Article

Solvent-Free Benzylolation of Glycerol by Benzyl Alcohol Using Heteropoly Acid Impregnated on K-10 Clay as Catalyst

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Abstract: Value addition to glycerol, the sole co-product in biodiesel production, will lead to reform of the overall biodiesel economy. Different valuable chemicals can be produced from glycerol using heterogeneous catalysis and these valuable chemicals are useful in industries such as cosmetics, pharmaceuticals, fuels, soap, paints, and fine chemicals. Therefore, the conversion of glycerol to valuable chemicals using heterogeneous catalysis is a noteworthy area of research. Etherification of glycerol with alkenes or alcohols is an important reaction in converting glycerol to various value-added chemicals. This article describes reaction of glycerol with benzyl alcohol in solvent-free medium by using a clay supported modified heteropolyacid (HPA), $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ /K-10 (Cs-DTP/K-10) as solid catalyst and its comparison with other catalysts in a batch reactor. *Mono-Benzyl glycerol ether* (MBGE) was the major product formed in the reaction along with formation of *di-benzyl glycerol ether* (DBGE). The effects of different parameters were studied to optimize the reaction parameters. This work provides an insight into characterization of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ /K-10 catalyst by advanced techniques such as surface area measurement, X-ray analysis, ICP-MS, FT-IR, and SEM. Reaction products were characterized and confirmed by using the GCMS method. The kinetic model was developed from an insight into the reaction mechanism. The apparent energy of activation was found to be 18.84 kcal/mol.

Keywords: glycerol; benzylolation; etherification; *mono-benzyl glycerol ether*; heteropolyacid

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1. Introduction

The sustainability of raw materials is the major challenge for the chemical and allied industries [1]. Biodiesel, a popular term for the fatty acid methyl esters, is an alternative to fossil fuels. As reported by He and Yang in their review on renewable and sustainable energy, the global market of glycerol is predicted to grow up to USD 2.52 billion by end of 2020, and biodiesel is predicted as a leading source for the production of glycerol, with more than 1400 kt production in the year 2017 [2]. As a result, glycerol production is climbing at an annual growth rate of >50% [3]. Thus, bio glycerol offers an opportunity as a potential building block to produce a variety of valuable derivatives [4–8] which have further applications as fuel additives [9], cryogenics [10], and in detergent, pharmaceutical, food, and cosmetic industries. Some of these industries use glycerol and its ethers as green solvents [11]. Glycerol on reaction with either alcohols or alkenes produces ethers which are used as fuel additives [12]. In the present work etherification of glycerol was carried out using solid acid catalysts. Depending up on the reaction parameters *mono*-, *di*- or *tri*- ether of glycerol can be formed. Glycerol mono ethers are also called as ‘solvo-surfactants’ owing to their dual characteristics of solvent as well as surfactant. Glycerol *tert*-butyl ethers are identified as alternate fuel additives to methyl *tert*-butyl ether (MTBE) in diesel and produced by etherifying glycerol with 2-butene or *tert*-butanol using acid

catalysts [13,14]. Properties such as acid strength, distribution of hydrophilic and lipophilic sites, and surface porosity of the catalyst are important in controlling the progress of the etherification reaction [15]. Dominguez et al. studied glycerol etherification with *tert*-butanol by Amberlyst-15, a cation exchange resin catalyst leading to 96% glycerol conversion after 180 min. at 90 °C for *tert*-butanol to glycerol molar ratio of 4:1 [16]. Gu et al. reported use of SO₃H catalysts to react glycerol with different alcohols such as benzyl alcohol, propargyl and allyl alcohols, olefins, to corresponding MAGEs in 60% to 90% yield [17]. Their method introduced a metal and salt free catalytic path for etherification of glycerol. Barrault et al. described 88% regioselective formation of α -monoalkyl glycerol ether at 80 °C over acid treated silica (SiO₂-SO₃H) [18]. Some reports are available on glycerol benzylation using benzyl alcohol by homogeneous as well as heterogeneous solid acid catalysis.

