPG showed a decreasing tendency towards selectivity. This result does bolster our previous interpretation that the production of propylene oxide might be through a possible dipropylene glycol active intermediate formed during the dehydration reaction of propylene glycol. More about the reaction path way of dehydration of propylene glycol is discussed in chapter 3.

Dehydration reaction at 370 °C and N₂ flow rate of 30 SCCM gave a selectivity of 10.85% to PO. At low temperature, the conversion of the reaction will be low. So, it is anticipated of obtaining lower selectivity to PO but, the reaction gives a higher selectivity to propylene oxide. The reason could be due to the fact that the lower temperature and lower residence time prevented PO from reacting further with other products thereby increasing the selectivity. This encouraged us to focus our attention to conduct reactions of propylene glycol at a lower temperature as discussed in section 2.5

2.4.3. Dehydration reaction with Na acac/MgO catalyst

Since Cs-ETS-10, a highly basic catalyst, gave a selectivity of 11 % to PO which is higher than Na/Al₂O₃ catalyst, reactions were conducted with another base catalyst, Na acac supported on nanocrystalline MgO. Figure 2.11 illustrates the selectivity to products over Na acac/MgO catalyst at 400 °C and at N₂ flow rate of 20 SCCM.

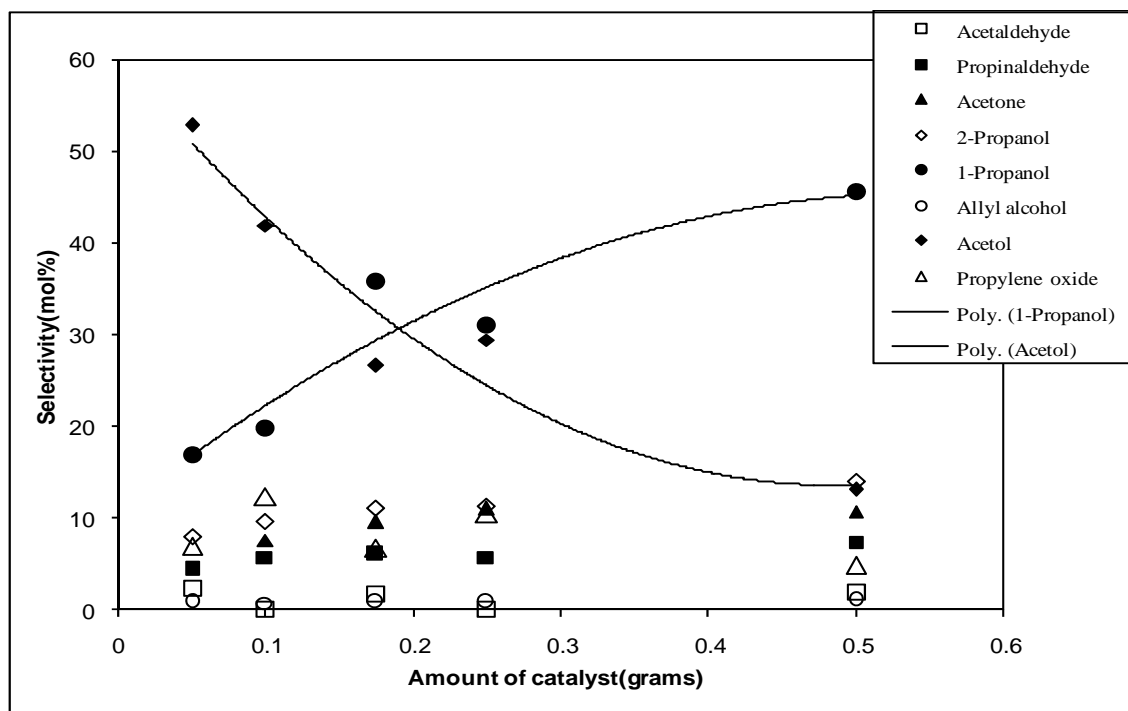


Figure 2.11: Selectivity of various products over Na acac/MgO catalyst at 400 °C and at N₂ flow rate of 20 SCCM

Initially the reaction was performed with 0.1 g of catalyst, reaction temperature of 400 °C and a N₂ flow rate of 20 SCCM. The selectivity to propylene oxide was found to be 12.33% (see Figure 2.11). In order to determine the effect of the amount of catalyst on the selectivity; 0.05, 0.175, 0.25, and 0.5 grams of catalysts were treated under the same reaction conditions. The highest selectivity to PO is shown for 0.1g of catalyst. The graph (Figure 2.11) shows a decreasing trend in selectivity as the amount of catalyst was increased more than 0.1 gram. Also, as the amount of catalyst was increased, there was an increase in the selectivity to the three alcohols: 2-propanol, 1-propanol and allyl alcohol and reduction in the production of acetol i.e. as the reaction progresses, the acetol initially formed over smaller amounts of catalyst reacts with other products formed and contributes to the increase in the production of the alcohols, especially 1-propanol.

A significant observation to be noted in this reaction is that there was no dipropylene glycol production over Na acac/MgO catalyst in contrast to the previously mentioned catalysts, Na/Al₂O₃ and Cs-ETS-10. As mentioned in section 2.4.2, Cs-ETS-10 gave a high selectivity to DPG (50-70%) and a selectivity of 11% to PO and; Na/Al₂O₃ catalyst gave a selectivity of 50%, 16% and 18% to propionaldehyde, acetone and 1-propanol, respectively, but provided a low selectivity to PO and DPG. The higher selectivity of DPG over Cs-ETS-10 catalyst could be explained due to the structure of ETS-10 i.e. its higher basicity and large pore structure might have aided in the production of DPG, which in turn lead to the production of PO. However, Na acac/MgO catalyst gave a selectivity of 12.33% to PO even though there was no production of DPG. Therefore, from this observation it could be studied that the reaction pathway of dehydration of propylene glycol to PO over Na acac/MgO catalyst does not occur through DPG as the reaction intermediate, but could be through some other reaction intermediate or it could

be a direct dehydration reaction. Chapter 3 discusses in detail about the reaction pathway of dehydration of propylene glycol.

In order to study the effect of temperature on the production of PO, the reactions were carried out at a range of temperatures over Na acac/MgO catalyst. The selectivity to products at different reaction temperatures is shown in Figure 2.12

