Article

Tuning the Catalytic Activity of Recyclable Heterogeneous Catalysts for the Direct Etherification Reaction of Glycerol Using Antagonistic Additives

Je Seung Lee *[ID], Eunji Jang [ID], Dae Won Kim and Seo Kyung Park

Department of Chemistry, Kyung Hee University, 26 Kyungheedae-ro, Dongdaemun-gu, Seoul 02447, Korea; eunji43513@naver.com (E.J.); david.pinkim@gmail.com (D.W.K.); tjrud1015@naver.com (S.K.P.)
* Correspondence: leejs70@khu.ac.kr; Tel.: +82-2-961-0458

Abstract: Using zeolite as a heterogeneous catalyst, the reaction conditions were optimized to increase the yield and selectivity of diglycerol (DG) and triglycerol (TG) in the direct etherification reaction of glycerol. By the addition of weakly acidic alkali metal-based inorganic salts ($NaHSO_4$ and $KHSO_4$), the selectivities and yields of DG and TG increased. Although the conversion of glycerol was lowered due to the role of the additive as an inhibitor, the reaction conditions were optimized by controlling the amounts and reaction times of the additives to increase the yields of DG and TG. Under the optimized condition, the glycerol conversion was as high as 85.4%, and the highest yields of DG and TG were observed as 54.1% and 21.3%, respectively. The recyclability of the catalysts was much enhanced by the influence of the additives suppressing the formation of oligomers.

Keywords: glycerol; etherification; diglycerol; triglycerol; alkali metal; zeolite; heterogeneous catalyst; antagonistic additive

1. Introduction

Polyglycerol, a product of the conversion of glycerol by etherification, has tremendous potential in a variety of fields including polymers, cosmetics, food, dispersants, pharmaceutical industry, lubricants, biomedical, or pharmaceutical delivery systems [1–4]. In particular, diglycerol (DG) and triglycerol (TG) are converted into derivatives such as fatty acid esters, which can be used as multifunctional additives for pharmaceuticals, cosmetics, foods, and polyurethans [1,2,5–10]. DG and TG can also be used as water-soluble plasticizers and emulsions. For this reason, interests in the selective conversion of glycerol to DG and TG have been steadily increasing [1,3,10,11]. However, scientific challenges such as the development of efficient and selective catalysts and the optimization of reaction conditions still remain in the selective production of desired short chains such as DG and TG through the etherification of glycerol [12]. Early research on the etherification of glycerol focused on the use of acidic homogeneous catalysts such as sulfuric acid, benzene sulfonic acid, dodecyl benzene sulfonic acid [13,14], as well as basic homogeneous catalysts such as hydroxides, carbonates, and oxides [15,16].

However, although the homogeneous catalyst has high activity, there is a disadvantage in that the selectivity of DG and TG is low due to the side reactions such as the increased formation of oligomer by the condensation reaction between the etherification products. Therefore, it is necessary to develop the efficient and selective catalysts and optimize the reaction conditions capable of directly condensing glycerol into DG and TG to overcome these shortcomings, and various studies have been conducted [17–25].

Research has compared homogeneous catalysts to heterogeneous catalysts such as basic porous solids and metal oxides, which have excellent selectivity and can be recovered and reused [23,24,26–29]. In particular, faujasites including zeolite beta, NaX, and NaY can be used as the selective catalysts for the production of DG and TG directly from

glycerol, and the results for the direct etherification of glycerol using zeolites have been being reported [15,30]. In addition, when Cs-exchanged zeolite was used as a catalyst, the conversion of glycerol and the selectivities of DG and TG were the highest among the tested zeolites, but the thermal instability has been reported as a disadvantage [31].

Although the selectivities of DG and TG can be increased by using the heterogeneous catalyst, the reaction temperature needs to be increased to increase the yield due to the lower reactivity of the heterogeneous catalyst than the homogeneous catalyst. Since the formation of oligomers is accelerated at high temperatures, the reduction of reaction time was attempted to decrease the formation of oligomers. However, there is a trade-off relationship between the reaction temperature and the reaction time, increasing the yield of DG and TG along with the conversion of glycerol, which was limited. To increase both the selectivities and yields of DG and TG, it is necessary to overcome the disadvantages of heterogeneous catalysts while taking advantages by optimizing the reaction condition. Recently, we have reported that the improved yield of DG and TG and suppressed the formation of oligomers in the presence of homogeneous catalysts at high temperatures by introducing the additives capable of moderating the activity of the homogeneous catalyst [25].

In this study, as an extension of the study and the last journey on the efficient conversion of glycerol to DG and TG under atmosphere pressure, the effect of additives on the moderating catalytic activity of heterogeneous catalysts was investigated. Especially, to optimize the reaction conditions for the selective production of DG and TG, the effects of varied reaction temperature, reaction time, and the amounts of additives on the heterogeneous catalytic etherification of glycerol were studied. In addition, as previously reported, the catalytic activity of zeolites was reduced after being reused 5 times, and this was also attempted to be overcome through additives.