The present work describes reaction of glycerol with benzyl alcohol using acid catalysts in a batch reactor. As shown in Scheme 1; *mono*-benzyl glycerol ether (MBGE) and *di*-benzyl glycerol ether (DBGE) were formed with *di*-benzyl ether as the by-product by sequential reaction of MBGE. MBGE is used as surfactant and fuel additive. Products MBGE and DBGE are important intermediates used for synthesis of various valuable products. The amino derivative of MBGE is used as an α and β adrenergic blocking agent while MBGE has application as an intermediate for the synthesis of anti-microbial active agents [19,20]. Many reactions of industrial practice are catalysed by acids which need to be replaced by solid acids and super acids to increase selectivity, process efficiency and for reducing the environmental footprint [21–39]. In this regard, heteropolyacids [21–25], acid treated clays [21,25], sulphated zirconia, and its modified versions including UDCaTs [26–33], supported heteropoly acids and particularly dodecatungstophosphoric acid (DTP) and cesium modified DTP on K-10 clay [34–39], and ion exchange resin [40] has been used for alkylation reactions. The other reactions include nitration, acylation, cracking, isomerization, oligomerization, and polymerisation, etc. Our research group has been at the forefront of designing, synthesis, characterization and application of such materials in a spectrum of chemical processes in the literature cited above. The above literature also showed that this cesium modified DTP on K-10 clay catalyst was found to be a stable and robust heterogeneous catalyst for wide range of types of acid catalysed unit operations and reaction conditions. This prompted and motivated us to undertake the study of efficacy and stability of this catalyst for glycerol benzylation.

Scheme 1. Reaction products for benzylation of glycerol with benzyl alcohol.

The best catalyst, 20% *w/w* Cs_{2.5}H_{0.5}PW₁₂O₄₀/K-10, was physico-chemically studied by advanced analytical techniques, such as surface porosimetry, ICPMS, FT-IR, X-ray diffraction, and SEM. Products were confirmed by mass spectroscopic method. Characterization of fresh as well as used catalyst was conducted to study the morphological and chemical changes in the catalyst during the reaction.

2. Result and Discussion

2.1. Efficacy of Different Catalysts

A series of solid acid catalysts was assessed to study their efficacy for benzylation of glycerol. Commercially available catalyst Amberlyst-15 was used along with 20% *w/w* DTP/K-10 and UDCaT-4 to evaluate their efficacy. Figure 1 compares the performance of 20% *w/w* Cs_{2.5}H_{0.5}PW₁₂O₄₀/K-10, Amberlyst-15, 20% *w/w* DTP/K-10, and UDCaT-4 catalysts. The purpose of screening a series of solid acid catalysts was to understand the effect of surface morphology, acid strength, and pore size distribution on glycerol conversion and its effect on selectivity towards MBGE. All these catalysts were screened at 150 °C, 1:3 glycerol to benzyl alcohol mole ratio for 4 h with 0.03 g/cm³ loading of catalyst. It was found that 20% *w/w* Cs_{2.5}H_{0.5}PW₁₂O₄₀/K-10 clay showed maximum (48%) conversion of glycerol with 76% selectivity for MBGE. The mass spectra of the MBGE (Figure S1) and DBGE (Figure S2) are enclosed as Supplementary Material.

Figure 1. Efficacy of different catalysts. Temperature: 150 °C. Catalyst loading: 0.03 g/cm³. Glycerol:BA mole ratio = 1:3, speed of agitation: 1000 rpm, reaction time: 4 h. (◆) MBGE; (✱) DBE; (▲) DBGE.

2.2. Product Profile

The published literature shows different product distribution as a result of type of catalyst and various reaction parameters for different solid acid catalysts. β -Zeolite and Amberlyst-35 gave MBGE as the main product whereas when *p*-toluenesulfonic acid (PTSA)

and K-10 montmorillonite clay were used as catalyst; the product di-benzyl ether was found in higher yield [41]. Reaction temperature has predominant effect on product distribution and course of reaction. Nature of catalyst support plays deciding role in controlling the reaction equilibrium by shifting it in forward direction as seen in montmorillonite clay by adsorbing the water of reaction formed during the course of the reaction. In the present study MBGE was the main product formed with 76% selectivity. *Mono*-benzyl glycerol ether and di-benzyl glycerol ether were extracted in ethyl acetate and were further isolated by column chromatography in hexane and ethyl acetate phase. The purified compound diluted in methanol and injected for direct mass analysis using +ve ESI (Electron Spray Ionisation) mode. The distinct peak at m/z 205 confirms the molecular ion peak (M^+) +23; whereas molecular weight for *mono*-benzyl glycerol ether is 182 m/z . The peak at m/z 295 confirms the (M^+) +23 whereas molecular ion (M^+) for *di*-benzyl glycerol ether is 272 m/z .

