CHAPTER 5
SYNTHESIS OF LONG ALKYL CHAIN ETHERS THROUGH ETHERIFICATION OF ETHYLENE GLYCOL
5.1. INTRODUCTION

Catalytic hydrogenation and/or fermentation of glycerol produces 1,2-propylene glycol, 1,3-propylene glycol and ethylene glycol as main products. Ethylene glycol and propylene glycol have found numerous important applications as building blocks for the synthesis of various valuable chemicals. Thus, the development of new routes for transforming biomass-based glycols into valuable products through innovative catalytic processes is of great relevance in the chemical industry (Parvulescu et al. 2010).

Etherification of bioglycerol or bio-based glycols can directly produce oxygenated fuel additives (Jereme et al. 2008). These products are also used as intermediates in pharmaceutical and agrochemical industries, non-ionic surfactants (Pagliaro et al. 2007), antimicrobial and antiseptic agents (Knifton 1995), and precursors for polymers (Diehl and Eggersperger 1997 and solvents (Queste et al. 2006) Long chain alkyl ethers of glycerol and other glycols were synthesized by using strong mineral acids or alkaline bases as catalysts and alkyl chlorides as alkylating reagents (Baer and Fisher 1941). Bio-based ethylene oxide or propylene oxide are used to produce corresponding alkyl ethers. However, the shortcomings of these processes are due to cumbersome reaction steps and generation of stoichiometric amounts of waste and corrosion of equipment (Smulders 2002). Heterogeneously catalyzed etherification of glycerol and other glycols with alkenes include the use of isobutene or butane (Melero et al. 2008; Klepacova et al. 2005), or cyclic alkenes catalyzed by ion-exchange resins and zeolites such as H-β and HY (Gu et al. 2008). (Zhang and Corma 2007) have reported direct synthesis of 1-octyl ether from the reaction of methanol with 1-octene in the presence of AuCl3/CuCl3 catalysts. H-β as catalyst has been used in the synthesis of long alkyl chain ethers from ethylene and propylene glycols (Ruppert et al. 2009) and in the etherification of glycerol with 1-dodecene (Okuhara et al. 1985). Hence, direct etherification of glycols with 1-octene catalyzed by heterogeneous system is desirable as it represents a greener and direct route.

In our laboratory, substantial research has been done on catalysis by heteropolyacids (HPA) and their modified version supported on K10 clay (Yadav and Doshi 2000; Yadav and Bokade 1996; Yadav 2005; Bokade and Yadav 2012), hexagonal
mesoporous silica (HMS) (Yadav and Manyar 2003; Yadav and Lande 2006), and Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ nano-particles on K10 clay (Yadav et al. 2003; Yadav and Asthana 2003). Etherification of glycerol has also been studied to prepare valuable ethers (Yadav et al. 2012). In this study, 20% w/w H$_3$PW$_{12}$O$_{40}$ (DTP)/K10 clay (Bokade and Yadav 2011), 20% w/w Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$/K10 (Cs-DTP/K10) and 20% w/w DTP/ZrO$_2$, were prepared and their catalytic activities were evaluated in the etherification of ethylene glycol, 1, 2 propylene glycol and glycerol with 1-octene. Effects of various reaction parameters such as speed of agitation, catalyst loading, glycol to 1-octene molar ratio and temperature on the conversion and selectivity are reported. Reaction mechanism and kinetics are also covered.

5.2. Experimental

5.2.1. Chemicals and catalysts

The following chemicals were procured from renowned companies and used without further purification: Ethylene glycol, 1-octene, dodecatungstophosphoric acid (DTP), montmorillonite K10 clay, cesium chloride, Amberlyst-35, zirconium oxide (M/s. Alfa Aesar, Canada), and ethanol (M/s. Sigma-Aldrich, Canada). All other chemicals were procured from Sigma-Aldrich.