2. Results and Discussion

Prepared Na^+ containing X-type zeolite (XZ-Na, Si/Al = 1.40, surface area = 541 m^2 g^{-1}, pore volume = 0.27 cm^3 g^{-1}) and K^+ containing X-type zeolite (XZ-K, Si/Al = 1.40, surface area = 465 m^2 g^{-1}, pore volume = 0.26 cm^3 g^{-1}) showed different physical properties (Figure S1 and Table S1 in Supplementary Materials) [32] from NaX (Si/Al ratio = 1.1, surface area = 868 m^2 g^{-1}, pore volume = 0.35 cm^3 g^{-1}), which was previously used as a catalyst for the etherification of glycerol [15].

Table 1 summarizes the results of the etherification reaction of glycerol by a basic heterogeneous catalyst containing an alkali metal, including the previously reported results. In general, the heterogeneous catalysts have the advantage of showing high selectivity for DG and TG compared to the homogeneous catalysts. To increase the yield of DG and TG, the reaction temperature or the reaction time need to be increased due to the low conversion of glycerol by the heterogeneous catalysts. However, because the formation of oligomers is promoted at high temperatures or increased reaction times, attempts have been made to reduce the formation of oligomers by reducing the reaction time. However, increasing both the selectivity and the yield of DG and TG by controlling the reaction time is limited, because there is a trade-off relationship between the reaction temperature and the reaction time. As shown in Table 1, when the reactions were carried out at the relatively low temperature, the high selectivities of DG and TG were observed. However, the yields of DG and TG were low due to the low conversion of glycerol. If the reaction was carried out for a long time to increase the conversion of glycerol, the production of oligomers was also increased.

Table 1. Comparison of the catalytic activity of heterogeneous catalysts containing alkali metal cation in the etherification reaction of glycerol [1].

Entry	Catalyst	Amount of Catalyst (wt.%)	Temp. (°C)	Time (h)	Conv. of Glycerol (%)	Selectivity (%)			Ref.
						DG	TG	Others	
1	NaX	4	260	9	68.8	68 (46.8)	22 (15.1)	10 (6.9)	[31]
2	Na mordenite	4	260	9	38.6	73 (28.2)	22 (8.5)	5 (1.9)	[31]
3	NaX	2	260	24	100	25 (25)	26 (26)	49 (49)	[15]
4	NaY	2	260	24	79	47.5 (37.5)	18.5 (14.6)	34 (26.9)	[15]
5	NaBeta	2	260	24	52.5	44.5 (23.4)	7.2 (3.8)	48.3 (25.3)	[15]
6	Li Ferrierite	2	200	8	35	77 (26.9)	16 (5.6)	7 (2.5)	[33]
7	Na Ferrierite	2	200	8	37	79 (29.2)	12 (4.5)	9 (3.3)	[33]
8	K Ferrierite	2	200	8	40	80 (32)	14 (5.6)	6 (2.4)	[33]
9	XZ-Na	3	280	2	79.4	64.7 (51.4)	27.6 (21.9)	7.7 (6.1)	[32]
10	XZ-Na [2]	3	280	2	76.3	66.6 (50.8)	26.7 (20.4)	6.7 (5.1)	This work
11	XZ-Na [2]	3	280	3	81.5	57.4 (46.8)	24.7 (20.1)	17.9 (14.6)	This work
12	XZ-K	3	280	2	89.3	53.6 (47.9)	24.5 (21.9)	21.9 (19.5)	[32]
13	XZ-K [3]	3	280	2	81.2	68.1 (55.3)	21.3 (17.3)	10.6 (8.6)	This work
14	XZ-K [3]	3	280	3	85.4	63.3 (54.1)	24.9 (21.3)	11.7 (10.0)	This work

[1] The numbers in parenthesis are the yields of each product. [2] 0.1 wt.% of $NaHSO_4$ was added. [3] 0.2 wt% of $KHSO_4$ was added.

The conversions of glycerol using 3 wt% of XZ-Na and XZ-K as catalysts at 280 °C for 2 h were 79.4% and 89.3%, respectively (Table 1, Entry 9 and 12). As previously reported, XZ-K showed higher conversion of glycerol than XZ-Na under the same reaction conditions due to the higher catalytic activity of K^+ cation than that of Na^+ cation [30,32,33].

The difference in reactivity according to the kind of alkali metal cation contained in zeolite is because the basicity of the alkali metal cation affects the strength of the catalytic activity for the etherification of glycerol. However, XZ-Na exhibited the higher selectivities and yields of DG and TG than XZ-K because the formation of oligomer was facilitated by K^+ cation. Recently, we reported that the yields of DG and TG were improved and the formation of oligomers was suppressed by introducing additives that can moderate the activity of homogeneous catalysts [25]. As an extension of the study on the efficient conversion of glycerol to DG and TG, the reaction time and the amounts of additives were adjusted to optimize the reaction conditions and the effect on heterogeneous catalytic etherification of glycerol for the selective production of DG and TG.

The results of the glycerol etherification for 2 h at 280 °C using 3 wt.% of XZ-Na and XZ-K as catalysts with varied amounts of $NaHSO_4$ and $KHSO_4$, which were introduced as additives, respectively, are shown in Figure 1. In both catalysts, as the amount of the additive increased, while the conversion of glycerol and the formation of oligomers decreased due to the suppressed activity of catalyst by the antagonistic inhibitor. The selectivity of DG increased steadily as the amount of additive increased. However, the yields of DG were observed as the highest when the amounts of 0.1 wt.% of $NaHSO_4$ and 0.2 wt.% of $KHSO_4$ were added to XZ-Na and XZ-K, respectively. The selectivity and yield of TG decreased due to the decreased activity of the catalyst as the amounts of additives increased.

