Article

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

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Abstract: X-type zeolite (XZ-Na) containing Na^+ as a cation was synthesized, and XZ-Li and XZ-K were prepared by exchanging the cations of XZ-Na with Li^+ and K^+ , respectively. The specific surface areas, structures, and chemical compositions of the prepared zeolites were analyzed by BET, XRD, and SEM-EDX. The activity of the direct and selective etherifications of glycerol to diglycerol (DG) and triglycerol (TG) were investigated using each zeolite XZ-M ($\text{M} = \text{Li}, \text{Na}$ or K) as a basic heterogeneous catalyst. The etherification reactions of glycerol were carried out at atmospheric pressure while controlling the reaction temperature, reaction time, and the amount of each zeolite. As the amount of each zeolite, reaction time, and reaction temperature increased, the conversion of glycerol also increased, but the selectivities of DG and TG decreased due to the increase in the production of oligomers. When each zeolite was used as a catalyst, the catalytic activity for the conversion of glycerol was observed as $\text{XZ-K} > \text{XZ-Li} > \text{XZ-Na}$, but the selectivities of DG and TG were observed as $\text{XZ-Li} > \text{XZ-Na} > \text{XZ-K}$. Especially, 3 wt.% of XZ-Li exhibited the excellent catalytic performance when the etherification of glycerol was optimized and carried out at 280°C for 2 h: the conversion of glycerol was 89.6% and the yields of DG and TG were 61.2 and 21.2%, respectively.

Keywords: glycerol; etherification; diglycerol; triglycerol; alkali metal; zeolite; heterogeneous catalysis

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1. Introduction

With increasing concerns about environmental pollution caused by petrochemical products such as microplastics, various studies are being conducted to convert biomass into useful eco-friendly materials [1,2]. In particular, interests in the process for producing diglycerol (DG) and triglycerol (TG) have recently increased due to their various application fields including pharmaceuticals, surfactants, cosmetics, food additives, lubricants, fatty acid ester emulsifiers, plasticizers, biodiesel additives and oligomeric liquid crystals [3–8].

Commercially, diglycerol has been prepared by distillation after hydrolysis of epichlorohydrin under basic conditions, but the process by selective etherification of glycerol is preferred due to the expensiveness of epichlorohydrin and corrosiveness of by-product such as HCl [9,10]. The selective etherification of glycerol can be proceeded under both acidic and basic conditions. However, the basic condition is more preferred because undesirable by-products such as acrolein are generated under acidic condition and polymerization occurs together, which lowers the selectivity of DG and TG [11,12].

As catalysts used in the etherification of glycerol, studies on homogeneous and heterogeneous catalysts have been conducted. The reaction rate of homogeneous catalysts is faster than that of heterogeneous catalysts. However, it is difficult to selectively obtain DG and TG using homogeneous catalysts because the selectivities of homogeneous catalysts for DG and TG are lower than that of the heterogeneous catalysts [12–14]. In recent

years, to overcome the disadvantages of homogeneous catalyst systems and increase the selectivities of DG and TG, researches on the direct etherification of glycerol using various basic heterogeneous catalysts including hydroxides, carbonates, basic porous solids and oxides of various metals have been being conducted [15–17]. Heterogeneous catalysts have relatively low reactivity compared to homogeneous catalysts, requiring high temperatures or long reaction times to increase the conversion of glycerol, but have several advantages over homogeneous catalysts. Porous materials such as crystalline zeolite have advantages of large surface area, selectivity according to the size and shape of pores, high thermal stability, and easy handling and recovery [17]. As shown in Table 1, for example, the heterogeneous catalysts require longer reaction time compared to the homogeneous catalysts. The conversion of glycerol was 83.8 and 72.8%, respectively, when reacted for 6 h at 260 °C using 0.5 mol% of NaOH and NaOAc as catalysts for homogeneous reaction (Table 1, Entry 1 and 2) [13]. Meanwhile, when 4 wt.% of NaX, a heterogeneous catalyst, was used as a catalyst at 260 °C for 9 h, the conversion of glycerol was only 68.8% (Table 1, Entry 3) [18]. However, the selectivities of DG and TG were higher in the heterogeneous catalysis than the homogeneous catalysis.