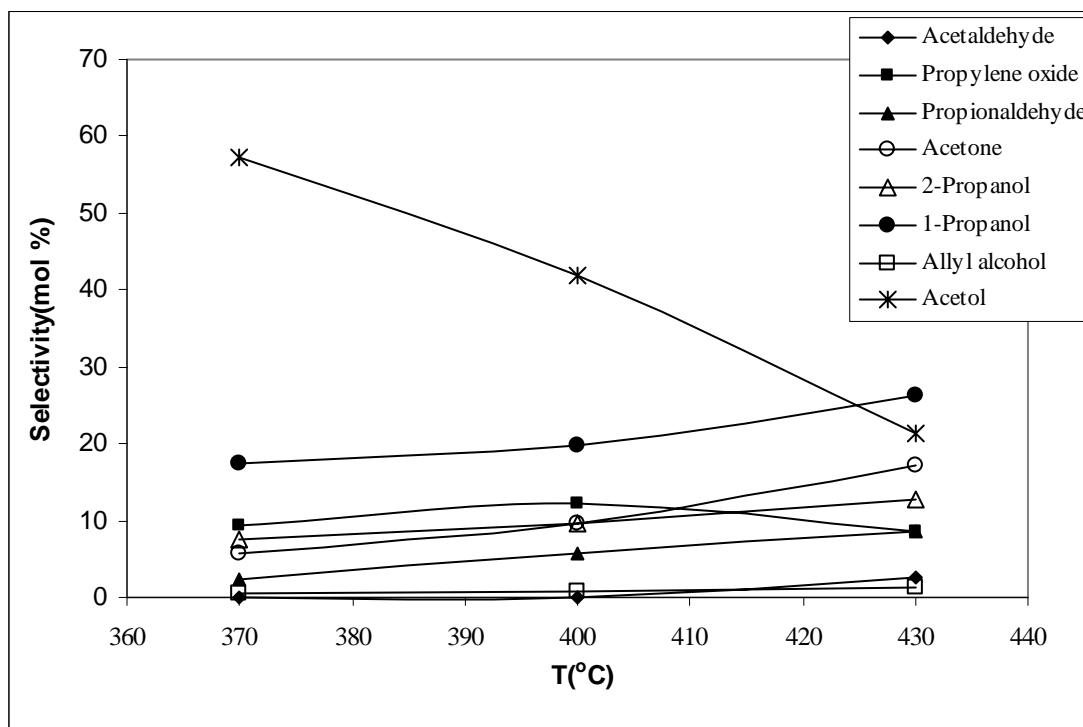


Figure 2.12: Selectivity to various products at different temperatures over 0.1g of Na acac/MgO catalyst at N₂ flow rate of 20 SCCM

A series of reaction runs were performed at temperatures ranging from 370 °C to 430 °C with 0.1 g of catalyst and N₂ flow rate of 20 SCCM. At 370 °C, the selectivity to PO was obtained as 9.3% and at 430 °C it was 8.71%. The graph (see Figure 2.12) indicates that as the temperature increases the selectivity to all products, except for acetol increases. This result also implies that, the acetol initially formed at low temperatures reacts further

with other products formed to increase the selectivity to alcohols and aldehydes. The optimum temperature for highest selectivity to propylene oxide is 400° C for Na acac/MgO catalyst. Also, Na acac/MgO gave a higher selectivity of 58% to acetol at 400° C when compared to the 10% and 40% selectivity over Cs-ETS-10 and Na/Al₂O₃ catalysts, respectively. The reason for this could be that the dehydrogenation of propylene glycol over an alkali metal supported on an oxide catalyst produce higher amounts of acetol compared to other types of catalysts [Organic Syntheses, 1943].

Next, we investigated the effect of residence time on the selectivity to products. Table 2.3 shows the selectivity to products at different N₂ flow rates

Table 2.3: Selectivity to various products formed with different N₂ flow rates over 0.1g of Na acac/ MgO catalyst at 400 °C

Products	20 SCCM (X=71)	30 SCCM (X=70)
Acetaldehyde	0.13	0
Propylene oxide	12.33	13.0
Propionaldehyhde	5.74	6.07
Acetone	9.59	10.48
2-Propanol	9.65	10.39
1-Propanol	19.87	20.32
Allyl alcohol	0.78	0.75
Acetol	41.89	39.00

The N₂ flow rate was increased from 20 SCCM to 30 SCCM with 0.1grams of catalyst at 400 °C. Increasing the flow rates did not affect the conversion rate of the products. Furthermore, the selectivity to the various products remained constant for both the flow rates. These results clearly indicate that the residence time did not have much effect on the selectivity to products over catalyst Na acac/MgO. When comparing Na acac/MgO catalyst with Cs-ETS-10, for the latter, lowering the reaction temperature and lowering the residence time increased the selectivity to PO by preventing PO from reacting further with the other products. This result led to the study of conducting reaction with propylene glycol under low temperature and low residence time via reactive distillation which is discussed in the next section 2.5.

2.5. Reactive distillation

As discussed in the previous sections, the selectivity to propylene oxide was reduced considerably due to its further reaction to other products. In order to prevent the propylene oxide produced from reacting further, it should be isolated from the reacting system soon after it was formed. To investigate on this, we conducted a set of experiments using a reactive distillation apparatus. The combination of chemical reaction with distillation in only one unit is called reactive distillation. The performance of reaction with separation in one piece of equipment offers distinct advantages over the conventional, sequential approach. The conversion of a reaction can be increased far beyond chemical equilibrium conversion due to the continuous removal of reaction products from the reactive zone. This may lead to low capital and investment costs and may be important for sustainable development due to a lower consumption of resources. Figure 2.13 gives a detailed description of the reactive distillation apparatus.