Figure 2 shows the influence of reaction time on the etherification of glycerol at 280 °C using 3 wt.% of XZ-Na as a catalyst with varied amount of $NaHSO_4$. Without additive, the yields of DG and TG were 51.4% and 21.9%, respectively, showing the highest values at 2 h (Table 1, Entry 9 and Figure 2a). The selectivity and yield of the oligomers increased steadily with the increased reaction time but decreased with the increased amount of $NaHSO_4$ (Figure 2). This is because the additive, which acts as a proton donor, inhibits the activity of catalyst as in homogeneous catalysis [25]. However, by the addition of $NaHSO_4$, the conversion of glycerol also decreased, resulting in lower yields of DG and TG compared to the condition without additives. For example, when 0.1 wt.% of $NaHSO_4$ was added and the reaction time was 2 h, the yields of DG and TG were 50.8% and 20.4%, respectively

(Table 1, Entry 10 and Figure 2b). This seems to be because the catalytic activity of XZ-Na was greatly affected and inhibited by NaHSO$_4$.
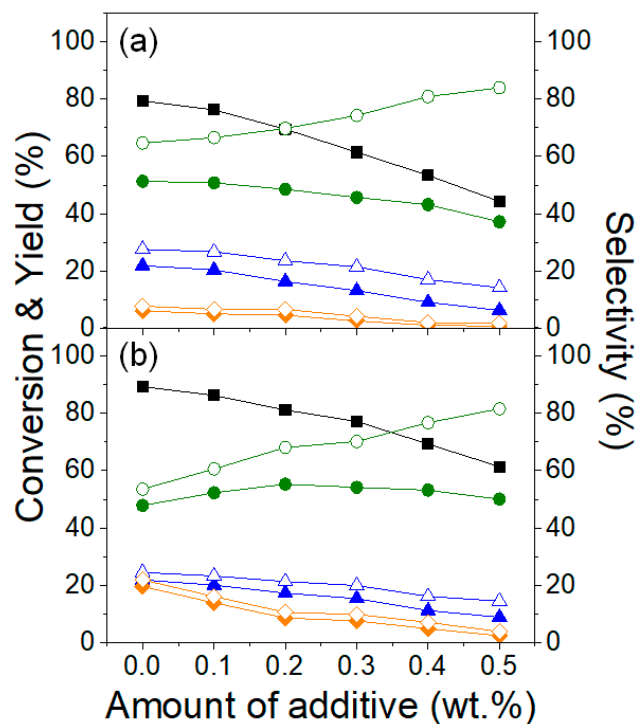

Figure 1. The influence of the amount of additive on the etherification reaction of glycerol: (**a**) Na-zeolite with NaHSO$_4$ and (**b**) K-zeolite with KHSO$_4$ (-■-: conversion of glycerol, -●-: yield of DG, -▲-: yield of TG, -◆-: yield of others -○-: selectivity of DG, -△-: selectivity of TG, -◇-: selectivity of others, the reaction temperature: 280 °C, the reaction time: 2 h).
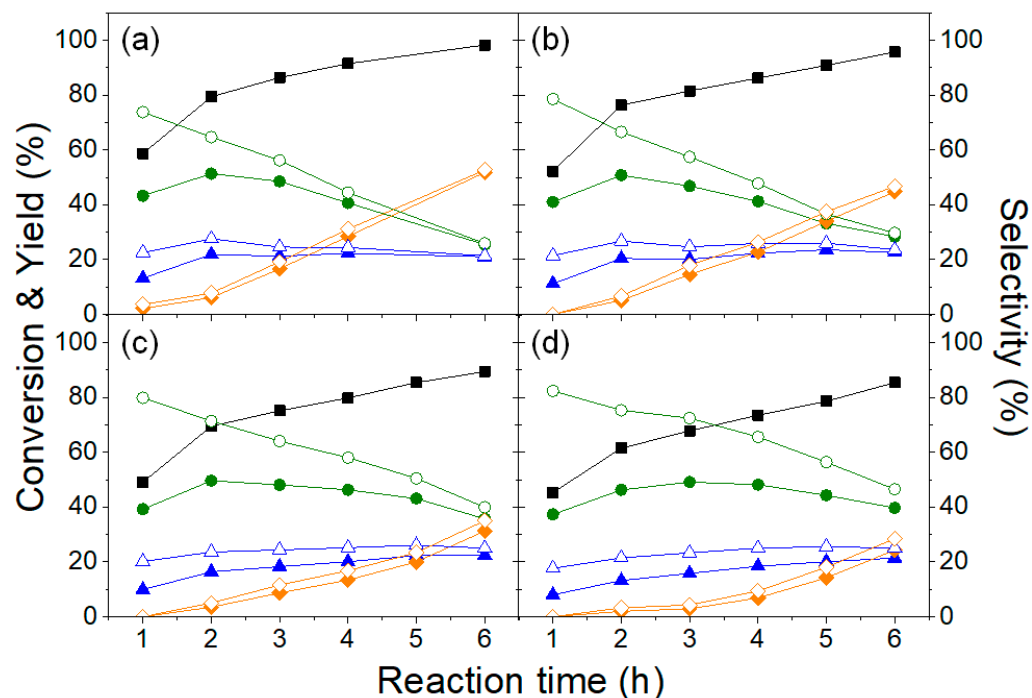

Figure 2. The influence of reaction time on the etherification reaction of glycerol in the presence of 3 wt.% of Na-zeolite with (**a**) 0 wt.%, (**b**) 0.1 w.t%, (**c**) 0.2 wt.%, and (**d**) 0.3 wt.% of NaHSO$_4$ (-■-: conversion of glycerol, -●-: yield of DG, -▲-: yield of TG, -◆-: yield of others -○-: selectivity of DG, -△-: selectivity of TG, -◇-: selectivity of others, reaction temperature: 280 °C).