2.3. Catalyst Characterization

Primary structures of K-10 supported DTP and cesium exchanged DTP were established by studying their FT-IR absorbance bands over DTP on K-10, bulk unsupported K-10, and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ having IR bands at approximately 1080 cm^{-1} (P–O bond in central tetrahedral), 985 cm^{-1} (W=O terminal bond), 895 cm^{-1} and 810 cm^{-1} (W–O–W bond) related with the asymmetric vibrations of Keggin polyanion [35] (Figure 2). $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ is characterized by splitting in the W=O band, suggesting direct interaction with the poly anion and Cs^+ cation. FT-IR study of 20% w/w DTP supported on K-10 and 20% w/w $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ /K-10 reveal that the primary Keggin structure remained undistorted in both cases when supported on K-10 clay. When characteristic peaks of bulk heteropoly acid and K-10 clay are overlaid on each other, no shift in the position of the peaks was observed for the supported catalysts. A sharp peak at 1630 cm^{-1} confirms the presence of H_3O^+ (Bronsted acidity). Water is bound as water of crystallization in DTP, while in $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ /K-10 it specifies the presence of partial H^+ ion attached to the polyanion (–O–H) and present in K-10 possibly as H_3O^+ [35].

Figure 2. FT-IR patterns of unsupported K-10, bulk DTP on K-10 and 20% w/w Cs-DTP/K-10.

BET (Brunauer, Emmett and Teller) surface area analysis results of prepared catalysts is presented in Table 1. Surface area of K-10 is $273\text{ m}^2/\text{g}$ which is more than that of

$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$ ($239.6 \text{ m}^2/\text{g}$). Plots from pore size distribution of these catalysts suggests that the average pore size of catalytic materials is found in the range of 5.0 to 6.5 nm suggesting that they fall in the mesoporous region of pore size, i.e., $>2 \text{ nm}$. The adsorption-desorption isotherm of DTP/K-10, bulk K-10, and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$ showed that they are of the form of Type IV isotherm type H_3 hysteresis loop, a feature of mesoporosity for solid materials. This study also helped to check any morphological changes had occurred in the catalysts after the completion of the reaction. Results in Table 1 show very marginal changes in the surface area, pore volume, and pore diameter of the catalyst after the reaction.

Table 1. Surface area, pore volume and pore diameter analysis.

Catalyst	BET Surface Area (m^2/g)	Single Point Total Pore Volume (cm^3/g)	Average Pore Diameter (4A/V by BET) (nm)
K-10	273.01 ± 0.84	0.392	5.749
Fresh Cs-DTP/K-10	239.61 ± 0.45	0.330	5.518
Regenerated Cs-DTP/K-10	223.49 ± 0.52	0.308	5.558

ICP-MS investigation of the catalyst was conducted to study any chemical changes and leaching (Table 2). Cs content was not detected in the reaction mass proving absence of any leaching of cesium metal whereas amount of tungsten is very small (0.075%) as compared with tungsten content in the fresh catalyst and hence negligible. This confirms that there was no leaching of either cesium or tungsten from the catalyst and hence chemical composition of the catalyst remains unchanged. As shown in Figure 3, SEM images of the Cs-DTP/K-10 catalyst before Figure 3a and after the reaction Figure 3b revealed no alteration in the surface morphology of the catalyst after the reaction. In summary, ICPMS and scanning microscope image studies reveal that chemical composition and morphological structure of the catalysts remain intact after the completion of the reaction.

Table 2. ICP-MS Study of the Catalyst.

Catalyst	Cs (ppm)	W (ppm)
Fresh $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$	18,999	116,708
Metal content in reaction mixture	Undetected	87.5

Figure 3. SEM images of (a) fresh Cs-DTP/K-10 catalyst and (b) used Cs-DTP/K-10.