In zeolites, the kind of alkali metal ions affects the strength of the basicity and catalytic activity. Barrault et al. reported the etherification of glycerol using base-modified microporous zeolites and mesoporous structures [19]. Cesium ion exchange zeolite (as heterogeneous catalyst) was less active than Na₂CO₃ (as homogeneous catalyst) but showed higher selectivity for DG and TG [19,20]. The effect of alkali metal ions on the basic strength of zeolites has been reported in the order of Cs⁺ > Rb⁺ > K⁺ > Na⁺ > Li⁺. The effect of the type of zeolite matrix was also studied. The activity of X, Y and beta-type zeolites containing Na⁺ as a cation at 260 °C was reported in the order of NaX > NaY > NaBeta. The concentrations of Na⁺ exist in NaX, NaY and NaBeta were 4.9, 2.3, and 0.7 mmol g^{−1}, respectively. The catalytic activity is mainly affected by the concentration of cations and NaX shortened the reaction time. However, the effect of the structure of each zeolite was not clearly observed [12,17]. The effect of the amount of impregnated alkali element on large-surface mesoporous scaffolds was also studied [12,21]. The conversion of glycerol increased with increasing the amount of Cs⁺, but the selectivities of DG and TG decreased. The decreased selectivity is by the accelerated formation of oligomers due to the high reactivity of Cs⁺. In addition, Cs⁺ leaching was observed during the reaction. It was explained that the size of Cs⁺ cations was too large to the X-type zeolite and the thermal stability reduced resulting in partial collapse of the porous structure of zeolite.

Table 1. Comparison of the catalytic activity of alkali metal cation containing catalysts 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	NaOH	0.5	260	6	83.8	24.5 (20.5)	19.5 (16.3)	56 (47.0)	[13]
2	NaOAc	0.5	260	6	72.8	38.7 (28.2)	31.9 (23.2)	29.4 (21.4)	[13]
3	NaX	4	260	9	68.8	68 (46.8)	22 (15.1)	10 (6.9)	[18]
4	Na mordenite	4	260	9	38.6	73 (28.2)	22 (8.5)	5 (1.9)	[18]
5	NaX	2	260	24	100	25 (25)	26 (26)	49 (49)	[12]
6	NaY	2	260	24	79	47.5 (37.5)	18.5 (14.6)	34 (26.9)	[12]
7	NaBeta	2	260	24	52.5	44.5 (23.4)	7.2 (3.8)	48.3 (25.3)	[12]
8	Li Ferrierite	2	200	8	35	77 (26.9)	16 (5.6)	7 (2.5)	[22]
9	Na Ferrierite	2	200	8	37	79 (29.2)	12 (4.5)	9 (3.3)	[22]
10	K Ferrierite	2	200	8	40	80 (32)	14 (5.6)	6 (2.4)	[22]
11	XZ-Li	3	260	6	54.2	71.3 (38.6)	21.1 (11.5)	7.6 (4.1)	This work
12	XZ-Na	3	260	6	43.1	62.9 (27.1)	14.4 (6.2)	22.7 (9.8)	This work
13	XZ-K	3	260	6	61.3	51 (31.3)	18.5 (11.3)	30.5 (18.9)	This work
14	XZ-Li	3	280	2	86.9	70.5 (61.2)	24.4 (21.2)	5.1 (4.5)	This work
15	XZ-Na	3	280	2	79.4	64.7 (51.4)	27.6 (21.9)	7.7 (6.1)	This work
16	XZ-K	3	280	2	89.3	53.6 (47.9)	24.5 (21.9)	21.9 (19.5)	This work

¹ The numbers in parenthesis are the yields of each product.