Figure 3 shows the influence of reaction time on the etherification of glycerol at 280 °C using 3 wt.% of XZ-K as a catalyst with varied amount of $KHSO_4$. Since the activity of XZ-K is higher than that of XZ-Na, the conversion of glycerol was 89.3% in a reaction time of 2 h without additive. The yields of DG, TG, and oligomers were 47.9%, 21.9%, and 19.5%, respectively, and the formation of oligomers increased rapidly with the increase in the reaction time (Table 1, Entry 12 and Figure 3a). $KHSO_4$ added to XZ-K more clearly exhibited the suppressed formation of oligomers than $NaHSO_4$ added to XZ-Na. Particularly, the formation of oligomers at 2–3 h was very suppressed, while the conversion of glycerol was maintained at a certain level, thereby obtaining high yields of DG and TG. When the etherification reaction of glycerol was carried out at 280 °C for 3 h in the presence of 3 wt.% of XZ-K and 0.2 wt.% of $KHSO_4$, the conversion of glycerol was 85.4%, and the yields of DG and TG were the highest values as 54.1% and 21.3%, respectively (Table 1, Entry 14 and Figure 3c). Therefore, the optimized conditions for the production of DG and TG through the catalytic direct etherification of glycerol using 3 wt.% of XZ-K as a catalyst at 280 °C were the addition of 0.2 wt.% of $KHSO_4$ and reacting for 3 h.
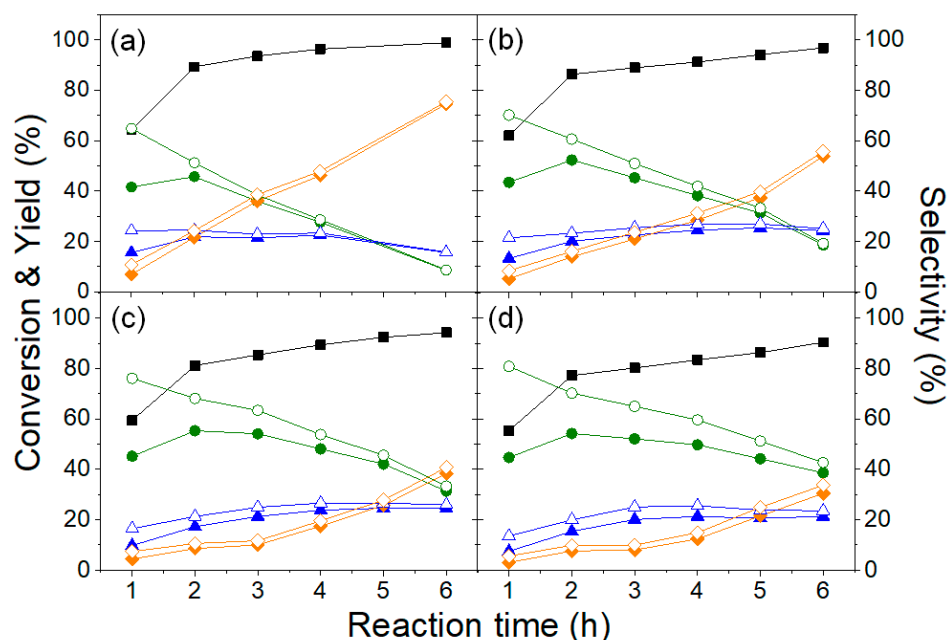

Figure 3. The influence of reaction time on the etherification reaction of glycerol in the presence of 3 wt.% of K-zeolite with (**a**) 0 wt.%, (**b**) 0.1 wt.%, (**c**) 0.2 wt.%, and (**d**) 0.3 wt.% of $KHSO_4$ (-■-: conversion of glycerol, -●-: yield of DG, -▲-: yield of TG, -◆-: yield of others -○-: selectivity of DG, -△-: selectivity of TG, -◇-: selectivity of others, reaction temperature: 280 °C).