X-ray diffraction study (Figure 4) of fresh and spent catalyst was conducted after recovering it by filtration post-reaction completion. It was then washed thoroughly with methanol followed by refluxed in methanol to remove the products and un-reacted glycerol from catalyst surface. The catalyst was calcined in furnace at 300 °C. It was observed that there was no crystallographic alteration in structure of the catalyst after the reaction. Keggin structure was observed to be preserved in the step of exchanging of proton of bulk DTP with Cs^+ ion. The XRD pattern of clay shows a sharp peak at a value of $2\theta = 26.20$, which belongs to quartz. It is also seen that there is no effect on this 2θ value after exchanging the K-10 clay with either bulk DTP acid or Cs^+ ion. The amorphous nature of K-10 was confirmed by background XRD reflection for K-10.

Figure 4. XRD patterns of Cs-DTP/K-10, Bulk DTP, K-10, and used catalyst.

Crystallinity of bulk DTP was seen to be lost while impregnating DTP on K-10. So, the effect of repeated use of catalyst on textural patterns of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$ was studied by recording the XRD patterns of the reused catalyst vis-à-vis fresh one. No change in crystallinity and textural patterns of the catalyst was observed. This study confirmed the catalyst is stable under the reaction conditions.

2.4. Parameter Optimization Study

2.4.1. Proof of Absence of External Mass Transfer Resistance

It was necessary to study the effect of external mass transfer resistance on the reaction and therefore effect of agitation on conversion was studied to establish the absence of external resistance. Experiments were conducted in the range between 600 and 1000 rpm with 0.03 g/cm^3 loading of the catalyst at 150 °C. Figure 5 shows that glycerol conversion remained practically the same above 800 rpm. Hence, in order to avoid mass transfer resistance, further experiments were carried out at 1000 rpm.

Figure 5. Effect of speed of agitation. Temperature: 150 °C, Catalyst loading: 0.03 g/cm³, Glycerol: BA = 1:3, reaction duration 4 h. (♦) 600 rpm; (■) 800 rpm; (▲) 1000 rpm.

2.4.2. Effect of Catalyst Loading

In the absence of any mass transfer resistance, the rate of conversion of glycerol is directly proportional to amount of catalyst used based on the total liquid phase of the reaction mass. Amount of catalyst was varied from 0.01 g/cm³ to 0.04 g/cm³ of the reactant. Figure 6 shows that glycerol conversion increases with increased number of active catalytic sites. Conversion remains nearly the same at 3% *w/v* onwards. Hence, further parameter optimization was performed at 0.03 g/cm³ of the catalyst loading.

Figure 6. Effect of catalyst loading. Speed of agitation: 1000 rpm, temperature: 150 °C, mole ratio Glycerol:BA = 1:3, reaction duration 4 h. (○) 0.01 g/cm³; (♦) 0.02 g/cm³; (■) 0.03 g/cm³; (▲) 0.04 g/cm³.

2.4.3. Effect of Mole Ratio of Glycerol to Benzyl Alcohol

Effect of mole ratio (Figure 7) was studied at glycerol to benzyl alcohol molar ratio in the range of 1:1 to 1:4 with otherwise similar reaction conditions. The conversion of glycerol increased as the benzyl alcohol concentration was found to be increased with respect to glycerol. Although the conversion of glycerol was increased with increased glycerol to benzyl alcohol mole ratio, selectivity towards MBGE decreased while the selectivity of by-product DBE increased, as shown in Figure 8. Therefore, to avoid more DBE formation, a 1:3 glycerol to benzyl alcohol mole ratio was taken for further study.

Figure 7. Effect of mole ratio of glycerol to benzyl alcohol. Speed of agitation: 1000 rpm, catalyst loading 0.03 g/cm^3 , temperature: 150°C , reaction duration: 4 h. (○) 01:01; (■) 01:02; (▲) 01:03; (◆) 1:4.

Figure 8. Effect of mole ratio on selectivity. Speed of agitation 1000 rpm, temperature 150°C , catalyst loading 0.03 g/cm^3 reaction duration 4 h. (◆) MBGE; (▲) DBE; (■) DBGE.

2.4.4. Effect of Temperature

The effect of temperature on conversion of glycerol was studied in the range between 130 and 160°C . Figure 9 shows that the reaction rate increases with increase in reaction temperature. Above 150°C , no significant increase in glycerol conversion was observed and therefore 150°C was taken as optimum. At higher temperature, intra-particle diffusion resistance was set in.