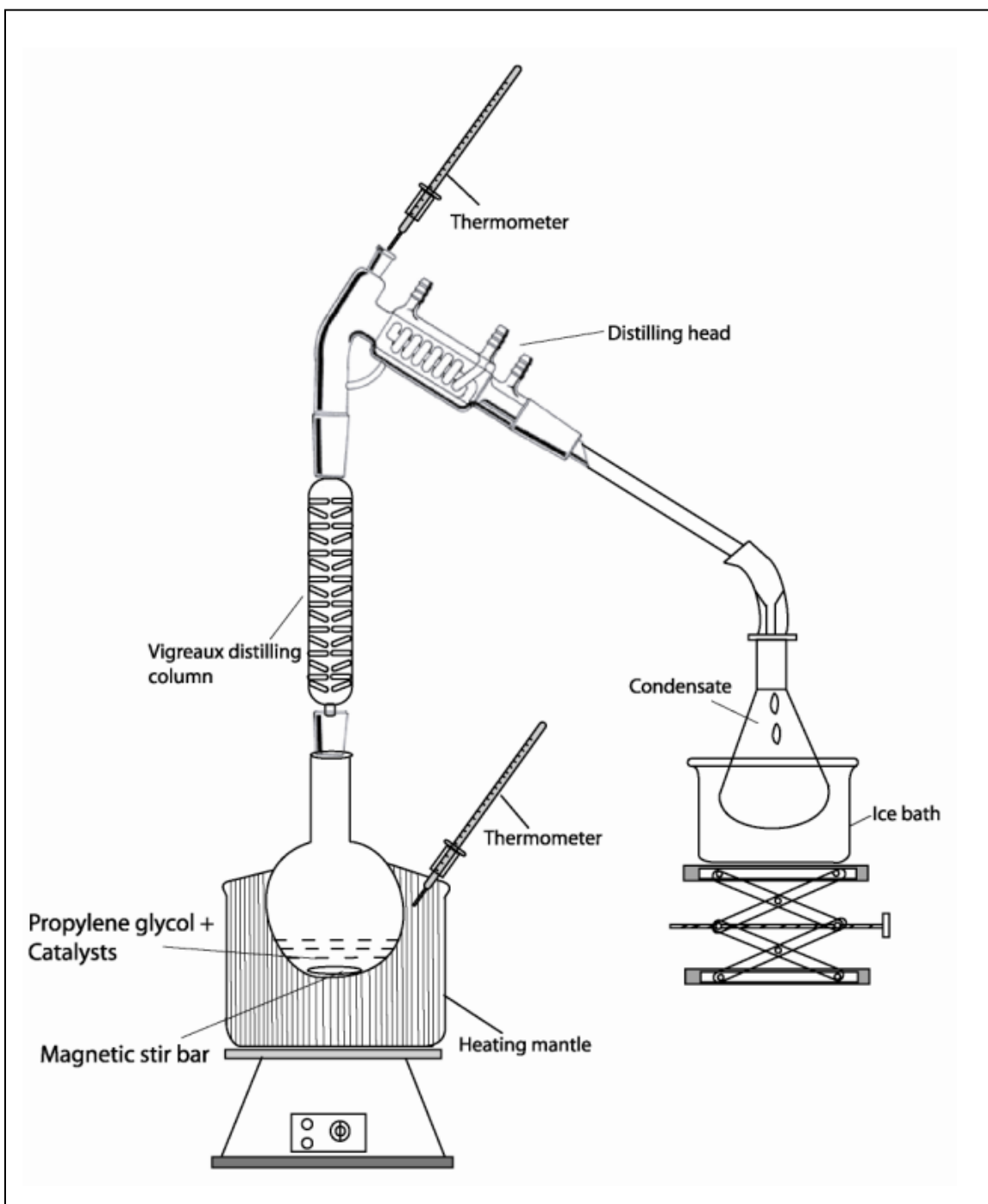


Figure 2.13: Reactive distillation apparatus

The reactive distillation apparatus consisted of a 100 ml round bottomed flask where the reactant and catalyst were stirred together. The mixture was heated to a reaction temperature of 189 °C because the boiling point of propylene glycol is 189 °C. A thermometer was fixed inside the heating mantle to ensure that the reaction temperature does not fall below 189 °C. The other components are the common distillation equipment like the Vigreux column, the condenser head and a pear shaped flask to collect the condensate formed. The pear shaped flask was kept inside an ice bath to cool the condensed vapors formed. A thermometer was affixed on the top of the distilling head to measure the temperatures of the products: acetaldehyde, propylene oxide, propionaldehyde, acetone, 2-propanol, 1-propanol, allyl alcohol, acetol, and dipropylene glycol, formed. Cooling water was circulated through the condenser head to cool the vapors rising through the column.

A variety of catalysts were studied for reactive distillation which includes ETS-10, Cs-ETS-10, Li acac/MgO, Na acac/MgO and potassium hydroxide. Initially, the reaction started with using ETS-10 catalyst (as discussed in Section 2.4.2) which was kept in the oven overnight at 120 °C to remove all moisture content present in the catalyst. About 0.1grams of ETS-10 and 20 ml of PG were reacted together in the distillation reacting flask and the reaction temperature was maintained at 189 °C. As the mixture is heated and boils, the vapor rises up in the column. The vapor condenses on the glass platforms (known as plates or trays) inside the column and runs back down into the liquid below, thereby refluxing the up-flow of the distillate vapor. The reactive distillation was carried out continuously for 5 hours and the condensate was collected. It was manually injected to the GC with the same specifications as described in section 2.3.3. The selectivity to PO and other products are given in Table 2.4.

Table 2.4: Selectivity to various products over 0.1g of ETS-10 at 189 °C

Products	ETS-10 (Condensate)	ETS-10 (Residue)
Acetaldehyde	9.52	12.56
Propylene oxide	1.85	1.05
Propionaldehyde	11.01	10.51
Acetone	9.31	6.95
2-Propanol	21.25	16.02
1-Propanol	27.96	18.45
Allyl alcohol	0.59	0.27
Acetol	3.52	3.22
Dipropylene glycol	14.99	30.97

From Table 2.4, it could be noted that the selectivity to PO is only 2% over ETS-10 catalyst with the condensate formed. This could be due to the fact that, since the reaction temperature was at 189 °C, the rate of reaction might have been really slow to produce any substantial amount of PO. The propylene glycol which remained in the reactive distillation flask, termed as residue, was also injected into the GC and the selectivity to products was also analyzed. The selectivity to PO did not show any progress. Hence, to check any improvement in the selectivity to PO, reactive distillation was conducted with more basic catalysts Cs-ETS-10 and potassium hydroxide at the same reaction conditions. The selectivity to PO and other products are shown in Table 2.5.

Table 2.5: Selectivity to various products over 0.1g of Cs-ETS-10 and KOH catalysts

Products	Cs-ETS-10 at 189 ° C (Residue)	Cs-ETS-10 at 385 ° C (Gas phase)	KOH at 189 ° C (Residue)
Acetaldehyde	6.34	0.62	3.63
Propylene oxide	12.43	11.06	9.08
Propionaldehyde	20.84	3.63	7.19
Acetone	1.66	2.10	17.86
2-Propanol	3.44	0.88	18.66
1-Propanol	0	1.72	22.13
Allyl alcohol	0	1.02	0.00
Acetol	4.52	1.18	0.00
Dipropylene glycol	50.77	77.79	21.45

The reactions with Cs-ETS-10 and KOH did not condense any of the products formed. In order to have a better understanding whether the catalysts were effective in producing PO, the residue in the distillation flask were injected into the GC. The selectivity to products for both liquid and gas phase is shown in Table 2.5. The selectivity to PO remains almost constant when comparing the liquid and gas phase reaction for Cs-ETS-10 catalyst. However, the selectivity to DPG decreased from 78% to 51% when performed in liquid phase. The reason could be the low reaction temperature which led to decreased selectivity to DPG and increased selectivity to propylene oxide, aldehydes, 2-propanol and acetol. Even though the low reaction temperature led to the low

selectivity to DPG, it also led to the low conversion rate. The selectivity to PO is obtained as 12% for Cs-ETS-10 and 9% for KOH. Even though the catalysts were effective in producing PO via reactive distillation, no distillation products were formed. The reason for this could also be low reaction temperature, which led to low conversion to products and hence no appreciable amount of products were formed to condense.

To investigate more on the selectivity to PO via reactive distillation, experiments were performed using Li acac/MgO and Na acac/MgO. The selectivity to products over Li acac/MgO as catalyst is shown in Table 2.6.

Table 2.6: Selectivity to various products over 0.1 g of Li acac/MgO at 189 °C

Products	Li acac/MgO (Condensate)	Li acac/MgO (Residue)
Acetaldehyde	3.06	2.33
Propylene oxide	6.82	4.47
Propionaldehyde	7.37	6.60
Acetone	20.00	18.23
2-Propanol	13.47	13.38
1-Propanol	41.36	49.72
Allyl alcohol	1.35	1.41
Acetol	1.26	1.05
Dipropylene glycol	5.31	2.81

The selectivity to propylene oxide in this case was obtained as 7% from the condensate formed. Li acac/MgO gave selectivity of 41% for 1-Propanol. On the other hand, when reactive distillation was carried out with Na acac/MgO as catalyst, there was no production of PO, giving low selectivity to propionaldehyde and acetol. Since the reaction was conducted at low temperature, which reduced the rate of reaction, thereby affecting the amount of the products formed.