The catalyst recycle was performed at 280 °C for 2 h in the presence of XZ-Na or XZ-K. After the completion of the reaction, the zeolite was separated from the liquid product mixture by the filtration followed by refluxing for 2 h in distilled water (50 mL). The dried XZ-Na or XZ-K was reused in the next cycle with a fresh charge of glycerol (50 g) and the appropriate amount of additive. As previously reported, when XZ-Na or XZ-K was used as a catalyst in the absence of additive, the conversion of glycerol decreased slightly with the cycle, although the selectivities of DG and TG were kept at a similar level [32]. We have reported that the decreased catalytic activity was due to the reduced specific surface area of zeolite by the generated oligomers, although the skeleton structure of the zeolite was maintained even after recycling. As shown in Figure 4 and Table S2, interestingly, the catalytic activity of XZ-Na and XZ-K was not deteriorated during 10 times of recycling in the presence of additives. This result appears to be due to the suppression of the formation of oligomers, especially long-chain oligomers, under the influence of additives, resulting in the declined reduction of the surface area of zeolites (Figure 5). The N_2 sorption isotherms

of XZ-K exhibited some hysteresis, which seems to be because a small amount of mesopores (with a pore size distribution of around 5 nm, Figure S2) are generated by relatively large K$^+$ cations, unlike XZ-Na, where only micropores exist. The reason that the yield and selectivity of the oligomer of XZ-K is higher than that of XZ-Na seems to be because not only the strong basicity of K$^+$ but also the presence of mesopores affect it. It was confirmed again through FT-IR spectra and XRD patterns that the skeletal structure of zeolites did not change even after repeated reuse (Figures S3 and S4). The IR peak between 900 and 1000 cm^{-1} is according to the asymmetric stretching of Si-O-Al. In the case of XZ-Na, the peak positions of the initial, 5th reuse, and 10th reuse were 961.4, 961.9, and 962.8 cm^{-1}, respectively, indicating that there was almost no structural change during the recycle. On the other hand, in the case of XZ-K, the peak positions of the initial, 5th, and 10th reuse were 961.4, 956.6, and 964.3 cm^{-1}, respectively. The Si/Al ratios for the initial, 5th, and 10th reuse catalysts of XZ-Na and XZ-K measured by EDX were 1.40, 1.39, 1.38, and 1.40, 1.40, 1.41, respectively (Figure S5 and Table S1). The IR peak position corresponding to Si/Al was obtained consistent with the previously reported experimental results and theoretical calculations [34–36]. Therefore, it appears that the rather large shift of the IR peak in reused XZ-K catalysts is due to the difference of mesopores rather than the altered the Si/Al ratio.
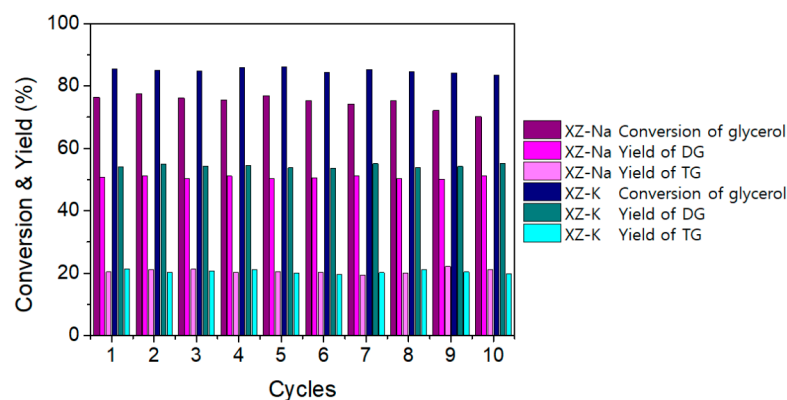

Figure 4. Recycling of XZ-Na and XZ-K for the etherification reaction of glycerol.
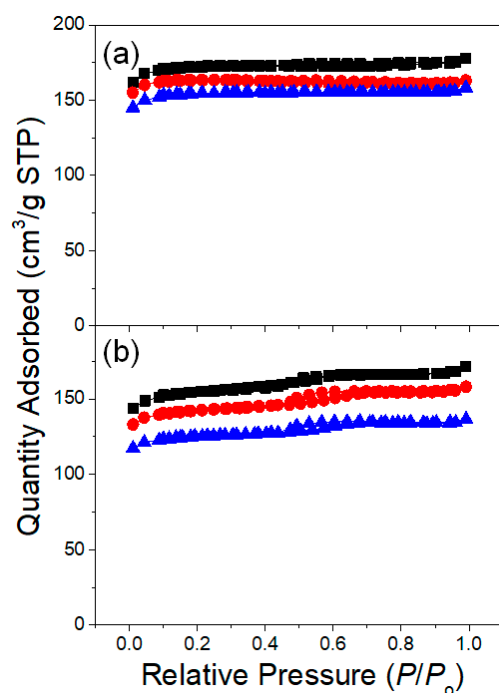

Figure 5. N$_2$ sorption isotherms of (**a**) XZ-Na and (**b**) XZ-K: (-■-) pristine zeolite, (-●-) after 5 recycles, (-▲-) after 10 recycles.

3. Materials and Methods

3.1. Materials

Aluminum isopropoxide, silica gel, sulfuric acid (98 wt.%, HPLC grade), and *t*-butanol were purchased from Sigma-Aldrich Chemical Co. (Yongin, Korea). Glycerol, NaOH, KCl, $NaHSO_4$, and $KHSO_4$ were purchased from Daejung Chemicals Co. (Seoul, Korea). Water (HPLC grade) was purchased from J. T. Baker Co. (Seoul, Korea). All the chemicals were used as received without further purification.

