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Solventless Catalytic Etherification of Glycerol Using Acetate Salts as Efficient Catalysts

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Diglycerol (DG) and triglycerol (TG) were synthesized via dehydrative etherification reaction of glycerol without solvent. The catalytic activities of alkali metal-acetate salts (LiOAc, NaOAc, and KOAc) for the etherification reaction of glycerol were investigated. Compared to the stronger basic catalysts, the less basic catalysts showed higher selectivity of DG and TG. A half mol % of LiOAc exhibited excellent selectivities of DG and TG as 52.5 and 30.4%, at 260 °C and 6 h. The dependence of reaction on the relative basicity and loading amount of catalyst, reaction time, and reaction temperature were investigated to elucidate the characteristics of etherification reaction of glycerol.

Keywords: Glycerol, Dehydrative etherification, Diglycerol, Triglycerol, Acetate

Introduction

Glycerol is one of the plentiful renewable resources for various chemical intermediates. Recently, glycerol has been produced in large quantities as a side-product during the production of biodiesel which could be prepared by the transesterification of triglyceride and methanol in the presence of catalyst.[1–3] Various methods for the transformation of surplus glycerol to more value-added materials such as epichlorohydrine,[4,5] glycerol carbonate,[6,7] glycidol,[8,9] and ally alcohol[10–12] have been reported.

Condensed glycerols including diglycerol (DG) and triglycerol (TG) which have been used as additives in pharmaceuticals, foods, cosmetics and also used as plasticizer, lubricant, dispersant, stabilizer, and wetting agent[13–16] in various fields were prepared by the reaction of glycerol and epichlorohydrine or glycidol industrially. However, the production of DG and TG using epichlorohydrine or glycidol has suffered by generating large amounts of salt as a by-product or high cost of raw material. To overcome the drawbacks of commercial methods, the etherification reaction of glycerol using base catalysts such as NaOH, KOH, CsOH, and Na_2CO_3 has been reported to convert the glycerol to DG and TG, directly.[3,17–19] Although, however, the etherification reaction of glycerol is a very simple reaction, the direct condensation reaction of glycerol needs harsh reaction condition. Moreover, this reaction is not easy to control because it is difficult to cease at two or three glycerol molecules.[20,21] For these reasons, DG and TG prepared by the direct etherification reaction of glycerol showed poor yield and selectivity due to the production of various side-products including oligomeric and polymeric compounds.[22]

In this work, we report the improved yields and selectivity of DG and TG in the etherification reaction of glycerol using sodium acetate (NaOAc) or potassium acetate (KOAc) as a catalyst. The key feature of this work is controlling the reactivity of the etherification reaction by adjusting the basicity of the catalyst to obtain the enhanced selectivity of DG and TG. We also investigated the effect of reaction temperature, reaction time and the amount of catalyst in the reaction to enhance the yields and selectivity of DG and TG.

Experimental

Materials. Glycerol, NaOH, KOH, lithium acetate (LiOAc), sodium acetate (NaOAc), potassium acetate (KOAc), *t*-butanol, sulfuric acid (98 wt.%, HPLC grade), and H_2O (HPLC grade) were purchased from Sigma-Aldrich Co. (Yongin, Korea). Water (HPLC grade) was purchased from J. T. Baker Co. (Seoul, Korea). All the chemicals were used as obtained without further purification.

Etherification Reaction of Glycerol. The etherification reactions of glycerol were performed using the proper amount of catalyst at the range of 220–280 °C and atmospheric pressure. Glycerol (50 g) was put into a round bottomed flask (100 mL) with magnetic stirring bar. The flask was placed on a heating mantle equipped with a temperature controller. The water generated during the etherification reaction was removed using a Dean-Stark apparatus.

Analysis of Reaction Mixtures. The reaction mixtures were analyzed using the high performance liquid chromatography (HPLC) equipped with an Aminex HPX-87H (Bid Rad) column and the reflective index (RI) detector.

The aqueous solution of H_2SO_4 (5 mM) was used as mobile phase with a flow rate of 0.6 mL min^{-1}. To quantitatively analyze the amount of glycerol, DG, and TG in the reaction mixture, each compound were calibrated using the aqueous solution of respective authentic sample with known concentration in the presence of *t*-butanol as an internal standard.