Recent studies on the catalytic activity according to the type of alkali metals have used two-dimensional and mesoporous ferrierite zeolite containing Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ as cations as catalysts [22]. The specific surface area of ferrierite zeolite was wide in the order of $\text{Na}^+ > \text{Li}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ in the range of $286\text{--}389\text{ m}^2\text{ g}^{-1}$, and the pore size of Cs^+ was the largest with the reverse order in the range of $2.33\text{--}2.47\text{ nm}$. The catalytic activity of ferrierite zeolite containing Rb and Cs^+ as cations was highest, but the conversion of glycerol was much lower than the homogeneous catalyst. The conversion of glycerol and the selectivity of DG was observed in the order of $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$, which is reported to be because $\sim 2\text{ nm}$ mesopores are optimal for the production of DG. Similar to the previous results, however, it has been reported that Cs^+ leached out and the catalytic activity decreased as the zeolite structure was partially collapsed.

Herein, we prepared X-type zeolites (XZ-M, M = Li, Na and K) containing different alkali metals as cations and analyzed physical properties such as specific surface area and alkali metal content. The direct etherification reactions of glycerol using prepared zeolites were carried out and the catalytic activity was systematically investigated (Scheme 1). The effect of different basic cations on the yields of DG and TG were compared and to optimize the reaction condition according to the results obtained. The etherification reactions of glycerol were carried out by controlling the reaction temperature, the reaction time, and the amount of catalyst to find the reaction conditions optimized for the production of DG and TG. To the best of our knowledge, this is the first study for increasing the conversion of glycerol and the yields of DG and TG in the heterogeneous catalytic etherification of glycerol through suppressing the formation of oligomers by optimizing the reaction conditions.

Scheme 1. Reaction scheme for the preparation of diglycerol and triglycerol by the direct etherification of glycerol.

2. Results and Discussion

Zeolite having a faujasite (FAU) structure is divided into X-type and Y-type which has a Si/Al molar ratio of 1.1 and 2.3, respectively [12]. In this work, we prepared X-type zeolite containing Na^+ as a cation through a hydrothermal method and exchanged the cation of the prepared zeolite to Li^+ and K^+ resulting in preparing three different X-type zeolites. Prepared zeolite containing Na^+ as a cation shows a characteristic FT-IR spectrum of FAU materials (Figure S1 in Supplementary Materials). The main asymmetric stretch occurs at 960 cm^{-1} with a shoulder at 1070 cm^{-1} and the symmetric stretches occur at 754 and 669 cm^{-1} . The bands at around 560 cm^{-1} is associated with the double 6 rings that connect the sodalite cages [23]. The shoulder appeared at 1070 cm^{-1} of XZ-Na shifted to 1035 and 1095 cm^{-1} in XZ-Li and XZ-K, respectively. This seems to be according to the different interaction between each cation and the skeleton structure of zeolite due to the difference in the size and hardness of each cation. Similarly, the symmetric stretching in XZ-Na at near 670 cm^{-1} became sharper in XZ-Li but broadened in XZ-K. Zeolites containing Li^+ or K^+ as a cation exhibited similar FT-IR spectra implying that the prepared zeolites have FAU structure. Figure S2 shows scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) measurement results of the manufactured zeolites.

As summarized in Table S1, cation modified zeolites have the structural characteristics of FAU and have a chemical composition close to X-type zeolite with a Si/Al molar ratio of 1.4, but there are some differences in chemical composition and physical properties from NaX (Si/Al = 1.1), NaY (Si/Al = 2.2) and NaBeta (Si/Al = 10.7) [12]. Therefore, the cation modified zeolites were denoted as XZ-M (M = Li, Na or K).

Figure 1 is the N₂ sorption isotherms of the XZ-M. The specific surface area of NaX reported in the literature was 868 m² g^{−1} and the pore volume was 0.35 cm³ g^{−1} [12], but the specific surface area of XZ-Na was 541 m² g^{−1} and the pore volume was 0.27 cm³ g^{−1} (Table S1). The specific surface area and pore volume decrease in the order of XZ-Li > XZ-Na > XZ-K because the smaller the size of the cations present in the zeolite having the same structure, the smaller the volume occupied by the cations [12]. From the result that the three zeolites show similar XRD patterns, it can be seen that the basic skeletal structure of XZ-M is the same (Figure 2). The peak values of XRD pattern of XZ-M (M = Li, Na and K) are agreed well with the standard values of X type zeolite (JCPDS data cards No. 39-0218). The crystallinities of XZ-Li, XZ-Na and XZ-K were calculated as 84.2, 87.7 and 78.9%, respectively (Table S1). The average size of crystalline can be calculated employing the Scherrer equation [24,25] as shown in Equation (1):