3.2. Preparation of XZ-Na and XZ-K

X-type zeolite was prepared using a modified literature method [32,37]. A white suspension was obtained by mixing sodium silicate gel prepared by dissolving 12.0 g of silica gel and 9.6 g of NaOH in 25 mL of deionized water and sodium aluminate prepared by dissolving 29 g of aluminum isopropoxide and 9.6 g of NaOH in 40 mL of deionized water. XZ-Na in the form of white powder obtained by standing the suspension in an oven at 90 °C for 4 h was washed with deionized water followed by drying under vacuum at 140 °C. XZ-K was obtained by dispersing XZ-Na in 4 M KCl aqueous solution and stirring at 80 °C for 24 h to exchange cation.

3.3. Characterization Methods

A Micromeritics TriStar analyzer was used to record the nitrogen adsorption isotherms at −196 °C. The samples were outgassed at 200 °C for 2 h under vacuum before each measurement. The total pore volume (V_{total}) was determined from the amount of N_2 uptake at $P/P_0 = 0.95$. The total specific surface area (S_{total}) was calculated using the Brunauer–Emmett–Teller (BET) method from the nitrogen adsorption data in the relative pressure (P/P_0) of 0.06–0.20 [38]. A field emission scanning electron microscope (FE-SEM, Hitachi, Model SU 8220, Tokyo, Japan) equipped with an EDS PV9761 detector at the acceleration voltage of 200 kV was used to investigate the morphology and structural properties of Na-zeolite. The FT-IR spectrum of zeolite was obtained using a Nicolet FT-IR spectrometer (iS10, Thermo Fisher Co., Waltham, MA, USA) equipped with a SMART MIRACLE accessory.

3.4. Etherification Reaction of Glycerol

First, 50 g of glycerol, an appropriate amount of zeolite, and additive were added to a round-bottomed flask (100 mL) with a stir bar, and the catalytic etherification reaction was carried out under atmospheric pressure. A Dean–Stark apparatus was used to remove the water generated during the etherification reaction.

3.5. Analysis of the Etherification Reaction Mixtures

The reaction mixture was analyzed using high-performance liquid chromatography (HPLC) equipped with an Aminex HPX-87H (Bid Rad, Hercules, CA, USA) column and a reflection index (RI) detector. An aqueous H_2SO_4 (5 mM) solution was used as a mobile phase with a flow rate of 0.6 mL min^{-1}. The amounts of glycerol, DG, and TG present in the reaction mixture were quantitatively analyzed using *t*-butanol as an internal standard. The conversion of glycerol, yields, and selectivities of DG, TG, and oligomers were calculated using the following equations:

$$\text{Moles of reacted glycerol} = \text{moles of glycerol taken} - \text{moles of unreacted glycerol}$$

$$\text{Moles of oligomers} = \text{moles of reacted glycerol} - \text{moles of DG and TG}$$

$$\text{Conversion of glycerol (\%)} = \frac{\text{moles of reacted glycerol}}{\text{moles of glycerol taken}} \times 100\%$$

$$\text{Yield of DG (\%)} = \frac{\text{moles of DG}}{\text{moles of glycerol taken}} \times 100\%$$

$$\text{Yield of TG (\%)} = \frac{\text{moles of TG}}{\text{moles of glycerol taken}} \times 100\%$$

$$\text{Yield of oligomers (\%)} = \frac{\text{moles of oligomers}}{\text{moles of glycerol taken}} \times 100\%$$

$$\text{Selectivity of DG (\%)} = \frac{\text{moles of DG}}{\text{moles of reacted glycerol}} \times 100\%$$

$$\text{Selectivity of TG (\%)} = \frac{\text{moles of TG}}{\text{moles of reacted glycerol}} \times 100\%$$

$$\text{Selectivity of oligomers (\%)} = \frac{\text{moles of oligomers}}{\text{moles of reacted glycerol}} \times 100\%$$

3.6. Catalyst Recycle

The recycling experiments of XZ-Na and XZ-K were performed at 280 °C for 2 h in the presence of additive. After the completion of the reaction, the liquid product mixture was removed by filtration, and the remaining solid catalyst was resuspended in distilled water (50 mL) and refluxed for 2 h. The solid catalyst recovered by the filtration and drying was reused in the next cycle with a fresh charge of glycerol and additive.

4. Conclusions

To moderate the catalytic activity of XZ-Na or XZ-K used as a catalyst for the dehydration etherification of glycerol, $NaHSO_4$ or $KHSO_4$ was added to each as an additive capable of acting as a proton donor, and the characteristics of the reaction were investigated. The conversion of glycerol and the yields and selectivities of DG, TG, and oligomeric compounds can be controlled by varying the amounts of additives and reaction time. The optimized reaction conditions to produce DG and TG with high yield using 3 wt.% of XZ-K as a catalyst at 280 °C were 0.2 wt.% of $KHSO_4$ and 3 h of reaction time. Under this condition, the glycerol conversion was as high as 85.4%, and the highest yields of DG and TG were observed as 54.1% and 21.3%, respectively. In addition, under the influence of the additive, the formation of oligomers, particularly long-chain oligomers, was suppressed, stably maintaining the catalyst activity even after repeated reuse.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal12020220/s1. Figure S1: SEM images and EDX data. Figure S2: N_2 isotherms. Figure S3: FT-IR spectra. Figure S4: XRD patterns of (a) XZ-Na and (b) XZ-K. Figure S5: EDX data of XZ-Na (a) pristine, (b) after 5th recycle, (c) after 10th recycle and XZ-K (d) pristine, (e) after 5th recycle, (f) after 10th recycle, respectively. Table S1: Structural characterization. Table S2: Recycling data.