5.2.2. Catalyst synthesis

Supported heteropolyacids (HPA) were synthesized by the incipient wetness technique. The following process was adapted to make 10 g of catalyst: 2 g of dodecatungstophosphoric acid (DTP) was dissolved in 20 ml methanol and it was added drop wise to 8 g K10 clay, under constant stirring until a thick paste was formed. The paste was kneaded to obtain fine powder. The mixture was further dried in oven to remove methanol at 120ºC for 2 h. It was calcined at 280ºC for 3 h to obtain DTP/K10 catalyst. Prior to use, the catalyst was dried in oven to remove moisture. Similar procedure was followed to synthesize 20% w/w DTP/ZrO$_2$. 20% w/w Cs-DTP/K10 was prepared as per our earlier work (Yadav et al. 2003; Yadav and Asthana 2003).
5.2.3. Catalyst characterization

X-ray powder diffraction (XRD) was performed using a Bruker D8 Advance series-II instrument Germany, with Cu Kα radiation, to analyze crystallinity and phase purity of synthesized catalysts. The XRD patterns were recorded by scanning the sample within the 2θ range of 10 to 80°. The specific surface area, pore volume and pore diameter of each sample were obtained from nitrogen adsorption-desorption isotherms measured in Micromeritics ASAP 2000 instrument and specific surface areas of all catalysts were calculated by using the BET model. Thermo gravimetric analysis (TGA) was performed in the range of 25 to 500°C using a Perkin Elmer Pyris Diamond instrument. Fourier transform infrared (FTIR) spectra were collected on a Perkin Elmer Spectrophotometer in the range of 400 to 4000 cm⁻¹ using a sample disk of 5% w/w catalyst weight in KBr powder.

5.2.4. Catalytic experiments and analytical methods

In a typical experiment, 0.12 mol alcohol (glycol or glycerol), 0.36 mol 1-octene and 0.01g/cm³ of catalyst were loaded in a 100 ml stainless steel Parr autoclave. The autoclave was flushed with nitrogen to remove moisture and then pressurized with an additional 1.5 MPa of nitrogen, in order to maintain 1-octene in the liquid phase during the course of reaction. The autoclave was heated to 140°C under continuous stirring at 800 rpm. When the autoclave reached the desired temperature, an initial sample was withdrawn and thereafter sampling was done at regular intervals of time. The product samples were dissolved in a known amount of ethanol for GC analysis. At the end of the reaction, the autoclave was cooled to room temperature; the catalyst was removed and separated by filtration. Analysis was carried out using GC (Hewlett Packard 5890 instrument with FID detector, and stabilwax column of length: 30m, ID: 0.25mm, DF: 0.50). The products were confirmed by GC-MS (Varian, Saturn 2000 instrument) using the same capillary column. The same procedure was used for the other alcohols.
5. 3. RESULTS AND DISCUSSION

5.3.1. Catalyst characterization

5.3.1.1. X-ray powder diffraction (XRD)

Preliminary experimental results show that the 20% w/w DTP/K10 was a promising catalyst for this process; hence all characterization studies were undertaken for this catalyst. The crystallinity and phase purity of the synthesized catalyst was determined by X-ray powder diffraction (XRD) (Bruker D8 Advance series-II instrument Germany) with Cu Kα radiation. The XRD patterns for K-10 shows one peak at \(2\theta=28.1^\circ\), which is due to quartz, and there is no effect on the \(2\theta\) value of quartz even after exchanging K-10 clay with DTP. It was observed that some peaks after DTP loading on K-10 clay in these XRD patterns confirmed that the DTP were properly loaded on K-10 clay, and improved the crystallinity of the catalyst. (Figure 5.1)
5.3.1.2. BET surface area analysis

The specific surface area, pore volume and pore diameter were determined by N₂ adsorption-desorption isotherms using a Micromeritics ASAP 2000 instrument. The catalyst samples were degassed under vacuum at 300°C for 3 h. The measurements were made using N₂ gas as the adsorbent and with a multipoint method. Isotherms were measured at liquid nitrogen temperature. Surface area, pore volume and pore diameter were calculated from N₂ adsorption-desorption isotherm using conventional BET method. The specific surface area of K-10 clay (270.75 m²/g) was found to decrease with DTP loading on K-10 clay which may be due to the blockages of pores by DTP loading on K-10 clay (Table 5.1).