The experiments with reactive distillation did not show any significant increase in the selectivity to PO, further studies in this field were discontinued. The low reaction temperature (189 °C) for reactive distillation caused low conversion which led to the slow production of products. Since no appreciable amount of products was formed, it is difficult to conduct experiments and study the effect of catalysts via reactive distillation. Also, the concept of reactive distillation is more complex and requires extensive research in this area to produce more valuable results.

2.6. Conclusions

This chapter mainly discusses about the dehydration reaction of propylene glycol over various catalysts by altering the reactor temperatures, amount of catalysts and flow rates of nitrogen to investigate on the selectivity to propylene oxide. Based on the reactions conducted, it can be concluded that smaller amount of catalysts gave higher selectivity to PO, by performing it at optimum reaction temperature range of 385-400 °C. As the amount of catalysts was increased, the PO initially formed over smaller amount of catalysts reacted with other products which were formed over larger amount of catalysts, which eventually contributed to the lower selectivity to PO. Three catalysts, Na/Al₂O₃,

Cs-ETS-10 and Na acac/MgO were studied for this experiment. The Na/Al₂O₃ resulted in low selectivity of 2% to PO, although it gave a high selectivity of 55% to propionaldehyde. Even though Cs-ETS-10 catalyst was active for PO production, it also produced higher amounts of dipropylene glycol which significantly reduced the selectivity of propylene oxide to 11%. The Na acac/MgO catalyst gave the highest selectivity of 12.33% to propylene oxide at 400 °C, 0.1 grams and N₂ flow rate of 20 SCCM. The Na acac/MgO catalyst also gave a reasonable selectivity of 58% to acetol with 0.1 grams of catalyst, at 370 °C, a N₂ flow of 20 SCCM, and 47% to 1-propanol with 0.5 grams of catalyst, at 400 °C, and a N₂ flow of 20 SCCM which was higher than the other two catalysts. The reactions with reactive distillation did not produce any significant results as the low reaction temperature led to low conversion.

CHAPTER 3

REACTION PATHWAY FOR DEHYDRATION OF PROPYLENE GLYCOL

3.1. Introduction

Chapter 3 discusses about the dehydration of propylene glycol over three main catalysts: Na/Al₂O₃, Cs-ETS-10 and Na acac/MgO at different mass of catalysts, reaction temperatures and residence times. Here, the 2-wt% Na/Al₂O₃, Cs-ETS-10 and Na acac/MgO gave maximum selectivity of 2%, 11% and 12.33%, respectively, to propylene oxide at various reaction parameters. Even though these catalysts, especially Cs-ETS-10 proved active for PO production, they also produced higher amounts of other various products like propionaldehyde, acetol, 1-propanol and dipropylene glycol. The selectivity to PO decreased considerably due to the formation of these products. In order to study whether these products are active intermediates in the formation of PO, it became necessary to obtain more information about the reaction pathway for the dehydration of propylene glycol.

To get a better understanding of the reaction mechanism of propylene glycol, the major products such as, acetol, 1-propanol (PrOH) and dipropylene glycol (DPG) were investigated as reactants over the three catalysts. This chapter is organized as follows. Section 3.2 discusses the catalyst preparations of the three main catalysts: sodium loaded on alkali modified alumina (Na acetate alumina), cesium chloride ETS-10 (Cs-ETS-10)

and sodium acetyl acetonate supported on magnesium oxide (Na acac/MgO). Section 3.3 discusses the experimental set up of the reaction process followed by the results and discussion, conclusion.

3.2 Catalyst preparation

The procedure for the preparation of all the three catalysts is explained in detail in Section 2.2.

3.3 Experimental section

3.3.1. Reactor set up

The dehydration reaction was conducted using a plug flow reactor system. The main components of the system include a plug flow reactor, a 4-port valve (Valco, Valve I), a gas chromatograph (Thermoquest Trace GC) and an air actuated 6-port GC gas sampling valve (Valco, UW-type- Valve II) which contains a 0.5 ml sample loop. A detailed description of the plug flow reactor is given in Figure.1 of Section 2.3.1

The plug flow reactor consists of a long piece of stainless steel tubing with an outer diameter (OD) of 0.25 inches and a length of 19.5 inches. This stainless steel tubing was sheathed by a 0.7 inches OD and 12inches long cylindrical brass rod, which acts as a heat sink and create more uniform temperatures throughout the length of the reactor. A type K thermocouple was inserted in the middle of the reactor to detect the temperature of the reactor during the entire process.

Some glass wool was placed inside the stainless steel reactor to support the catalyst bed in the middle of the reactor. The catalyst was pelletized to 30-40 mesh size and was loaded into the reactor carefully to obtain maximum uniformity of the catalyst bed. Once the catalyst was properly loaded, the reactor was placed inside an Omega ceramic cylindrical heater (870 W and 120 V) and connected to the temperature controller I (Cole-Parmer, Series 6890010).

Here, the valve-I was used to check whether the reactants were bypassed or passed through the reactor i.e., with or without reacting with the catalyst. Initially, the feed (DPG, acetol or 1-propanol), and nitrogen (carrier gas) were bypassed through the reactor until the flow of reactants became steady, which was determined by sampling the reactant stream to the GC to find the relative concentration of the reactant. This was done by analyzing the trace of the reactant in the GC. Once the concentration of the feed attained a steady state, valve-I was turned clockwise to start the flow of reactants through the catalyst bed of the reactor. The reactants continuously flowed through the catalyst bed for 8-9 hours and sampling to the GC was performed simultaneously. Analysis of the GC trace from the product stream of the plug flow reactor provided the data for the formation of PO and other products like acetaldehyde, propionaldehyde, acetone, 2-propanol, 1-propanol, allyl alcohol, acetol, propylene glycol and dipropylene glycol.

3.3.2. Catalyst pre-treatment

The pelletized catalyst was loaded into the reactor and the treatment process involved the ramping of the catalyst from room temperature to 500 °C in 8 hours with a N₂ flow rate of

20 SCCM. Then, the catalyst was heated for a period of 4 hrs at 500 °C, after which it was cooled to the appropriate temperature at which the dehydration reaction was investigated.

3.3.3. Dehydration reaction

The dehydration reaction was conducted with a pre-treated catalyst at a specific reactor temperature. The feed was loaded into a 10 ml gas tight syringe and was injected to the feed stream using a syringe pump (Cole-Parmer Instrument Company, 74900 series). The flow rate of the feed was 0.5 ml/hr for DPG and 1 ml/hr for acetol and 1-propanol. The flow rate of nitrogen (carrier gas) was maintained at 20 SCCM using a mass flow controller (Sierra Instruments, 110 VAC). The stainless steel tubing in the plug flow reactor system was heated using flexible electric heating tapes (Thermolyne), while the valves (valve-I and valve-II) were encased in heated enclosures and temperature of both heating tapes and the valve enclosures were controlled by temperature controller II (Love Controls Division, 16A series). The temperature of the heat traced tubing and that of the heated valve enclosures were maintained at a certain appropriate temperature, depending upon the boiling points of the corresponding feed used. These temperatures ensured that the reactants remained in the vapor phase throughout the entire process and to the point where it is injected to the GC. When Valve I was in the bypass position, the reactant vapors were injected to the GC through a sample loop for the trace to be analyzed and when the sample was not injected to the GC, the effluents were collected in a trap and nitrogen was vented to a fume hood.