Author Contributions: Conceptualization, J.S.L.; methodology, S.K.P. and J.S.L.; formal analysis, D.W.K. and E.J.; investigation, S.K.P. and D.W.K.; data curation, D.W.K. and E.J.; writing—original draft preparation, S.K.P. and J.S.L.; writing—review and editing, J.S.L.; visualization, S.K.P.; supervision, J.S.L.; project administration, J.S.L.; funding acquisition, J.S.L. All authors have read and agreed to the published version of the manuscript.

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

References

1. Wilms, D.; Stiriba, S.; Frey, H. Hyperbranched polyglycerols: From the controlled synthesis of biocompatible polyether polyols to multipurpose applications. *Acc. Chem. Res.* **2010**, *43*, 129–141. [CrossRef] [PubMed]
2. Calderón, M.; Quadir, M.A.; Sharma, S.K.; Haag, R. Dendritic polyglycerols for biomedical applications. *Adv. Mater.* **2010**, *22*, 190–218. [CrossRef] [PubMed]
3. Salehpour, S.; Dubé, M.A. Towards the sustainable production of higher-molecular-weight polyglycerol. *Macromol. Chem. Phys.* **2011**, *212*, 1284–1293. [CrossRef]

4. Yadav, J.D.; Kulkarni, P.R.; Vaidya, K.A.; Shelke, G.T. Niosomes: A review. *J. Pharm. Res.* **2011**, *4*, 632–636.
5. Magana, J.R.; Esquena, J.; Solans, C.; Rodriguez-Abrew, C. Deconstruction of technical grade diglycerol isostearate enables the controlled preparation of hexosomes and liposomes. *J. Mol. Liquids* **2021**, *343*, 117594. [CrossRef]
6. Younes, G.R.; Marić, M. Bio-based thermoplastic polyhydroxyurethanes synthesized from the terpolymerization of a decarbonate and two diamines: Design, rheology, and application in melt blending. *Macromolecule* **2021**, *54*, 10189–10202. [CrossRef]
7. Bowman, L.-P.; Younes, G.R.; Marić, M. Effects of poly(propylene glycol)-based triamine on the sol/gel curing and properties of hybrid non-isocyanate polyurethanes. *Macromol. React. Eng.* **2022**, 2100055. [CrossRef]
8. Nda-Umar, U.I.; Ramli, I.; Taufiq-Yap, Y.H.; Muhamad, E.N. An overview of recent research in the conversion of glycerol into biofuels, fuel additives and other bio-based chemicals. *Catalysts* **2019**, *9*, 15. [CrossRef]
9. Varma, R.S.; Len, C. Glycerol valorization under continuous flow conditions-recent advances. *Curr. Opin. Green Sustain. Chem.* **2019**, *15*, 83–90. [CrossRef]
10. Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J.; Lindner, F. Improved utilisation of renewable resources: New important derivatives of glycerol. *Green Chem.* **2008**, *10*, 13–30. [CrossRef]
11. Stefani, S.; Kurniasih, I.N.; Sharma, S.K.; Böttcher, C.; Servin, P.; Haag, R. Triglycerol-based hyperbranched polyesters with an amphiphilic branshed shell as novel biodegradable drug delivery systems. *Polym. Chem.* **2016**, *7*, 887–898. [CrossRef]
12. Zhou, C.C.; Beltramini, J.N.; Fan, Y.; Lu, G.M. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. *Chem. Soc. Rev.* **2008**, *37*, 527–549. [CrossRef] [PubMed]
13. Harvey, S.B.; Shen, S. One Phase Production of Polyglycerol Esters. U.S. Patent US5585506A, 17 December 1996.
14. Medeiros, M.A.; Araujo, M.H.; Augusti, R.; de Oliveira, L.C.; Lago, R.M. Acid-catalyzed oligomerization of glycerol investigated by electrospray ionization mass spectrometry. *J. Braz. Chem. Soc.* **2009**, *20*, 1667–1673. [CrossRef]
15. Krisnandi, Y.K.; Eckelt, R.; Schneider, M.; Martin, A.; Richter, M. Glycerol upgrading over zeolites by batch-reactor liquid-phase oligomerization: Heterogeneous versus homogeneous reaction. *Chem. Sustain. Chem.* **2008**, *1*, 835–844. [CrossRef] [PubMed]
16. Richter, M.; Krisnandi, Y.K.; Eckelt, R.; Martin, A. Homogeneously catalyzed batch reactor glycerol etherification by $CsHCO_3$. *Catal. Commun.* **2008**, *9*, 2112–2116. [CrossRef]
17. Garti, N.; Aserin, A.; Zaidman, B. Polyglycerol esters—optimization and techno-economic evaluation. *J. Am. Oil Chem. Soc.* **1981**, *58*, 878–883. [CrossRef]
18. Ayoub, M.; Khayoon, M.S.; Abdullah, A.Z. Synthesis of oxygenated fuel additives via the solventless etherification of glycerol. *Bioresour. Technol.* **2012**, *112*, 308–312. [CrossRef]