$$r = (0.94 \times \lambda) / (B \times \cos\theta) \quad (1)$$

where λ , B and 2θ are the wave length of X-ray radiation, the full-width at the half-maximum of diffraction peak and the diffraction angle, respectively. The crystalline size was calculated from the peak of 16° (331) and 27° (642) and the average crystalline size of XZ-Li, XZ-Na and XZ-K were calculated as 34.1, 36.6, 39.3 nm, respectively.

Figure 1. N₂ sorption isotherms of zeolite XZ-Li (■), XZ-Na (●) and XZ-K (▲).

The direct etherification reaction of glycerol was carried out using XZ-M (M = Li, Na or K) as a catalyst under atmospheric pressure. The by-product, generated water during the reaction, was removed with a Dean-Stark apparatus. Table 1 shows the results of the etherification reaction of glycerol using the heterogeneous catalysts including zeolites and clays bearing alkali metal cation. Under similar reaction conditions, although the reactivity of the heterogeneous catalysts was lower than that of the homogeneous catalysts, the selectivity of heterogeneous catalysts for DG and TG was higher than that of the homogeneous catalysts. Each 0.5 wt.% of NaOH and NaOAc, the homogeneous catalysts, converted 83.8 and 72.8% of glycerol, respectively, during a reaction time of 6 h at 260 °C (Table 1, Entry 1 and 2) [13]. However, the selectivities of DG and TG were 24.5 and 19.5%

for NaOH and 38.7 and 31.9% for NaOAc, respectively. Although the glycerol conversion of the weak base NaOAc was lower than that of the strong base NaOH, the selectivities of DG and TG were higher in the weak base. Heterogeneous catalysts containing the same alkali metal cations require larger amounts of catalysts and longer reaction times due to the lower catalytic activity of heterogeneous catalysts than homogeneous catalysts. As shown in Table 1, Entry 3, 4 wt.% of NaX and over 9 h of reaction time was required to obtain a glycerol conversion similar to NaOAc at 260 °C [18].

Figure 2. XRD patterns of XZ-M (M = Li, Na and K).

As the result of etherification reaction carried out using 3 wt.% of XZ-Na as a catalyst at a temperature of 260 °C for 6 h, the conversion of glycerol was 43.1%, and the selectivities of DG and TG were 62.9 and 14.4%, respectively (Table 1, Entry 12). As a result of the reaction at 260 °C for 9 h using 4 wt.% of NaX, the conversion of glycerol was 68.8%, and the selectivities of DG and TG were 68 and 22%, respectively (Table 1, Entry 3). When reacted for 24 h using 2 wt.% of NaX at 260 °C, the conversion of glycerol reached 100%, but the selectivities of DG and TG were 25% and 26%, respectively (Table 1, Entry 5). It can be seen that even if the amount of catalyst is reduced by half, the amount of oligomer produced increases in proportion to the reaction time. In addition, the reaction was carried out at 200 °C for 8 h using 2 wt.% of Na Ferrierite, the selectivity of DG was as high as 79% as shown in Table 1, Entry 9. However, the yield of DG was only 29.2% because the conversion of glycerol was only 37%. In the industrial process, not only the selectivities of DG and TG are important, but also it is necessary to increase the actual yields of DG and TG by increasing the conversion of glycerol as well.