The gas chromatograph (GC) was operated with a capillary column and flame ionization (FID) detector to separate and analyze the components injected to the GC. For analyzing a sample inside the GC, a trace method was developed beforehand, because no two peaks could be seen overlapped in the GC trace. For this reaction, the method developed earlier for the study of dehydration of propylene glycol was used. The GC parameters chosen for the experiments were: oven temperature of 35°C, right inlet temperature of 225°C, split flow of 15 ml/min, split ratio of 30, carrier gas (He) flow rate of 0.5 ml/min, detector base temperature of 225°C and the flow rates of air, hydrogen(H₂) and make up helium (He) were 350,35,50 ml/min respectively.

The sample was injected to the GC automatically using a 6-port valve (valve-II). This valve consisted of a 0.5 ml sample loop to ensure that the sample volume injected to the GC remained constant for every injection. A representation of a GC trace with dipropylene glycol as reactant is shown in Figure 3.1

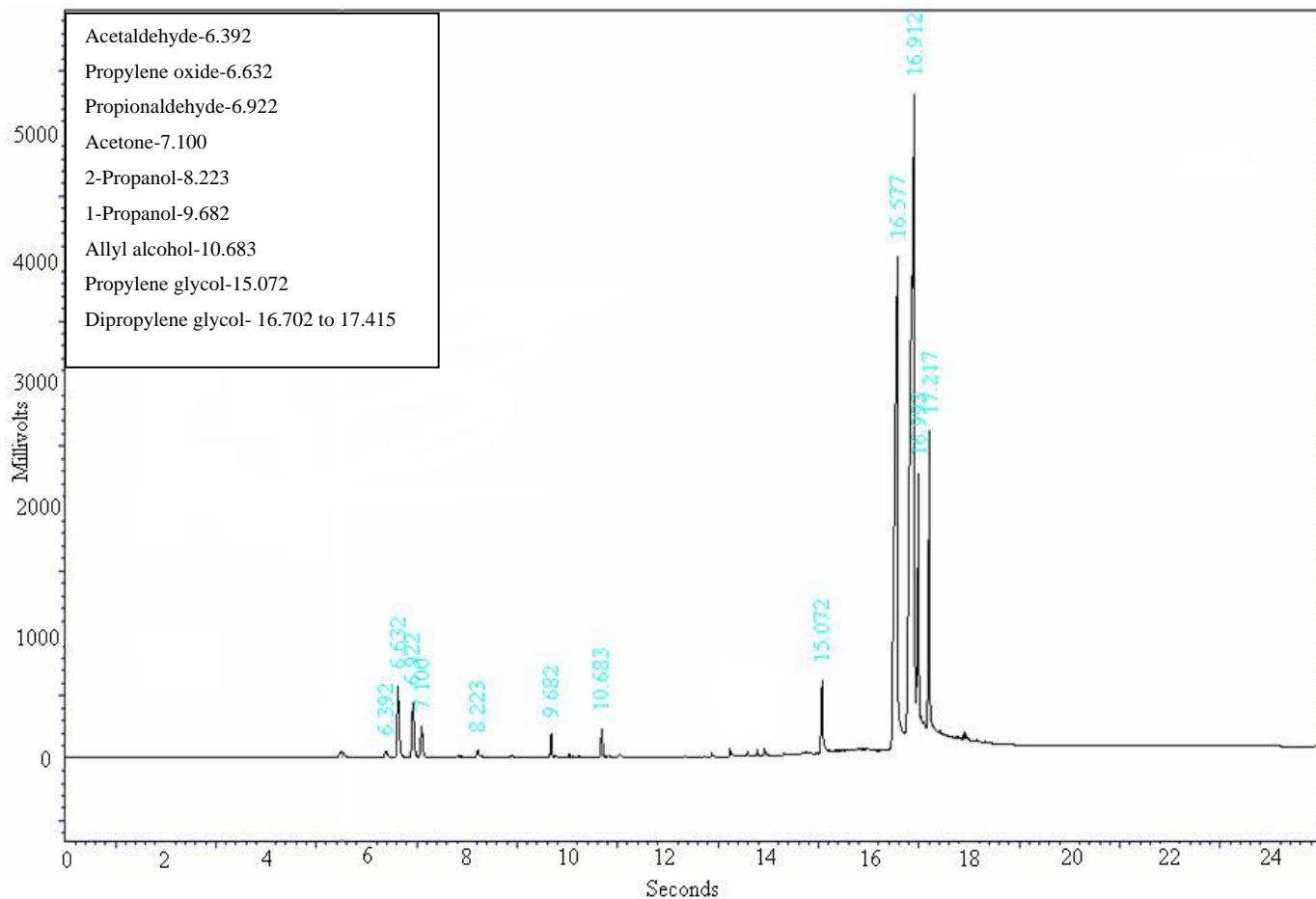


Figure 3.1: GC trace of a sample performing the dehydration of dipropylene glycol over Cs-ETS-10 catalyst

Refer Section 2.3.4 for the analysis and calculations of the selectivity to various products.

Equation 1 and equation 2 provides details for the calculation of response factors and selectivity of products, respectively.

3.4. Results and discussion

3.4.1. Dehydration reaction with Na/Al₂O₃ catalyst

The dehydration of propylene glycol over 2-wt% Na/Al₂O₃ catalyst gave 2% selectivity to PO, as discussed in Section 2.4.1. In order to get a better understanding of the reaction pathway of dehydration of propylene glycol over 2-wt % Na/Al₂O₃ catalyst; pure dipropylene glycol, 1-propanol and acetol were separately injected as feed at a temperature of 400°C and at a N₂ flow rate of 20 SCCM. The selectivity to various products formed from these three reactions and also from the reaction with propylene glycol (see Section 2.4.1) is given in Figure 3.2.