Table 5.1: BET surface areas of studied catalysts

<table>
<thead>
<tr>
<th>No.</th>
<th>Catalyst</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K-10 clay</td>
<td>270.7</td>
<td>0.39</td>
<td>5.86</td>
</tr>
<tr>
<td>2</td>
<td>20% DTP-K10</td>
<td>174.0</td>
<td>0.28</td>
<td>6.64</td>
</tr>
<tr>
<td>3</td>
<td>20% Cs-DTP-K10</td>
<td>170.0</td>
<td>0.38</td>
<td>5.64</td>
</tr>
<tr>
<td>4</td>
<td>20% DTP-ZrO₂</td>
<td>146.2</td>
<td>0.22</td>
<td>3.26</td>
</tr>
<tr>
<td>5</td>
<td>Amberlyst-35</td>
<td>52.0</td>
<td>0.39</td>
<td>23.5</td>
</tr>
</tbody>
</table>

5.3.1.3. Thermo gravimetric analysis (TGA)

The thermo gravimetric analysis (TGA) of selected catalysts were carried out on bulk DTP, K-10 clay and 20% w/w DTP/K-10 catalysts by using a TGA Perkin Elmer Pyris Diamond instrument to determine the thermal stability of the catalyst. The TGA was performed to obtain weight loss as a function of temperature in the range of 25 to 500°C (Figure 5.2). The TGA of bulk DTP shows a weight reduction of about 7% up to 200°C due to the loss of free and adsorbed water. Then the bulk DTP was found to be thermally stable up to 500°C. The TGA of K-10 clay shows a steady loss of about 12% up to 500°C,
which is due to the removal of physisorbed and interlayer water and the dehydroxylation caused by the breaking of structural OH-groups of support (Silva et al. 2009). The TGA of 20% DTP/K-10 catalyst showed about 5% weight loss within the temperature range of 50-400°C, due to the loss of adsorbed water molecules. Then there is gradual loss about 2% up to 500°C, which seems to increase thermal stability of DTP supported on K-10 clay. This may be due to the bonding interaction between DTP and K-10 clay.

![Thermo gravimetric analysis of catalyst](image.png)

**Figure 5.2: Thermo gravimetric analysis of catalyst**

### 5.3.1.4. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectra of catalyst samples were collected on a Perkin Elmer Spectrophotometer (Figure 5.3). Catalyst samples were prepared by mixing 5% catalyst weight in KBr powder. A pellet was made by applying 10 tone pressure. All catalyst samples were scanned in the range of 400 to 4000 cm⁻¹. The IR spectra for bulk
DTP are shown at 1090 cm\(^{-1}\) (P-O in central tetrahedral), at 1010 cm\(^{-1}\) (terminal W=O), and one small band nearby at 960 cm\(^{-1}\) (W-O-W) associated with the asymmetric vibrations of the Kegginpolyanion. On K-10 supported catalysts, some of the characteristic Keggin bands are seen at 980 and 830 cm\(^{-1}\) and other bands are exhibited as in case of K-10 clay. The FTIR for 20% w/w DTP/K10catalyst shows that the primary Keggin structure is retained.

![FTIR spectra of catalysts](image)

**Figure 5.3: FTIR spectra of catalysts**

### 5.3.2 Etherification of ethylene glycol with 1-octene

The reaction products showed both mono- (major) and di-etherified species as given in Scheme 1 which is due to consecutive reactions.
5.3.2.1. Catalyst screening