Figure 9. Effect of temperature. Speed of agitation: 1000 rpm, Mole ratio Glycerol:BA = 1:3, catalyst loading 0.03 g/cm³, reaction time 4 h. (○) 130 °C; (◆) 140 °C; (▲) 150 °C; (■) 160 °C.

2.5. Reaction Mechanism and Kinetic Model

Mechanism of this reaction suggests that there are three competing reactions occurring during the benzylation of glycerol. Those reactions as shown in Scheme 2 involve: (i) reaction of in-situ formed benzyl cation with glycerol to form *mono*-benzyl glycerol ether (MBGE) (ii) reaction of MBGE with another benzyl cation to form *di*-benzyl glycerol ether (DBGE) and (iii) etherification of benzyl alcohol with another molecule of it to form *di*-benzyl ether (DBE). The reaction mechanism of S_N² type was suggested with formation of benzyl cation on catalyst surface following a second order rate equation. Camila et al reported that MBGE was the major product formed over β -zeolite and Amberlyst-35, whereas DBGE was formed in higher yield over K-10 and PTSA, although self-etherification of benzyl alcohol was observed in all the cases [41].

Scheme 2. Reaction mechanism: Benzylation of glycerol.

The kinetic model was deduced based on above results. Understanding mechanism of the etherification reaction is necessary to develop a kinetic model for this reaction. Reaction

mechanism is assumed to be consisted of; weak adsorption of reactants on surface of the catalyst, reaction occurring on the surface and desorption of product molecules from the surface as shown in Scheme 2.

Weak adsorption of glycerol (A) on a vacant catalyst site S is given by

Similarly, the adsorption of benzyl alcohol (B) on the vacant catalyst site is represented as:

The surface reaction of AS with BS on the adjacent sites leads to the formation of MBGE (ES) and water (WS) on the catalytic sites

Desorption of MBGE and water is shown as

Now, total concentration of the sites, C_t can be expressed as:

$$C_t = C_S + C_{AS} + C_{BS} + C_{ES} + C_{WS} \quad (6)$$

This can also be expressed as:

$$C_t = K_A C_A C_S + K_B C_B C_S + K_E C_E C_S + K_W C_W C_S \quad (7)$$

Alternatively, the concentration of vacant sites is:

$$C_S = \frac{C_t}{(1 + K_A C_A + K_B C_B + K_E C_E + K_W C_W)} \quad (8)$$

Assuming the surface reaction (C) is a rate determining step, then rate of reaction of A is given by,

$$-r_A = -\frac{dC_A}{dt} = k_2 C_{AS} C_{BS} - k'_2 C_{ES} C_{WS} \quad (9)$$

$$\frac{-dC_A}{dt} = \frac{k_2 \{K_A K_B C_A C_B - (K_E K_W C_E C_W) / K_2\} C_t^2}{(1 + K_A C_A + K_B C_B + K_E C_E + K_W C_W)^2} \quad (10)$$

When the reaction is away from the equilibrium,

$$-\frac{dC_A}{dt} = \frac{k_2 C_t^2 K_A K_B C_A C_B}{(1 + \sum K_i C_i)^2} \quad (11)$$

$$= \frac{k_w C_A C_B}{(1 + K_i C_i)^2} \quad (12)$$

where $k_w = k_2 C_t^2 K_A K_B$ and w is amount of catalyst loading. Assuming that the adsorption constants are very small, then the above equation becomes:

$$-\frac{dC_A}{dt} = k_w C_A C_B \quad (13)$$

Let $C_{B0}/C_{A0} = M$ molar ratio of glycerol to benzyl alcohol at initial time $t = 0$. Then, Equation (13) can be expressed in terms of fractional conversion as below:

$$\frac{dX_A}{dt} = kwC_{A0}(1 - X_A)(M - X_A) \quad (14)$$

up on integration this leads to

$$\ln\left(\frac{(M - X_A)}{M(1 - X_A)}\right) = k_1(M - 1)t \quad (15)$$

where $k_1 = kwC_{A0}(M - 1)$

Thus, from Equation (15) a plot of $\ln\left(\frac{(M - X_A)}{M(1 - X_A)}\right)$ Vs t gave a good fit at various reaction temperatures, thereby validating the model (Figure 10). Values of the rate constants at various reaction temperatures were estimated from Figure 10. And Arrhenius plot was used to calculate the apparent energy of activation of the reaction as 18.84 kcal/mol (Figure 11).