The conversion of glycerol and selectivities of DG and TG with XZ-Na were lower than those with NaX at the same reaction temperature due to the less amount of XZ-Na and shorter reaction time than NaX. Another reason to consider is that the lower contents of Na⁺ cation in XZ-Na than that in NaX due to the higher Si/Al ratio of XZ-Na than that of NaX (the molar ratios of Si/Al in XZ-Na and NaX are 1.4 and 1.1, respectively). It was necessary to control the reaction conditions, nevertheless, because XZ-Na exhibited the higher selectivity of oligomer than NaX. Under the same conditions, as shown in Table 1, Entry 13, the glycerol conversion of XZ-K was higher than that of XZ-Na, and the selectivity of XZ-K to DG and TG was lower than that of XZ-Na. It is because the catalytic activity of K⁺ is higher than that of Na⁺ and this result is agreed to the previous report [19,20,22]. Interestingly, XZ-Li (Table 1, Entry 11) showed lower the conversion of glycerol than XZ-K but higher than XZ-Na. It may due to the larger surface area and amount of alkali metal

cation per weight in XZ-Li than XZ-Na and XZ-K. However, the selectivities of DG and TG have the order of XZ-Li > XZ-Na > XZ-K depending on the basicity of the cation (Table 1, Entry 11, 12 and 13).

Figure 3 shows the results of etherification of glycerol at 260 °C for 6 h using different amounts of each XZ-M (M = Li, Na and K). Similar to the previously reported basic catalysts, the conversion of glycerol increased with increasing the amount of XZ-M. As the amount of XZ-M increased, however, the production of oligomers also increased, leading to the decreased selectivities of DG and TG. In particular, this tendency was remarkable at over 3 wt.% of XZ-M. At over 5 wt.% of XZ-M, the increase in the conversion of glycerol became small. This result seems to be because more oligomers were generated during the same reaction time resulting in increased viscosity of the reaction mixture. Therefore, it can be seen that the optimized amount of the catalyst capable of suppressing the formation of oligomers while increasing the selectivities and yields of DG and TG is 3 wt.%.

Figure 3. The influence of the amount of (a) XZ-Li, (b) XZ-Na and (c) XZ-K on the etherification reaction of glycerol (—■—: conversion of glycerol, —●—: yield of DG, —▲—: yield of TG, —◆—: yield of others —○—: selectivity of DG, —△—: selectivity of TG, —◇—: selectivity of others, reaction temperature: 260 °C, reaction time: 6 h).

Figure 4 shows the effect of the reaction time at a temperature of 260 °C using 3 wt.% of XZ-M as a catalyst. Similar to the result of increasing the amount of catalyst, the conversion of glycerol increased as the reaction time elongated, but the selectivities of DG and TG decreased with increasing the amounts of oligomers. Up to 2–3 h, the selectivities of DG and TG decreased and increased, respectively, indicating that the formation of oligomers was proceeded slowly in the early stage of the etherification of glycerol. From these results, in the early stage of the reaction, it can be seen that the production of DG and the conversion of DG to TG were the main reaction. In the time period after 3 h, XZ-Li showed increased selectivity of TG, but XZ-Na and XZ-K did not show significant differences. These results implied that Li⁺ cation carried out the conversion of DG to TG faster than that of TG to oligomers, but Na⁺ and K⁺ cations facilitated the conversion of TG to oligomers. In addition, XZ-Na and XZ-K exhibited the decreased selectivity of DG and increased selectivity of oligomers as elongating the reaction time comparing to XZ-Li. Therefore, it is conceivable that DG and TG exist in the reaction mixture are converted into oligomers larger than tetramers as the reaction proceeded.

Reducing the reaction time was required since the production of oligomers increased as the reaction time increased. As a result of performing the etherification reactions of glycerol for 2 h at 260 °C using 3 wt.% of XZ-M, the conversion of glycerol was very low (for XZ-Li, XZ-Na and XZ-K were 16.9, 13.5 and 19.7%, respectively) but DG was selectively obtained (the selectivity of DG for XZ-Li, XZ-Na and XZ-K were 88.8, 88.7 and 73.1%, respectively). Based on these results, the reaction time was reduced to 2 h to suppress the formation of oligomers. The etherification reactions of glycerol were carried out for 2 h while varying the reaction temperature in the range of 260 to 290 °C (Figure 5). As the reaction temperature increased, the conversion of glycerol and the selectivity of TG and oligomers increased while the selectivity of DG decreased. The conversion at