Results and Discussion

The direct condensation reactions of glycerol were performed in the presence of base catalyst at an ambient pressure. The water generated as a by-product during the reaction was removed by Dean-Stark apparatus. A comparison of base catalysts used in the etherification reaction of glycerol including the previously reported results performed by other groups was shown in Table 1. The catalysts which have relatively strong basicity, LiOH, NaOH, KOH, CsOH, and Na_2CO_3 ($pK_b = 3.67$), showed high conversions of glycerol but low selectivities of DG and TG. Meanwhile, the catalysts which have relatively weak basicity,[23,24] $NaHCO_3$ ($pK_b = 10.33$), LiOAc ($pK_b = 6.79$), NaOAc ($pK_b = 6.58$), and KOAc ($pK_b = 6.10$), exhibited lower conversion of glycerol and higher selectivities of DG and TG than which have stronger basicity implying that the further etherification reaction of DG or TG was not effectively proceeded by the weak bases.[17,25,26]

The effects of reaction temperature in the presence of catalyst were investigated by varying the reaction temperature in the range of 200–280 °C. As shown in Figure 1, all catalysts showed very low conversion of glycerol but high selectivity of DG at 200 and 220 °C. With elevating the reaction temperature, however, the conversion of glycerol drastically increased and the selectivity of DG decreased with increasing that of TG and other products. The selectivities of TG showed maximum as 30.4, 31.9, and 25.1% for LiOAc, NaOAc, and KOAc, respectively, at 260 °C and the selectivity of other products kept increasing indicating that DG was produced at early stage of the reaction. TG

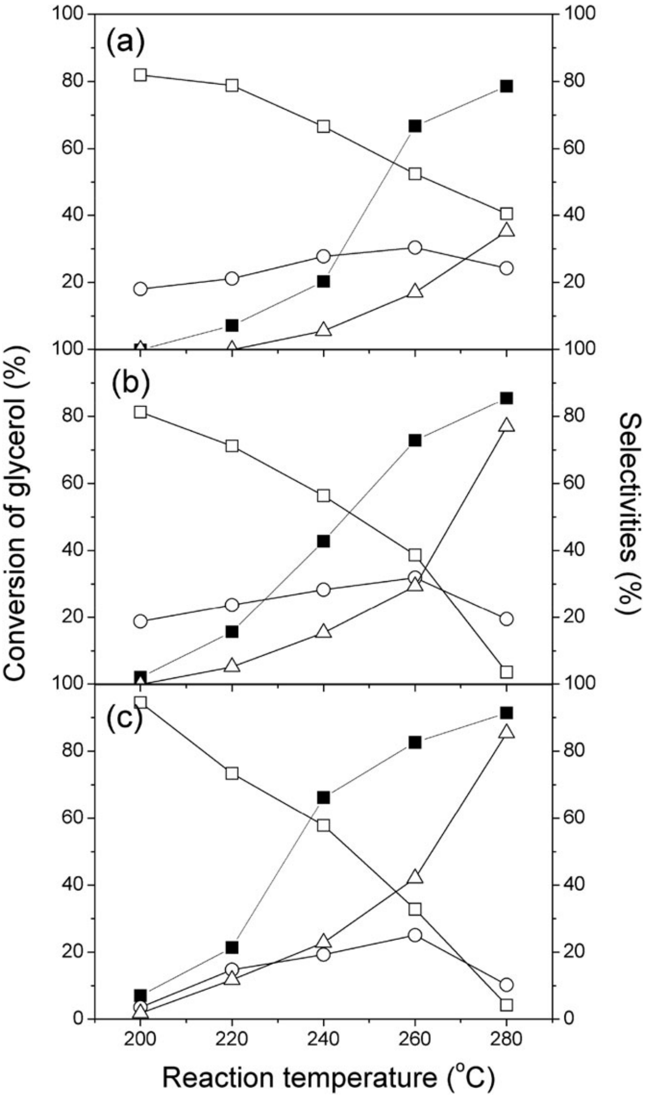

Figure 1. The dependence of reaction temperature on the etherification reaction of glycerol in the presence of (a) LiOAc, (b) NaOAc, and (c) KOAc (—■—: Conversion of glycerol, —□—: Selectivity of DG, —○—: Selectivity of TG, —△—: Selectivity of others, the amount of catalyst: 0.5 mol% and reaction time: 6 h).

Table 1. Etherification reactions of glycerol with base catalysts at 260 °C.