Figure 10. Second order plot. (♦) 130 °C; (■) 140 °C; (▲) 150 °C.

2.6. Catalyst Reusability Study

Catalyst stability and reusability are of paramount importance during the development of catalyst for new processes. The catalyst was collected, separated, and thoroughly washed thrice by refluxing with methanol for 2 h. Washed catalyst was dried in oven to make it free from moisture and used for the study. Figure 12 shows the activity and selectivity of the catalyst for this reaction. As shown in Figure 12, a slight decrease in glycerol conversion was observed. During this reusability study fresh catalyst was not used to top up in second and third use of the catalyst. Going further, efficacy of catalyst may not show much change for this reaction when switch to vapor phase mode. Based on reaction rate per unit mass of the catalyst, it remains practically the same, which means the catalyst is stable and active. As described in the above sections, results of SEM, surface area measurement and EDAX analysis of the fresh as well as used catalyst showed that the catalyst is stable and there are no structural nor chemical changes having occurred in the catalyst. ICP-MS results showed that there was no leaching of metal in the reaction volume.

Figure 11. Arrhenius Plot.

Figure 12. Reusability study. (■) Conversion; (□) MBGE; (■) DBGE; (▨) DBE.

3. Experimental Section

3.1. Chemicals

All the required chemicals were purchased from well-known firms and used with no further purification. Glycerol was purchased from Merck Ltd., Canada. Benzyl alcohol (99%); cesium chloride (99.9%) and hexahydrate dodecatungstophosphoric acid (DTP) were purchased from Alfa Acer, Canada. Montmorillonite- K-10 clay was sourced from Fluka, Germany. Methanol was obtained from Merck Ltd., Canada.

3.2. Catalyst Synthesis

$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}/\text{K-10}$ (20% *w/w*) catalyst was prepared by a well-developed method in our laboratory and reported elsewhere. It was prepared by using incipient wetness method. Clay was dried at 120 °C in oven for 3 h prior to its use. Methanolic solution of CsCl was (10 cm³) was added to the pre-dried clay. Volume of methanol used was roughly estimated as the pore volume of the clay. This slurry was vigorously stirred at 120 °C for 1 h. This dried solid material was further treated by impregnation using alcoholic solution of DTP in 10 cm³ methanol and mixed thoroughly and thereafter the solvent was again evaporated by drying in air. It was subjected to calcination for 3 h at 300 °C. Prior to use, it was oven dried for 3 h.

3.3. Experimental Setup

An autoclave (350 cm³ volume capacity Parr reactor) having a four-bladed pitched-turbine impeller was used to carry out the reactions. Temperature of the reaction was attained using PID controller and kept constant at the accuracy level of ± 1 °C of the set value. The calculated weighed amount of the reactants followed by weighed dried catalyst were placed into the reactor. Heating was started to allow to attain the temperature at the desired value. A zero-hour sample was taken out. Agitation was started. Additional samples were withdrawn at regular time intervals till 4 h of the reaction time to study the progress of the reaction.

3.4. Reaction Procedure

For a typical reaction 0.205 mol glycerol was taken to react with 0.820 mol benzyl alcohol (BA) (1:4 mol ratio, glycerol to BA) with 2.98 g of fresh catalyst; making 0.03 g/cm³ of catalyst loading with respect to the total reaction volume. Nitrogen was purged to displace air from the reactor, if any. Experiments were performed at desired values of temperature and speed of agitation with solvent-free conditions.

3.5. Method of Analysis

Reaction progress was monitored by taking out clear liquid samples timely after minimizing the speed of agitation of the reaction to zero hence allowing the catalyst to get settle down at the bottom. Analysis of clear samples was carried out using gas chromatography (Agilent Technology, Santa Clara, CA, USA, Model # 7890 A) equipped with HT Stabilwax capillary thin column (0.25 mm i.d $\times$ 30 m) and flame ionization detector (FID). Being the limiting reactant; conversion of the reaction was calculated based on glycerol. DBGE and MBGE were characterized by mass spectroscopy. Products were separated by column chromatographic extraction using ethyl acetate as solvent.