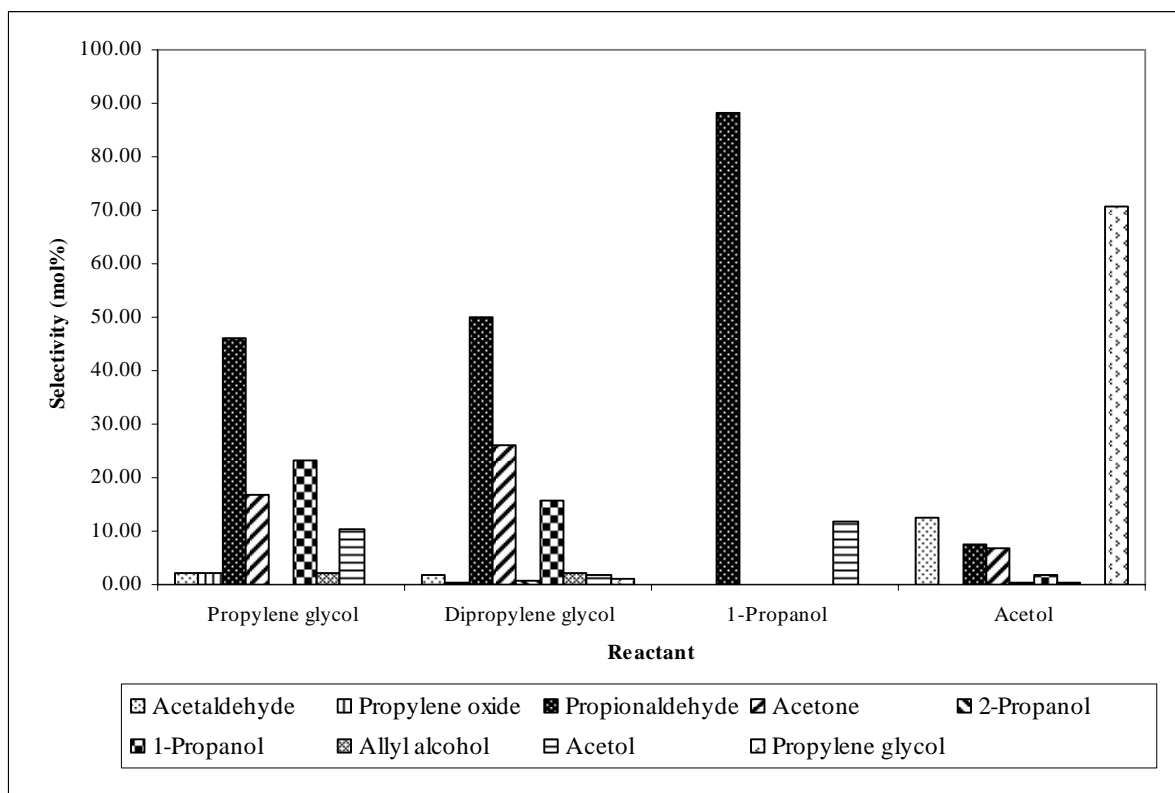


Figure 3.2: Selectivity to various products over 0.1 g of 2-wt% Na/Al₂O₃ at 400 °C and at a N₂ flow rate of 20 SCCM

From Figure. 3.2, it could be noted that PO is produced only during the dehydration of propylene glycol over Na/Al₂O₃ as catalyst. When DPG, 1-propanol and acetol were used as a reactant, there is no trace of PO formed. It is apparent from these results that the reaction pathway to the dehydration of propylene glycol over 2-wt% Na/Al₂O₃ may not be through a particular reaction intermediate like dipropylene glycol, 1-propanol and acetol but rather a direct dehydration.

3.4.2. Dehydration reaction with Cs-ETS-10 catalyst

As discussed in Section 2.4.2 of the previous chapter, the reactions of propylene glycol with Cs-ETS-10 as catalyst gave a selectivity of 11% to PO and 80% to DPG. Also, it could be noted that as the production of dipropylene glycol increased, the production of propylene oxide also increased suggesting that dipropylene glycol could act as an active intermediate in the formation of propylene oxide. To get a better understanding of this reaction pathway, dehydration reaction was performed with DPG as the reactant over Cs-ETS-10 catalyst. Figure 3.3 illustrates the selectivity to propylene oxide with both PG and DPG as reactants over 0.1 grams of Cs-ETS-10 catalyst, at 400 °C and a N₂ flow rate of 20 SCCM.

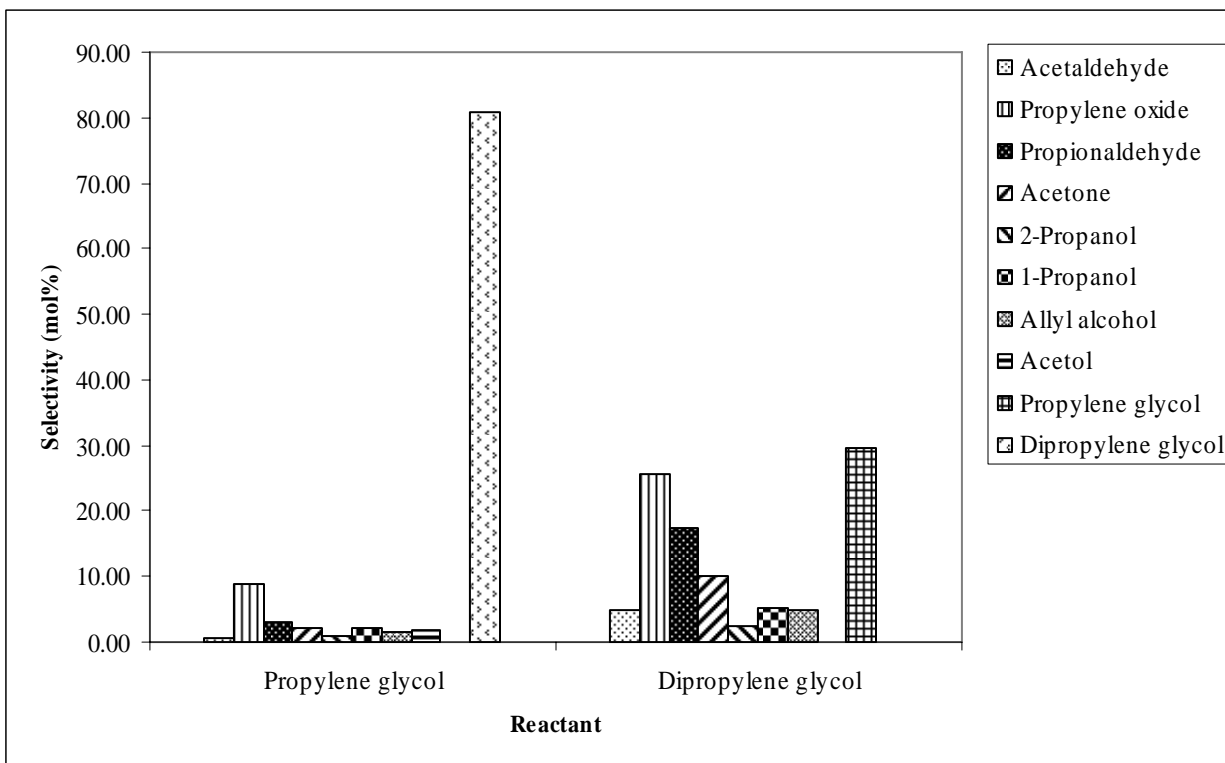


Figure 3.3: Selectivity to various products over 0.1 g of Cs-ETS-10 at 400 °C and N₂ flow rate of 20 SCCM