The etherification of ethylene glycol with 1-octene was carried out using different solid acid catalysts such as 20% w/w Cs-DTP/K-10, 20% w/w DTP/ZrO\textsubscript{2} and 20% w/w DTP/K-10 and cation exchange resin Amberlyst -35 with the following conditions: temperature 140\degree C, ethylene glycol:1-octene molar ratio of 1:3, speed of agitation 800 rpm, catalyst loading 0.03 g cm\textsuperscript{-3}, and N\textsubscript{2} pressure of 1.5 MPa, in a solventless system. Each run was conducted for a reaction time of 5 h and average of three runs was taken with a standard deviation of ±2.5. The activities were as follows: 20%w/w DTP/K-10 (best) > 20%w/w Cs-DTP/K-10 > 20% w/w DTP/ZrO\textsubscript{2} > Amberlyst-35 (Figure 5.4). 20% w/w DTP/K-10 catalyst gave the highest ethylene glycol conversion of 72%. This can be attributed to the more number of active sites spread on a high surface area (174.0 m\textsuperscript{2}/g) and showing super acidic properties. The acid strength of DTP/K-10 is 0.423 mmol g\textsuperscript{-1} (Yadav and Lande 2006) as compared to 20% w/w Cs-DTP/K-10. 20% w/w Cs-DTP/K-10 gave somewhat less conversion of 67% vis-a-vis 20% w/w DTP/K-10. This is due to somewhat less number of acidic sites (0.405 mmol g\textsuperscript{-1}) and surface area (170 m\textsuperscript{2}/g) as compared to 20% w/w DTP/K-10. Whereas 20% w/w DTP/ZrO\textsubscript{2} gave 58% conversion, which can be attributed to its less surface area (146 m\textsuperscript{2}/g) and less acidity; it is due to the support zirconia. It is reported that K-10 clay is better support for etherification reactions of glycols (Yadav et al. 2003). Whereas Amberlyst-35 shows the least conversion of
ethylene glycol at 30% because it has very less surface area (52 m²/g) and less available acidity as compared to other tested catalysts. Hence 20% w/w DTP/K10 catalyst was used for further study.

![Catalyst screening](image_url)

**Figure 5.4: Catalyst screening for etherification of ethylene glycol with 1-octene**

Reaction conditions: Reaction conditions; Temperature 140°C, molar ratio (ethylene glycol:1-octene) of 1:3, speed of agitation 800 rpm, catalyst loading of 0.03 g cm⁻³, N₂ pressure 1.5 MPa, reaction time of 5 h

5.3.2.2. Effect of speed of agitation

Effect of speed of agitation was studied in the range of 600-1000 rpm with 0.03 g.cm⁻³ catalysts loading at 140°C and ethylene glycol to 1-octene molar ratio of 1:3 for 5 h (Figure 5.5). It was observed that there was a marginal increase in conversion of
ethylene glycol when speed of agitation was increased from 600 to 800 rpm and not much change in the conversion was observed from 800 to 1000 rpm. Hence further experiments were carried out at 800 rpm to ensure that external mass transfer effects did not influence the reaction.

![Graph showing conversion vs time](image)

**Figure 5.5: Effect of speed of agitation on etherification of ethylene glycol with 1-octene using 20% DTP/K-10 catalyst**

Reaction conditions; Temperature 140°C, Molar ratio (ethylene glycol:1-octene) of 1:3, catalyst loading 0.03 g cm⁻³, N₂ pressure 1.5 MPa, reaction time 5 h. (●) 600 rpm; (●) 800 rpm; (▲) 1000 rpm

**5.3.2.3. Effect of mole ratio**

Effect of ethylene glycol to 1-octene molar ratio was studied at 1:1, 1:2, 1:3, and 1:4 at 140°C. Ethylene glycol conversion was increased with increasing molar ratio. At
1:1 mole ratio, the conversion was 57% which increased to 72% at 1:3 mole ratio. Further increase in mole ratio up to 1:4 did not increase the conversion much. Hence mole ratio of 1:3 was found optimum and used for further study. The selectivity of 2-(octan-2-yloxy) ethanol (C8 ether) did not increase much when mole ratio increased form 1:1 to 1:4 and it was found almost similar for all the cases. In the case of mole ratio of 1:3, the selectivity of 2-(octan-2-yloxy) ethanol (C8 ether) and 1,2-bis(octan-2-yloxy) ethane (C16 ether) was 80% and 14%, respectively. For 1:4 mole ratio, selectivity of 1,2-bis(octan-2-yloxy) ethane (C16 ether) increased from 14 to 16% whereas 2-(octan-2-yloxy) ethanol (C8 ether) selectivity was almost the same. Hence mole ratio of 1:3 was selected to be optimum and considered for further studies (Figure 5.6).