19. Ayoub, M.; Inayat, A.; Hailegiorgis, S.M.; Bhat, A.H. *Advanced Materials Research*; Trans Tech Publications: Zurich, Switzerland, 2016; Volume 1133, pp. 33–37.
20. Karam, A.; Sayoud, N.; Vigier, K.D.O.; Lai, J.; Liebens, A.; Oldani, C.; Jérôme, F. Heterogeneously-acid catalyzed oligomerization of glycerol over recyclable superacid Aquivion® PFSA. *J. Mol. Catal. A Chem.* **2016**, *422*, 84–88. [CrossRef]
21. Barros, F.; Moreno-Tost, R.; Cecilia, J.A.; Ledesma-Muñoz, A.L.; De Oliveira, L.; Luna, F.; Vieira, R.S. Glycerol oligomers production by etherification using calcined eggshell as catalyst. *Mol. Catal.* **2017**, *433*, 282–290. [CrossRef]
22. Lee, J.H.; Park, S.K.; Ryu, J.; Lee, H.; Lee, J.S. Solventless catalytic etherification of glycerol using acetate salts as efficient catalysts. *Bull. Korean Chem. Soc.* **2018**, *39*, 722–725. [CrossRef]
23. Barros, F.J.S.; Cecilia, J.A.; Moreno-Tost, R.; de Oliveira, M.F.; Rodríguez-Castellón, E.; Luna, F.M.T.; Vieira, R.S. Glycerol oligomerization using low cost dolomite catalyst. *Waste Biomass Valorization* **2020**, *11*, 1499–1512. [CrossRef]
24. Ebadipour, N.; Paul, S.; Katryniok, B.; Dumeignil, F. Alkaline-based catalysts for glycerol polymerization reaction: A review. *Catalysts* **2020**, *10*, 1021. [CrossRef]
25. Han, T.; Lee, J.S. Positive effect of antagonistic additives on the homogeneous catalytic etherification reaction of glycerol. *Catalysts* **2021**, *11*, 1000. [CrossRef]
26. Gholami, Z.; Abdullah, A.Z.; Lee, K. Dealing with the surplus of glycerol production from biodiesel industry through catalytic upgrading to polyglycerols and other value-added products. *Renew. Sustain. Energy Rev.* **2014**, *39*, 327–341. [CrossRef]
27. Sangkhum, P.; Yanamphorn, J.; Wangriya, A.; Ngamcharussrivichai, C. Ca—Mg—Al ternary mixed oxides derived from layered double hydroxide for selective etherification of glycerol to short-chain polyglycerols. *Appl. Clay Sci.* **2019**, *173*, 79–87. [CrossRef]
28. Padula, I.D.; Santos, B.M.A.; Rodrigues, A.P.H.; Gastelois, P.L.; Mendes, I.M.C.; Portilho, M.F.; Oliveira, L.C.A.; Oliveira, C.C. Niobium-modified hydrotalcite catalysts: Sustainable conversion of waste glycerol to valuable chemicals. *Appl. Catal. A Gen.* **2020**, *606*, 117814. [CrossRef]
29. Aloui, M.; Cecilia, J.A.; Moreno-Tost, R.; Ghorbel, S.B.; Zina, M.S.; Rodríguez-Castellón, E. Glycerol etherification towards selective diglycerol over mixed oxides derived from hydrotalcites: Effect of Ni loading. *J. Sol.-Gel Sci. Technol.* **2021**, *97*, 351–364. [CrossRef]
30. Barrault, J.; Clacens, J.; Pouilloux, Y. Selective oligomerization of glycerol over mesoporous catalysts. *Top. Catal.* **2004**, *27*, 137–142. [CrossRef]
31. Cottin, K.; Clacens, J.; Pouilloux, Y.; Barrault, J. Preparation of diglycerol and triglycerol by the direct polymerization of glycerol in the presence of the new solid catalysts. *Ocl-Ol. Corps Gras Lipides* **1998**, *5*, 407–412.
32. Park, S.K.; Kim, D.W.; Lee, S.Y.; Lee, J.S. Direct etherification reaction of glycerol using alkali metal cation (Li^+, Na^+ and K^+) containing X-type zeolites as heterogeneous catalysts: Optimization of the reaction conditions. *Catalysts* **2021**, *11*, 1323. [CrossRef]

33. Zafari, R.; Kharat, A.N. Evaluation of mesoporous modified ferrierite zeolite performance in production of diglycerol from glycerol. *Rev. Roum. de Chim.* **2018**, *63*, 95–101.
34. Byrappa, K.; Kumar, B.V.S. Characterization of zeolites by infrared spectroscopy. *Asian J. Chem.* **2007**, *19*, 4933–4935.
35. Król, M.K.; Jeleń, P. The effect of heat treatment on the structure of zeolite A. *Materials* **2021**, *14*, 4642. [CrossRef] [PubMed]
36. Król, M.; Koleźyński, A.; Mozgawa, W. Vibrational spectra of zeolite Y as a function of ion exchange. *Molecules* **2021**, *26*, 342. [CrossRef] [PubMed]
37. Balkus, K.J.; Ly, K.T. The preparation and characterization of an X-type zeolite: An experiment in solid-state chemistry. *J. Chem. Educ.* **1991**, *68*, 875. [CrossRef]
38. Kruk, M.; Jaroniec, M. Gas adsorption characterization of ordered organic−inorganic nanocomposite materials. *Chem. Mater.* **2001**, *13*, 3169–3183. [CrossRef]