				Selectivity (%)			
Catalyst	Amount of catalyst (mol %)	Reaction time (h)	Conversion of glycerol (%)	DG	TG	Others	Ref.
Na_2CO_3	1.74	8	96	24	35	41	25
$NaHCO_3$	0.22	8	75	27	12	61	26
LiOH[a]	7.7	6	100	33	ND	ND	3
CsOH	0.18	8	74	32	21	47	17
NaOH	0.50	6	83.8	24.5	19.5	56	this work
KOH	0.50	6	91.9	18.9	14.5	66.6	this work
LiOAc	0.50	6	66.7	52.5	30.4	17.1	this work
NaOAc	0.50	6	72.8	38.7	31.9	29.4	this work
KOAc	0.50	6	82.6	32.8	25.1	42.1	this work

[a] Reaction temperature = 240 °C.

would be generated by the etherification reaction of produced DG and unreacted glycerol. Other products including tetra- and longer oligomeric ethers were resulted from the further etherification reaction of produced DG or TG with glycerol, DG or TG existing in the reaction mixture as reported.[3,22]

The effect of reaction time was investigated by varying the etherification reaction time from 1 to 8 h at 260 °C. As showed in Figure 2, increasing the reaction times led to increase the conversion of glycerol and to decrease the selectivity of DG. The selectivity of TG and other products increased slowly with increasing the reaction time. The selectivity of TG in the presence of LiOAc kept increasing in the reaction condition. However, in the presence of NaOAc and KOAc, the maximum selectivities of TG were observed as 31.9 and 26.6%at 6 and 4 h, respectively. The selectivity of other products also increased slowly with increasing the reaction time and the increasing rate were corresponding to the basicity of catalyst. The conversion of glycerol was inversely proportional to the selectivity of DG because the increased concentration of DG in the reaction mixture could be subjected on further dehydration reaction which gave oligomeric ethers. As shown in Figures 1 and 2, the catalyst which had higher basicity showed the higher conversion of glycerol but exhibited the lower selectivities of DG and TG than the catalyst which had lower basicity suggesting that the further dehydrative etherification reaction of produced DG was proceeded efficiently in the presence of catalyst which had stronger basicity.

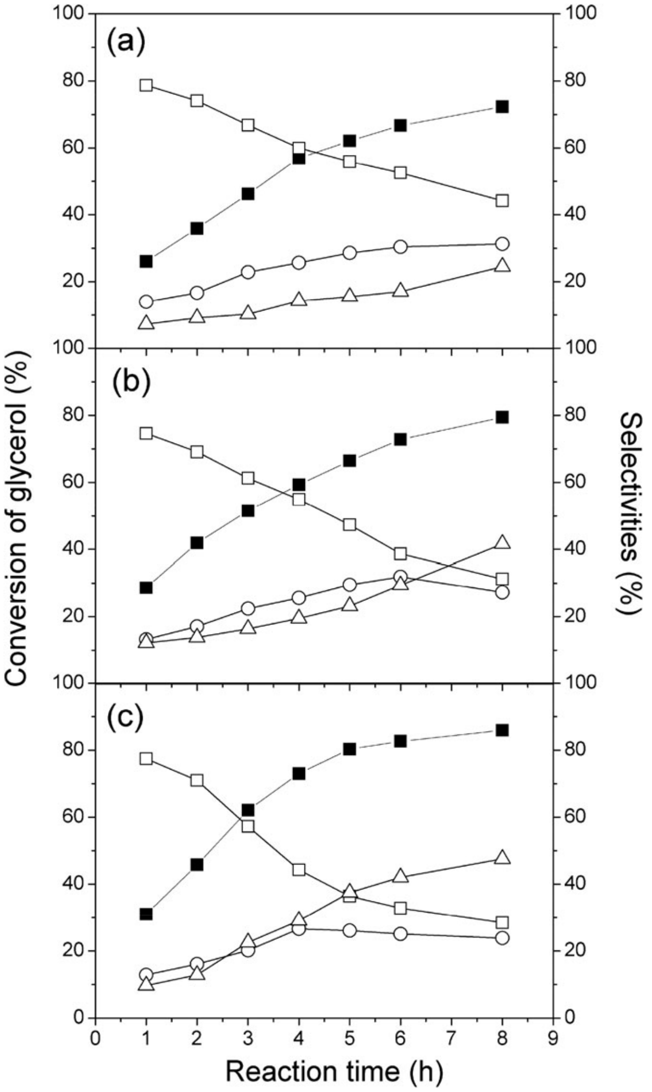

Figure 2. The dependence of reaction time on the etherification reaction of glycerol in the presence of (a) LiOAc, (b) NaOAc, and (c) KOAc (—■—: Conversion of glycerol, —□—: Selectivity of DG, —○—: Selectivity of TG, —△—: Selectivity of others, the amount of catalyst: 0.5 mol% and reaction temperature: 260 °C).