**Figure 5.6: Effect of mole ratios on etherification of ethylene glycol with 1-octene**

Reaction conditions; Temperature 140°C, speed of agitation 800, catalyst loading 0.03 g cm⁻³, N2 pressure 1.5 MPa, reaction time 5 h. (♦) 1:1; (■) 1:2; (▲) 1:3; (×) 1:4
5.3.2.4. Effect of catalyst loading

The effect of catalyst loading on the conversion of ethylene glycol was studied from 0.01 to 0.04 g cm\(^{-3}\) of total reaction mixture at 140\(^\circ\)C for 5 h. With increase in catalyst loading, the conversion of ethylene glycol increased. This is due to the increase in total number of active sites and availability of large surface area of the catalyst. In the absence of external mass transfer resistance, the rate of reaction is directly proportional to catalyst loading. Hence with increase in catalyst loading from 0.01 to 0.04 g cm\(^{-3}\), the conversion of ethylene glycol increased from 37 to 74%. After 0.03 g cm\(^{-3}\) catalyst loading, there was no major increase in conversion of ethylene glycol. Hence 0.03 g cm\(^{-3}\) catalyst loading was found as the optimum and was chosen for reusability studies. The initial rate of reaction, given as change in fractional conversion with respect to time (\(\frac{dX}{dt}\)) was directly proportional to catalyst loading (Figure 5.7).

![Figure 5.7: Plot of initial rate of reaction vs catalyst loading](image-url)

\[ y = 159.7x \]
\[ R^2 = 0.996 \]

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5.3.2.5. Effect of reaction temperature

Ethylene glycol conversion and selectivity to 2-(octan-2-yloxy) ethanol (C8 ether) was studied in the temperature range of 120 to 150°C. With increase in temperature, the conversion of ethylene glycol also increased from 40% at 120 °C to 81 % at 150 °C (Figure 5.8). At 150°C, the initial rate of reaction was high and also the formation of by-products increased from 6 to 11% (Scheme 5.2). To reduce formation of byproducts, 140°C was taken as an optimum temperature.

Scheme 5.2: Observed by-products of etherification of ethylene glycol at 150 °C
Figure 5.8: Effect of temperature on etherification of ethylene glycol with 1-octene

Reaction conditions: Molar ratio (ethylene glycol:1-octene) of 1:3, speed of agitation 800 rpm, catalyst loading 0.03 g cm⁻³, N₂ pressure 1.5 MPa, reaction time 5 h. (♦) 120°C; (■) 130°C; (▲) 140°C; (×) 150°C

5.3.2.6 Product selectivity profile

The product selectivity profile of etherification of ethylene glycol with 1-octene by using 20% w/w DTP/K10 catalyst was studied with the following conditions: temperature 140°C, catalyst loading 0.03 g cm⁻³, molar ratio of ethylene glycol: 1-octene is 1:3, speed of agitation 800, nitrogen pressure 1.5 MPa, reaction time 5 h. (Figure 5.9) shows conversion of ethylene glycol and selectivity to 2-(octan-2-yl)oxy) ethanol (C₈ ether), 1,2-bis(octan-2-yl)oxy) ethane (C₁₆ ether) and other byproducts after 5 h. It was found that the conversion of ethylene glycol was 72% at 5 h. Initially C₈ ether selectivity was found to be 85% which decreased gradually to 80% and C₁₆ ether selectivity increased from 9% to 14% at 5 h. Selectivity of C₈ ether and C₁₆ ether did not change with time which was due to the use of lower mole ratio of ethylene glycol: 1-octene of 1:3. The byproducts in this study were acetaldehyde and di-ethylene glycol at 6% in 5 h. These byproducts were formed due to dehydration and self-condensation of ethylene glycol respectively in presence of acid catalyst and higher temperature.
Figure 5.9: Product selectivity profile