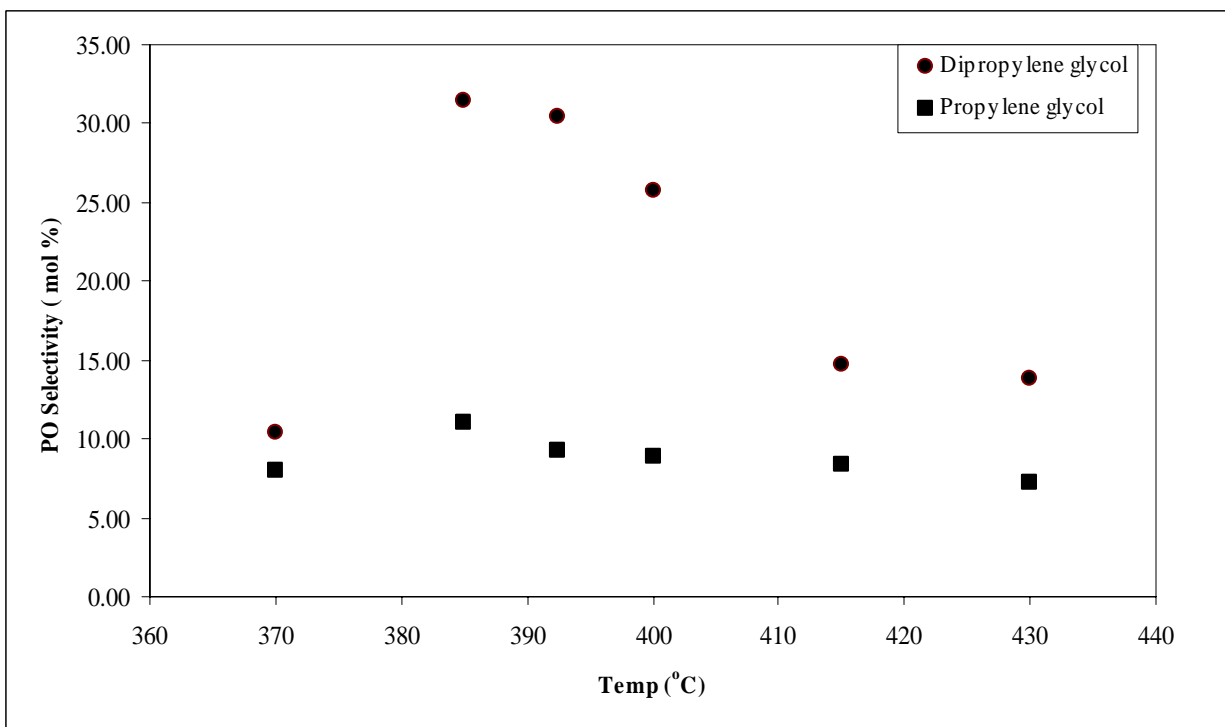


Figure 3.4: Selectivity to PO at various temperatures with 0.1 g of Cs-ETS-10 catalyst and at a N₂ flow rate of 20 SCCM

From Figure.3.3, it could be observed that the selectivity to PO increased to 26% when DPG is used as the feed at 400 °C. In order to further investigate on this, a series of reactions were conducted at a temperature range of 370- 430°C with dipropylene glycol as the reactant. From Figure 3.4, the highest selectivity to PO is observed as 11% at a temperature of 385°C during the dehydration of propylene glycol. However, it could be noted that when dipropylene glycol is used as feed, the highest selectivity to PO is also obtained at 385°C, which is 33%. As the selectivity to DPG decreases after 392.5°C, the selectivity to PO also reduces, leading us to a possible conclusion that the dehydration of PG to propylene oxide over Cs-ETS-10 catalyst could be through dipropylene glycol as the reaction intermediate. The DPG produced during dehydration, might have undergone further dehydration, which eventually led to the production of propylene oxide. Even though DPG appears to be an active intermediate in the production of PO, from Figure 3.4, one could observe that it also produced other various products like acetaldehyde, propionaldehyde, acetone and alcohols i.e. for instance, when 1 mole of DPG reacts to form PO, the other mole of DPG reacts to form the other products. Hence, the maximum selectivity to propylene oxide obtained by dehydration of propylene glycol over Cs-ETS-10 catalyst would be limited to 50% via DPG as the active intermediate. Therefore, catalysts for enhanced PO production must go through a direct dehydration step to be economically viable process rather than through an active intermediate.

3.4.2. Dehydration reaction with Na acac/MgO catalyst

The dehydration reaction of propylene glycol over Na acac/MgO as catalyst gave a selectivity of 12.33% at 400°C. There was no production of dipropylene glycol during

this reaction (see Section 2.4.2). However, it gave a selectivity of 22% and 42% to 1-propanol and acetol, respectively. In order to investigate on the reaction pathway of the dehydration of propylene glycol; 1-propanol, acetol and also DPG were injected as feed over Na acac/MgO as catalyst. The selectivity to various products formed from these three reactions and also from the reaction with propylene glycol is given in Figure 3.4.

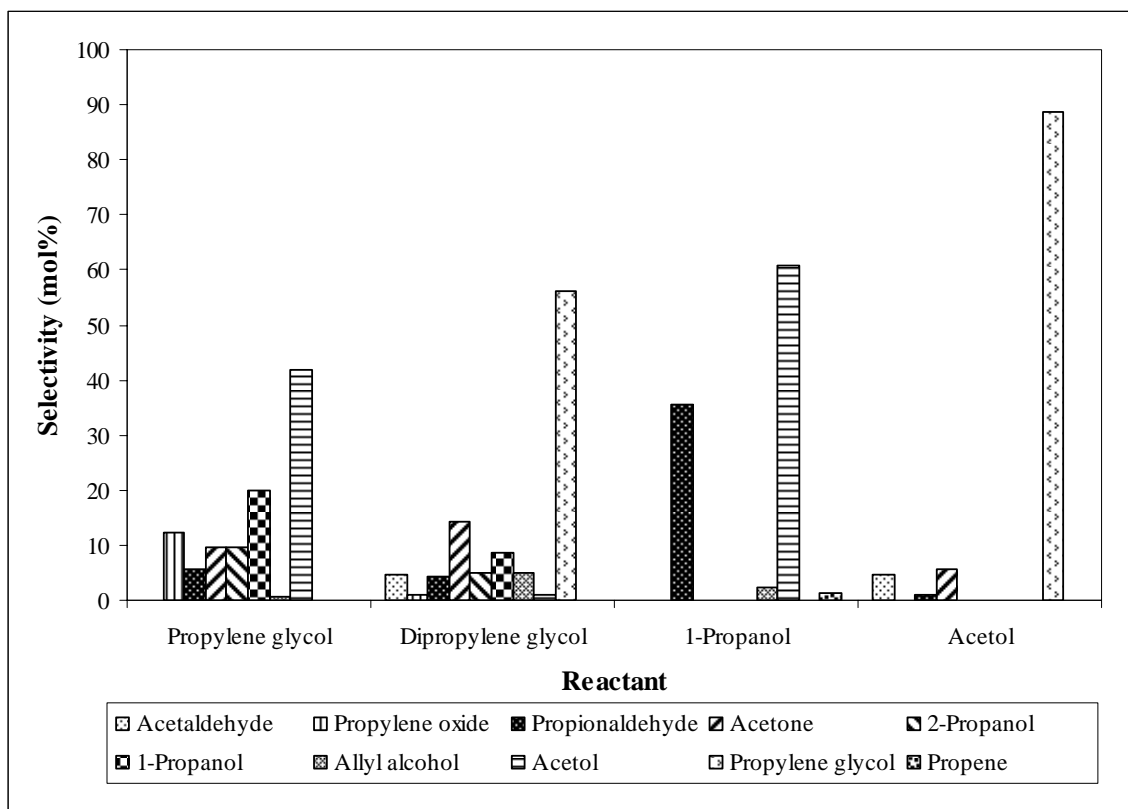


Figure 3.5: Selectivity to various products over Na acac/MgO at 400 °C and at a N₂ flow rate of 20 SCCM

All the reactions were conducted at a temperature of 400°C and N₂ flow rate of 20 SCCM over 0.1 grams of Na acac/MgO catalyst. From Figure 3.3, it could be observed that PO is produced from the dehydration of propylene glycol and DPG. However, there is no production of DPG during the dehydration of propylene glycol over Na acac/MgO

catalyst. Hence, it appears that the dehydration of propylene glycol to PO over Na acac/MgO catalyst could not be through DPG as the reaction intermediate. Furthermore, the reactions with 1-propanol and acetol did not produce any trace of propylene oxide which could lead to the conclusion that the dehydration of propylene glycol over Na acac/MgO catalyst might not be through a particular intermediate like DPG in the case of Cs-ETS-10 catalyst but rather a direct dehydration process.