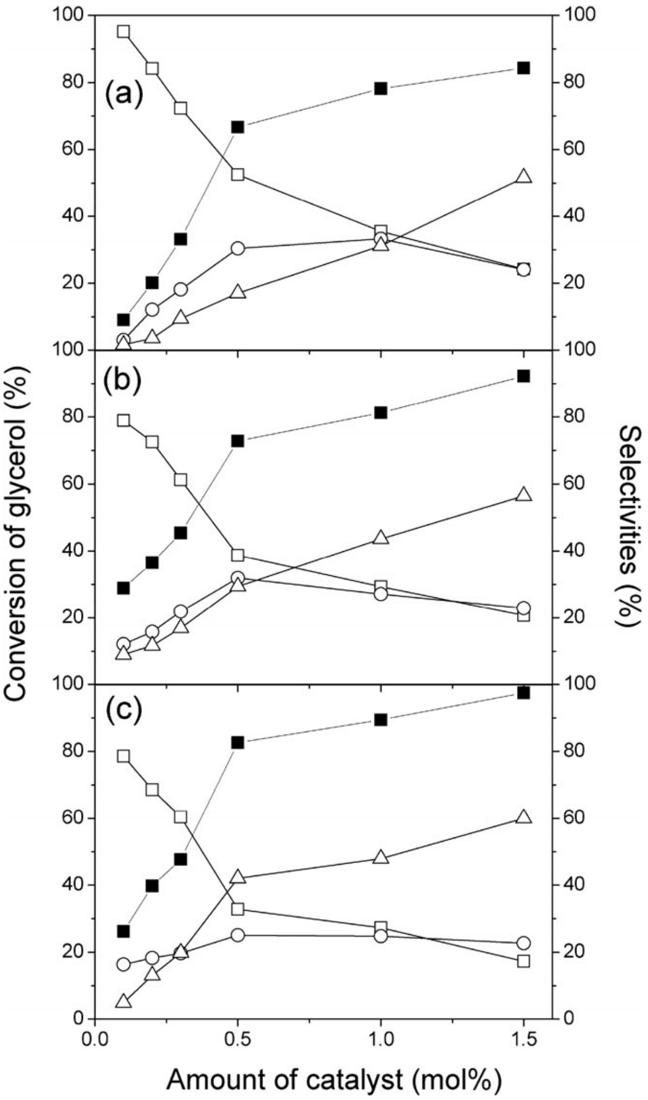

Figure 3. The dependence of amount of (a) LiOAc, (b) NaOAc, and (c) KOAc on the etherification reaction of glycerol (—■—: Conversion of glycerol, —□—: Selectivity of DG, —○—: Selectivity of TG, —△—: Selectivity of others, reaction time: 6 h, reaction temperature: 260 °C).

The etherification reactions of glycerol were executed for 6 h at 260 °C with varied amount of each catalyst. As shown in Figure 3, the conversion of glycerol steeply increased with increasing the amount of catalyst up to 0.5 mol % but the increasing rate of conversion reduced at over 0.5 mol % due to the increased viscosity of reaction mixture resulted from the increased DG, TG, and other oligomeric products. With larger amount of catalyst, the selectivities of DG and TG were lower but the selectivity of other products was higher than with smaller amount of catalyst. The selectivity of TG exhibited the maximum at 1.0, 0.,5 and 0.5 mol % of LiOAc, NaOAc, and KOAc, respectively. In the presence of catalyst over 1.0 mol % oligomeric other products were observed as major product.

Conclusion

The dehydrative etherification reactions of glycerol have been performed without solvent using LiOAc, NaOAc, or KOAc as the catalyst at an ambient pressure. The conversion of glycerol and the selectivities of DG, TG, and other oligomeric compounds could be controlled by varying the basicity and amount of catalyst. The dependences of the etherification reaction of glycerol on the reaction time and reaction temperature were also investigated. 0.5 mol % of LiOAc showed an excellent catalytic performance with the selectivities of DG and TG as 52.5 and 30.4%, respectively, at 260 °C and 6 h.

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