290 °C slightly increased than at 280 °C due to the increased viscosity by the increased etherification products, particularly oligomers, at high temperature. Interestingly, XZ-Li, XZ-Na and XZ-K showed the highest yields of DG as 61.2, 51.4, and 47.9%, respectively, at 280 °C (Table 1, Entry 14, 15 and 16). During the reaction for 2 h, the production of DG and TG occurred faster than the conversion to oligomers at a temperature below 280 °C but the conversion to oligomers proceeded rapidly at 290 °C. In the etherification using XZ-K as a catalyst, the yield and selectivity of oligomers increased linearly as the reaction temperature increased (Figure 5c). However, when XZ-Li or XZ-Na were used as a catalyst, the yield and selectivity of oligomers were low and those of DG and TG kept increase in the temperature range of 260–280 °C (Figure 5a,b). Therefore, when the etherification reaction of glycerol was carried out using 3 wt.% of XZ-M for 2 h, the optimum reaction temperature for DG and TG production was 280 °C.

Figure 4. The influence of reaction time on the etherification reaction of glycerol: (a) XZ-Li, (b) XZ-Na and (c) XZ-K (■: conversion of glycerol, ●: yield of DG, ▲: yield of TG, ◆: yield of others, ○: selectivity of DG, △: selectivity of TG, ◇: selectivity of others, amount of zeolite: 3 wt.%, reaction temperature: 260 °C).

Figure 5. The influence of the reaction temperature on the etherification reaction of glycerol: (a) XZ-Li, (b) XZ-Na and (c) XZ-K (■: conversion of glycerol, ●: yield of DG, ▲: yield of TG, ◆: yield of others, ○: selectivity of DG, △: selectivity of TG, ◇: selectivity of others, amount of zeolite: 3 wt.%, reaction time: 2 h).

These results are also confirmed through the reaction results according to the amount of XZ-M at each temperature of 260–290 °C (Figures S3–S5). At 260 and 270 °C, the conversion of glycerol tended to increase proportionally with increasing amount of XZ-M. The yields of DG and TG also increased as the amount of XZ-M increased. However, at 280 and 290 °C, the conversion of glycerol increased in proportion to the amount of catalyst until the amount of XZ-M reached to 3 wt.%. But at more amounts of XZ-M, the increase in glycerol conversion slowed down. This is because the etherification reaction is accelerated and the viscosity of the reaction mixtures increases using large amount of XZ-M at high temperature. Especially, the highest yields of DG and TG were obtained at 280 °C when

3 wt.% of XZ-M was used. In addition, XZ-Li and XZ-Na showed very low oligomer formation under the same reaction conditions, but XZ-K showed relatively high oligomer formation due to the basicity of the K^+ cation. This trend was more pronounced at 290 °C: the formation of oligomers increased rapidly as increasing the amount of XZ-M. Therefore, it can be conceivable that the temperature of 280 °C and the use of 3 wt.% of XZ-M are the optimal reaction conditions for 2 h of reaction time.

The effect of reaction time on the etherification reaction using 3 wt.% of catalyst at 280 °C was also investigated (Figure 6). As the reaction time increased, the conversion of glycerol steadily increased, but the rate of increase in the conversion flattened out slightly after 2 h due to the increased viscosity of the reaction mixture as the reaction proceeded as described above. The yields of DG and TG increased until 2 h. After 2 h, however, the yield of DG decreased but the yield of TG was maintained at a similar level at 2 h. The yield and selectivity of oligomers increased rapidly from the beginning of the reaction using XZ-K, but XZ-Li and XZ-Na showed a rapid increase after 2 h. When XZ-Li or XZ-Na was used as a catalyst at 280 °C, the main reactions occurred during the first 2 h were the etherification of glycerol to produce DG and the conversion of DG to TG by the etherification of DG and glycerol. After 2 h, however, the formation of oligomers was accelerated through the reaction of the DG and TG with glycerol, DG and TG present in the reaction mixture. After 2 h, particularly, as the amount of unreacted glycerol remaining in the reaction mixture was reduced, the reaction between DG and/or TG became main reaction, and the amount of oligomer increased, thereby increasing the viscosity of the reaction mixture. Therefore, the optimal reaction conditions for preparing DG and TG using 3 wt.% of XZ-Li, XZ-Na or XZ-K as a catalyst are a reaction temperature of 280 °C and a reaction time of 2 h. Especially, at 280 °C for 2 h, 3 wt.% of XZ-Li showed a high glycerol conversion of 86.9% and suppressed the selectivity and yield of the oligomers to 5.1 and 4.5%, respectively (Table 1, Entry 14). The selectivities and yields of DG and TG were 70.5, 24.4% and 61.2, 21.2%, respectively, showing excellent performance.