3.5. Conclusions

The reaction pathway for the dehydration of propylene glycol to propylene oxide over three main catalysts: 2-wt% Na/Al₂O₃, Cs-ETS-10 and Na acac/MgO were investigated. To get a better understanding of the reaction pathway of propylene glycol, the major by-products, acetol, 1-propanol and dipropylene glycol were investigated as a feed over the three catalysts. The dehydration reaction of propylene glycol to propylene oxide over the catalysts 2-wt% Na/Al₂O₃ and Na acac/MgO did not occur through a particular reaction intermediate but via a direct dehydration since there was no increase in the selectivity to PO when pure dipropylene glycol, 1-propanol and acetol were used as the reactants. However, for the dehydration reaction of propylene glycol to PO over Cs-ETS-10 catalyst, a potential reaction intermediate to the production of propylene oxide was identified as dipropylene glycol. Even though DPG appears to be an active intermediate in the production of PO, it also could undergo dehydration directly to form other various products like acetaldehyde, propionaldehyde, acetone and alcohols. Hence, the maximum selectivity to propylene oxide obtained by dehydration of propylene glycol over Cs-ETS-10 catalyst would be limited to 50% via DPG as the active intermediate. Therefore,

catalysts for enhanced PO production must go through a direct dehydration step to be an economically viable process rather than through an active intermediate.

CHAPTER 4

SUMMARY AND FUTURE WORK

4.1. Summary

The objective of this work was to identify catalysts and reaction conditions necessary for the production of propylene oxide from propylene glycol derived from glycerin, a co-product from biodiesel production. A variety of catalysts were prepared and investigated for this study, but only three of the more active catalysts; Na/Al₂O₃, Cs-ETS-10 and Na acac/MgO, are presented here. The dehydration reaction was performed in a plug flow reactor and selectivity to acetaldehyde, propionaldehyde, acetone, 2-propanol, 1-propanol, allyl alcohol, acetol, and dipropylene glycol was analyzed using a Gas Chromatograph (FID). The mass of catalysts, reaction temperatures, residence times were altered to optimize the selectivity to propylene oxide formed. The highest selectivity to PO was obtained as 12.33% over 0.1 grams of Na acac/MgO catalyst at 400 °C and at a N₂ flow rate of 20 SCCM. The flow rate of propylene glycol fed was 1 ml/hr. Even though Cs-ETS-10 catalyst was active for PO production, it also produced higher amounts of dipropylene glycol which significantly reduced the selectivity to propylene oxide. The Na/Al₂O₃ resulted in a low selectivity of 2% to PO, although it gave a high selectivity of 55% to propionaldehyde.

From the reactions conducted with the above catalysts, it was observed that the selectivity to propylene oxide was reduced considerably due to its further reaction to other products.

To investigate this, a set of experiments were conducted using a reactive distillation apparatus to remove the PO formed from the system. The reactions with reactive distillation did not produce any improved selectivity to PO as the low reaction temperature led to low conversion.

The reaction pathway for the dehydration of propylene glycol to propylene oxide over the three main catalysts was also investigated. The major by-products, acetol, 1-propanol and dipropylene glycol were fed as reactants over the three catalysts. The dehydration of propylene glycol to propylene oxide over the catalysts 2-wt% Na/Al₂O₃ and Na acac/MgO did not appear to occur through a reaction intermediate but rather a direct dehydration process. However, for the dehydration reaction of propylene glycol to PO over Cs-ETS-10 catalyst, a potential reaction intermediate to the production of propylene oxide was identified as dipropylene glycol. Even though DPG appears to be an active intermediate in the production of PO, it also could undergo dehydration directly to form other various products like acetaldehyde, propionaldehyde, acetone and alcohols. Hence, the maximum selectivity to propylene oxide obtained by dehydration of propylene glycol over Cs-ETS-10 catalyst would be limited to 50% via DPG as the active intermediate. Therefore, catalysts effective for enhanced PO production must go through a direct dehydration step to be an economically viable process rather than through an active intermediate.

4.2. Future work

Among the ETS-10 catalysts investigated, Na supported on ETS-10 produced results different from ion-exchanged ETS-10 catalysts. Dehydration of propylene glycol performed over 0.1 grams of 1.2 wt% Na/ETS-10 and 2.4 wt% Na/ETS-10 catalysts at 400 °C and at a N₂ flow rate of 20 SCCM are given in Table 4.1

Table 4.1: Selectivity of products over 0.1 g of 1.2 wt% Na/ETS-10 and 2.4 wt% Na/ETS-10 catalysts at 400 °C and at a N₂ flow rate of 20 SCCM

<i>Catalyst</i>	<i>Propylene oxide</i>	<i>Propionaldehyde</i>	<i>Alcohols</i>	<i>Acetone</i>	<i>Dipropylene glycol</i>
1.2%Na/ETS-10	7.0	19.3	13.2	13.08	53.8
2.4%Na/ETS-10	10.3	28.7	15.6	14.46	10.7

From Table 4.1, the selectivity to PO for 1.2 wt% and 2.4 wt% Na/ETS-10 catalysts is observed as 7.0 % and 10.3%, respectively. As the Na loading on ETS-10 is doubled, there is a decrease in the production of DPG which contradicts the results obtained from ion-exchanged ETS-10 catalysts examined. For Cs-ETS-10 catalysts, selectivity to PO was reduced due to the higher production of DPG. Therefore, the dehydration of propylene glycol over Na/ETS-10 catalysts is advantageous for the production of PO, since the selectivity to PO can be increased by increasing the Na loading on ETS-10, which in turn decreases the selectivity to DPG. As explained in section 2.4.2, the formation of DPG appears to be occurring due to the reaction taking place inside the

active pores in the Cs-ETS-10 catalyst. However, in Na/ETS-10 catalysts, Na loaded on to the ETS-10 occupies the pores inside the ETS-10 structure thereby reducing the active pore volume of the catalyst. In effect, the formation of DPG is reduced, which in turn increases the selectivity to PO. More research in this area needs to be conducted to explain the increased selectivity to PO. Also, more base catalysts need to be investigated which may provide a direct dehydration route to the production of PO rather than via an active intermediate.

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