Reaction conditions; Temperature 140°C, molar ratio (ethylene glycol:1-octene) of 1:3, speed of agitation 800 rpm, catalyst loading 0.03 g cm⁻³, N₂ pressure 1.5 MPa, reaction time 5 h. (■) Conversion (■) Selectivity of C8 ethers; (▲) Selectivity of C16 ethers; (☆) Selectivity of others

5.3.2.7. Reaction mechanism and kinetics

In the case of present studies, it is essential to understand the reaction mechanism to develop a suitable model. The initial rate data were analyzed on the basis of Langmuir-HinsHELWOOD-Hougen-Watson (LHHW) mechanism. From the initial rate data, the following analysis was found to be most appropriate. Scheme 5.3 can be used to arrive at the LHHW type of mechanism.
The rate data could be interpreted using weak adsorption of all species. This is a consecutive reaction wherein at the used conditions; the predominant reaction is the first reaction where more that 80% selectivity is to the mono-ether. Thus, simple second order reaction kinetics could be written:

\[-r_A = \left( -\frac{dC_A}{dt} \right) = kwC_AC_B \]

\[\frac{dX_A}{dt} = kC_Aw(1-X_A)(M-X_A)\]
Synthesis of long alkyl chain ethers through etherification of ethylene glycol

\[
\ln \left( \frac{(M - X_d)}{M(1 - X_d)} \right) = k_i t
\]  
(5.3)

\[
k_i = C \cdot k_w
\]  
(5.4)

\[
M = \frac{C_{B_0}}{C_{A_0}}
\]  
(5.5)

Thus, in consonance with Eq. 3, a plot of \( \ln \left( \frac{(M - X_d)}{M(1 - X_d)} \right) \) Vs \( t \) was made at different catalyst loadings (w) to get straight lines passing through origin; the slopes of each line divided by \( C \cdot (M - 1) \) gives the average \( k \) values (Figure 5.10). The rate of reaction is proportional to the number of active sites present on the surface. It would therefore mean that the reaction mechanism is LHHW type with very weak adsorption of both the reactants in the absence of any diffusional resistance. The values of \( k \) were also found at different temperatures at the same \( w \) and \( M \) (Figure 5.11). (Figure 5.12) gives the Arrhenius plot, from which the apparent activation energy was calculated as 15.23 kcal/mol. The high value of activation energy also supported the fact that the overall rate of reaction is not influenced by external mass transfer or intra-particle diffusion resistance and it is intrinsically kinetically controlled reaction on active sites.
Figure 5.10: Slope $k_1$ vs Catalyst loading ($w$) (g/cm$^3$)
Figure 5.11: Second order plot of \(-\ln \{\frac{(M-XA)}{M(1-XA)}\}\)

\[y = 0.0052x \quad R^2 = 0.9998\]
\[y = 0.0036x \quad R^2 = 0.9993\]
\[y = 0.0023x \quad R^2 = 0.9993\]
\[y = 0.0014x \quad R^2 = 0.9982\]
5.3.2.8 Catalyst reusability

Catalyst reusability study was carried out by performing the reaction under optimized reaction conditions of temperature 140°C, speed of agitation 800 rpm, molar ratio of ethylene glycol to 1-octene is 1:3, 0.03 g cm$^{-3}$ catalyst loading, $N_2$ pressure is 1.5 MPa, reaction time of 5 h (Figure 5.13). After completion of the reaction, the catalyst was recovered by filtration from reaction mixture, washed with methanol and then calcined at 280°C for 3 h, in flowing air to remove adsorbed material from the catalyst. The loss of catalyst was about 2 to 3 % during these operations which was made up by the fresh catalyst, and catalyst reusability study was carried out. This catalyst showed good activity without changing the selectivity of 2-(octan-2-yloxy) ethanol (C8 ether) and 1,2-bis(octan-2-yloxy) ethane (C16 ether), even after three reaction cycles.