3.6. Catalyst Characterization

3.6.1. Fourier Transform Infrared Spectroscopy (FTIR)

FT-IR spectroscopic study of the catalysts were conducted by using Agilent Technology, USA make spectrophotometer. Dried catalyst was mixed with KBr of spectroscopic grade to prepare thin pellet which were then subjected to several scans before recording the fine spectra. The catalyst was thoroughly characterized during its preparation phase as well as after the reaction.

3.6.2. Surface Area Analysis

Measurement of surface area and porosity of the catalyst was carried out by N₂ gas adsorption-desorption technique on ASAP Micromeritics 2010 instrument, USA. Catalysts samples pre-treated under high vacuum for 4 h at 300 °C were subjected to BET surface area measurement at 77 K. N₂ adsorption-desorption isotherms of fresh and spent catalysts were deduced by using the conventional BET and BJH (Barrett, Joyner and Halenda) methods.

3.6.3. Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

ICPMS study of the catalyst was carried using model Nexlon 300D, PerkinElmer, USA, to confirm the metal composition of the catalyst and to ensure that no leaching of the metal from catalyst into the reaction mass was observed.

3.6.4. Scanning Electron Microscopy (SEM)

SEM images of the catalyst surface were captured using (SU 30 microscope, JEOL, Tokyo, Japan) instrument. Dried catalyst sample was mounted on studs and sputter coated with a thinner film of platinum to make the catalyst surface conducting.

3.6.5. X-ray Diffraction Study (XRD)

Bruker AXS powder diffractometer D8 with Cu-K α (1.54 Å) radiation was used to generate XRD patterns to study textural patterns and crystallinity of the catalyst.

4. Conclusions

Glycerol benzylation with benzyl alcohol was studied using different catalysts. among which 20% *w/w* Cs-DTP/K-10 was the best solid acid catalyst in solvent-free condition with more than 70% selectivity towards MBGE. MBGE and DBGE are valuable chemicals derived from glycerol and find application as important pharmaceutical intermediates. The effect of reaction parameters on the rate of reaction was studied. Reaction mechanism was discussed; an overall second order rate equation was deduced and validated with 18.84 kcal/mol as apparent energy of activation. The described reaction is one of the methods to produce valuable chemicals from glycerol. Thorough characterization of the catalyst was carried out to establish that the catalyst is robust and recyclable. It is a green process.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2073-4344/11/1/34/s1>, Figure S1: Mass Spectra of mono benzyl glycerol ether. *m/z* 205, Figure S2: Mass Spectra of dibenzyl glycerol ether.

Author Contributions: The project was conceptualized by G.D.Y. The experiments and characterizations of catalysts were performed by D.P.T. in India and Canada under the supervision of G.D.Y. and A.K.D. The original draft was written by D.P.T. which was discussed and revised by G.D.Y. and A.K.D. Funding and lab facilities were provided by A.K.D. in Canada. All authors have read and agreed to the published version of this manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

A	Reactant species A—Glycerol
AS	Chemisorbed A
B	Reactant species B—Benzyl alcohol
BS	Chemisorbed B
E	Product mono benzyl glycerol ether (MBGE)
ES	Chemisorbed product
W	Water
C_A, C_B	Concentration of A and B (mol/cm ³)
C_{A0}, C_{B0}	Initial concentration of A and B (mol/cm ³)
C_{AS}, C_{BS}	Concentration of A and B on solid catalyst surface (mol/g cat)
C_{ES}, C_{WS}	Concentration of E and W at solid catalyst surface (mol/g cat)
C_S	Concentration of vacant sites (mol/g cat)
C_t	Total concentration of sites (mol/g cat)
r_A	Rate of disappearance of A (mol/cm ³ /s)
K_A	Equilibrium constant for adsorption of A on catalyst surface (L mol ⁻¹)
K_B	Equilibrium constant for adsorption of B on catalyst surface (L mol ⁻¹)
k_2	Surface reaction rate constant for forward reaction (L mol ⁻¹ min ⁻¹)
k'_2	Surface reaction rate constant for reverse reaction (L mol ⁻¹ min ⁻¹)
K_P	Equilibrium constant for adsorption of P on catalyst surface (L mol ⁻¹)
K_W	Equilibrium constant for adsorption of W on catalyst surface (L min ⁻¹)
S	Vacant site
T	Time
W	Catalyst loading (g/cm ³ of liquid phase)
X_A	Fractional conversion of A

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