Figure 6. The influence of reaction time on the etherification reaction of glycerol: (a) XZ-Li, (b) XZ-Na and (c) XZ-K (—■—: conversion of glycerol, —●—: yield of DG, —▲—: yield of TG, —◆—: yield of others —○—: selectivity of DG, —△—: selectivity of TG, —◇—: selectivity of others, amount of zeolite: 3 wt.%, reaction temperature: 280 °C).

The catalyst recycle was conducted with glycerol in the presence of XZ-M (M = Li, Na and K) at 280 °C for 2 h. After the completion of the reaction, the liquid product mixture was removed by the filtration, and the remaining solid catalyst was resuspended in distilled water (50 mL) followed by refluxing for 2 h. The solid catalyst recovered by the filtration and drying under vacuum was reused for the next cycle with a fresh charge of glycerol (50 g). As shown in Figure 7 and Table S2, the conversion of glycerol was found to decrease with the cycle, but the drop in the conversions of glycerol of XZ-Li, XZ-Na and XZ-K after five cycles were 5.7, 8.2, and 11%, respectively, demonstrating the stability of XZ-M. After five recycles, in addition, the yields of DG of XZ-Li, XZ-Na and XZ-K were decreased by 4.4, 5.3, and 6.4%, and the yields of TG were decreased by 1.7, 2.2, and 3.1%, respectively. The

yields decreased due to the decreased conversion of glycerol, but the selectivity was kept at a similar level implying that the catalytic activities of XZ-M were kept constant during the recycles. The decreased conversion of glycerol according to the cycle seems to be due to the decreased specific surface area of XZ-M as the cycle increases, as shown in Figure S6. This seems to be because the oligomer formed during the repeated reactions blocks some pores. Although the specific surface areas of zeolites were reduced by repeated reactions, it can be confirmed that the skeletal structure is maintained through XRD spectra (Figure S7).

Figure 7. Recycling of XZ-M for the etherification reaction of glycerol.

3. Materials and Methods

3.1. Materials

Silica gel, aluminum isopropoxide, *t*-butanol and sulfuric acid (98 wt.%, HPLC grade) were purchased from Sigma-Aldrich Chemical Co. (Yongin, Korea). Glycerol, NaOH, LiCl and KCl 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. Characterization Methods

Nitrogen adsorption isotherms were recorded on a Micromeritics TriStar analyzer at $-196\text{ }^{\circ}\text{C}$. Prior to the measurement, the samples were outgassed under vacuum at $200\text{ }^{\circ}\text{C}$ for 2 h. 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 [26]. Field emission scanning electron microscope (FE-SEM, Hitachi, Model SU 8220, Tokyo, Japan) equipped with EDS PV9761 detector at the acceleration voltage of 200 kV were used to investigate the morphology and structural properties of the zeolites. FT-IR spectra of zeolites were obtained using a Nicolet FT-IR spectrometer (iS10, Thermo Fisher Co., Waltham, MA, USA) equipped with a SMART MIRACLE accessory. The X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (XRD-6000, Shimadzu Co., Nakagyo-ku, Kyoto, Japan).