$y = -7.666x + 12.94$

$R^2 = 0.999$

Figure 5.12: Arrhenius plot
Reaction conditions: Temperature 140°C, Molar ratio (ethylene glycol:1-octene) of 1:3, speed of agitation 800, catalyst loading 0.03 g cm⁻³, N₂ pressure 1.5 MPa, reaction time of 5 h. ( ■) Conversion ( □) Selectivity of C8 ethers; ( ■) Selectivity of C16 ethers: ( ■) Selectivity of others

**5.3.2.9 Substrate scope and product selectivity**

20% w/w DTP/K10 catalyst was used in etherification of glycerol and 1,2-propylene glycol at optimized reaction conditions. In all substrates, higher selectivity of 2-(octan-2-yloxy) ethanol (C8 ether) was obtained. The conversion and selectivity to the 2-(octan-2-yloxy) ethanol (C8 ether) was influenced by both the type of alcohol and the catalyst used. In the case of glycerol, the conversion was very less (20%), but the
selectivity towards C8 ether was good at 78%. In the case of 1,2-propylene glycol, conversion of 69% was obtained with 82% selectivity of C8 mono ethers. With ethylene glycol, 72% conversion was achieved with 80% selectivity towards 2-(octan-2-yloxy) ethanol (C8 ether) ether (Table 5.2). It is reported in the published literature that the size and hydrophilic/hydrophobic properties of the alcohols influence the etherification activity on the heterogeneous catalyst system. Glycols are more hydrophobic than glycerol and in the absence of solvent they can react better with the alkenes. The hydrophobic characteristics increase in the series of 1,2 propylene glycol > ethylene glycol > glycerol. Hence ethylene glycol and 1,2 propylene glycol gave more conversion as compared to glycerol.

Table 5.2: Substrate scope of alcohols for etherification activity with 1-octene using 20% DTP/K-10 catalyst

<table>
<thead>
<tr>
<th>Substrate</th>
<th>(% Conversion)</th>
<th>(% Selectivity)</th>
<th>(%) Selectivity</th>
<th>(% Selectivity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol</td>
<td>72</td>
<td>80</td>
<td>14</td>
<td>06</td>
</tr>
<tr>
<td>1,2 Propanediol</td>
<td>69</td>
<td>82</td>
<td>13</td>
<td>05</td>
</tr>
<tr>
<td>Glycerol</td>
<td>20</td>
<td>78</td>
<td>12</td>
<td>10</td>
</tr>
</tbody>
</table>

Reaction conditions: temperature 140°C, speed of agitation 800 rpm, molar ratio of ethylene glycol to 1-octene is 1:3; 0.03 g cm⁻³ catalyst loading, N₂ pressure is 1.5 MPa, reaction time of 5 h

5. 4. CONCLUSIONS

Etherification of ethylene glycol was studied with 1-octene, in a solventless system by using heterogeneous solid acid catalysts. The type of solid acid catalyst used strongly influences the activity of the etherification process. Also hydrophilicity of the alcohols is responsible in the etherification process. 20% w/w DTP/K-10 was the best catalyst which was robust and recyclable. Effect of several parameters was studied and
Synthesis of long alkyl chain ethers through etherification of ethylene glycol

optimized with detailed characterization of the selected catalyst. Kinetic model was
developed and validated. These results showed the potential of using heterogeneous solid
acid catalysts such as 20% (w/w) DTP/K10 for green synthesis of valuable long alkyl 2-
(octan-2-yloxy) ethanol (C8 ether) and 1,2-bis(octan-2-yloxy) ethane (C16 ether) from
various bio-based alcohols.
5.5 NOMENCLATURE

A  Ethylene glycol
B  1-octene
C  Mono-octyl ether
C_A Concentration of ethylene glycol, mol cm^{-3}
C_B Concentration of 1-octene, mol cm^{-3}
C_C Concentration of mono-octyl ether mol cm^{-3}
C_D Concentration of di-octyl ether mol cm^{-3}
M  Molar ratio of initial concentration of B to A
k_1 Pseudo-rate constant, min^{-1}
-r_A Rate of reaction, mol/cm^3/min
t  Time, min
w  Catalyst loading, g/cm^3
X_A Fractional conversion of A