3.3. Preparation of Zeolites

X-type zeolite was prepared using modified literature method [23]. 12.0 g of silica gel and 9.6 g of NaOH were dissolved in 25 mL of deionized water to prepare the sodium silicate gel. 29 g of aluminum isopropoxide and 9.6 g of NaOH were dissolved in 40 mL of deionized water to prepare the sodium aluminate. Clear sodium aluminate solution and 100 mL of deionized water were added to the sodium silicate gel and stirred to form the suspension of white solids. The mixture was transferred to a Teflon lined-autoclave and

placed in an oven at 90 °C for 4 h. The white zeolite crystals were neutralized by washing with deionized water followed by drying under vacuum at 140 °C.

10 g of prepared zeolite containing Na⁺ as a cation was put into each 100 mL of 4 M LiCl and 4 M KCl aqueous solution, respectively. After stirring at 80 °C for 24 h, the mixture was filtered and washed twice with deionized water. The cation exchange process was repeated twice. Cation exchanged zeolite was put in 100 mL of deionized water and stirred at 80 °C. After 24 h, the mixture was filtered and washed with deionized water. This process repeated three times. Each zeolite was put into a vacuum oven and dried under reduced pressure at 140 °C for 2 days.

3.4. Heterogeneous Catalysis of Glycerol

The catalytic reaction of glycerol was carried out by putting glycerol (50 g) and an appropriate amount of zeolite in a round bottomed flask (100 mL) with a stir bar. The flask was equipped with a Dean-Stark apparatus for removing the water generated during the etherification reaction. The reaction was carried out under atmospheric pressure with varying the temperature in the range of 260–290 °C using temperature controller and thermocouple.

3.5. Analyzing the Reaction Mixtures

High performance liquid chromatography (HPLC) was used for analyzing the reaction mixture: HPLC was equipped with Aminex HPX-87H (Bid Rad, Seoul, Korea) column and a refractive index (RI) detector. An aqueous solution of H₂SO₄ (5 mM) was used as the mobile phase and the flow rate was 0.6 mL min^{−1}. The amounts of glycerol, DG and TG present in the reaction mixture were quantitatively analyzed by calibrating each compound using an aqueous solution of each authentic sample of known concentration using *t*-butanol as an internal standard.

3.6. Catalyst Recycle

The catalyst recycle was conducted with glycerol in the presence of XZ-M (M = Li, Na and K) at 280 °C for 2 h. After the completion of the reaction, the liquid product mixture was removed by the filtration, and the remaining solid catalyst was resuspended in distilled water (50 mL) followed by refluxing for 2 h. The solid catalyst recovered by the filtration and drying under vacuum was reused for the next cycle with a fresh charge of glycerol (50 g).

4. Conclusions

X-type zeolite XZ-M (M = Li, Na, and K), the basic porous solids, were prepared and used as a catalyst to carry out direct etherification of glycerol. XZ-M has similar structural properties of NaX, a previously reported basic heterogeneous catalyst, but there are slight differences in specific surface area and chemical composition. The basicity and catalytic activity of the cations included in XZ-M has been reported in the order of K⁺ > Na⁺ > Li⁺. The measured surface area was observed in the order of XZ-Li > XZ-Na > XZ-K. The reaction temperature increased and the reaction time was shortened to make the reaction rate fast and to reduce the formation of oligomers because XZ-M had lower catalytic activity than NaX. As a result of direct etherification of glycerol at 280 °C for 2 h using 3 wt.% of XZ-Li as a catalyst, the conversion of glycerol was 86.9%, and the selectivities and yields of DG and TG were 70.5, 24.4% and 61.2, 21.2%, respectively. Therefore, DG and TG were efficiently produced by increasing the reaction temperature without significantly increasing the amount of the heterogeneous catalyst within short reaction time.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11111323/s1>, Figure S1: FT-IR spectra, Figure S2: SEM images and EDX data, Figure S3: The influence of the amount of XZ-Li at different temperature, Figure S4: The influence of the amount of XZ-Na at different temperature, Figure S5: The influence of the amount of XZ-K at different temperature, Figure S6: N₂ isotherms, Figure S7: XRD patterns, Table S1: Structural characterization, Table S2: Recycling of XZ-M.

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