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Synthesis of Glycerol Carbonate by Transesterification of Glycerol with Urea Over Zn/Al Mixed Oxide

Young Bok Ryu[1,2], Jae Ho Baek[1], Yangdo Kim[2,*], and Man Sig Lee[1,*]

[1] *Korea Institute of Industrial Technology (KITECH), Ulsan 681-802, South Korea*
[2] *School of Materials Science and Engineering, Pusan National University, Busan 609-735, South Korea*

Reactions of glycerol carbonate using glycerol and urea have been carried out previously using $ZnSO_4$ and ZnO catalysts, and high yields have been reported using $ZnSO_4$ as catalyst. However, this salt is soluble in glycerol, and recycling of catalyst is difficult after the reaction. In this study, we prepared a mixed metal oxide catalyst using Zn and Al, and this catalyst consisted of a mixture of ZnO and $ZnAl_2O_4$. We confirmed the conversion of glycerol and the yield of glycerol carbonate of the amount of Al. As a result, we obtained a yield of 82.3% and a conversion of 82.7%. In addition we obtained high yield in recycling of catalyst. The yield of the glycerol carbonate increases with an increase of acid and base site of catalysts and the highest catalytic activity was obtained when acid/base ratio was approx. 1. From this result, we may conclude that the acid and base site density and ratio of catalysts were very important parameters in the synthesis of glycerol carbonate from urea and glycerol.

Keywords: Glycerol, Glycerol Carbonate, Catalyst, Metal Oxide.

1. INTRODUCTION

Glycerol is a synthesis intermediate for the preparation of a large number of compounds via oxidation, etherification, esterification, transesterification, polymerization, and so on.[1–3] One important glycerol derivative is the glycerol carbonate (GC) which is widely used as protic solvent (in resins and plastics), additive, and as chemical intermediate. Due to its low toxicity, low evaporation rate, low flammability, and moisturizing ability, GC is used as wetting agent for cosmetics and carrier solvent for medical preparations. Glycerol carbonate is a relatively new material in the chemical industry with a large potential as a novel component of gas-separation membranes, a solvent for several types of materials, and biolubricant owing to its adhesion to metallic surfaces and resistance to oxidation, hydrolysis, and pressure.[4–6] The main methods for the preparation of GC are based on the reaction of glycerol with a carbonate source (phosgene, a dialkyl carbonate[7] or an alkylene carbonate), urea, and carbon monoxide, and oxygen.[8,9] Concerning the preparation of GC from urea and glycerol, the same authors have patented a process for preparing GC using metallic or organometallic salts, or supported metallic compounds.[8,10–13] As described above, the reaction between urea and glycerol has been performed using zinc sulfate ($ZnSO_4$) and zinc oxide (ZnO) catalyst. High yields are reported using $ZnSO_4$ as catalyst,[11,12,14,15] however, this salt is soluble in glycerol and the reaction takes place under homogeneous catalysis with the catalysts being partially recovered after the reaction.

In this research, we produced a binary metal oxide catalyst to facilitate, the synthesis of glycerol carbonate using glycerol and urea. We produced this binary catalyst by using Zn and Al, and we evaluated the change in the yield of glycerol carbonate and the conversion of glycerol in the synthesis reaction, as well as the differences in the characteristics of the catalyst as a function of the mixed molecular ratios of Zn and Al. We researched the reasons why the conversion and yield increased.

2. EXPERIMENTAL DETAILS

2.1. Production of Catalyst

The catalyst was produced through general co-precipitation by mixing Zn and Al oxides. First, we dissolved zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$, Aldrich] and aluminum nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$, Aldrich] until the concentration of metallic salts reached 1.2 M in distilled water according to a different molecular ratio. Then, we mixed sodium nitrate ($NaNO_3$, Aldrich) with

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[*] Authors to whom correspondence should be addressed.

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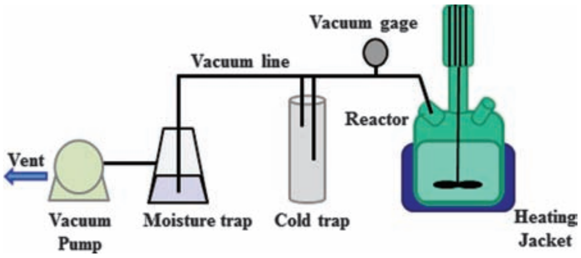

Figure 1. Schematic diagram of the experimental apparatus for reaction.

sodium hydroxide (NaOH, Yakuri) to induce precipitation of the metallic salts, reaching a final pH of 6.0. The solution was aged at a temperature of 50 °C for 18 h. We then filtered the particles, and removed any impurities, such as alkali ions by using distilled water. The particles were dried at a temperature of 100 °C for 24 h, and then, Zn–Al mixed oxide catalyst was produced by calcination for 6 h at a temperature of 450 °C in ambient atmosphere.

2.2. Reaction Procedure

The outline for the synthesis of glycerol carbonate in this research is shown in Figure 1. A 100 ml round-bottom glass flask was used in the synthesizing reaction. First, we agitated 0.2 mol of glycerol (Aldrich) and 0.2 mol of urea (Aldrich) at a constant speed. We simultaneously heated the glycerol and urea to 140 °C (the reaction temperature) and added the catalyst. We used 5 wt% of the catalyst as the weight ratio compared with the glycerol. The ammonia gas, which was produced during the reaction, was removed through a vacuum line connected to a synthesizer, and the vacuum within the chemical reactor was kept constant at 30 mbar. The synthesis of glycerol carbonate was completed in a total reaction time of 5 h, and then, both the yield of the glycerol carbonate and the conversion of glycerol were calculated by analyzing the sample using gas chromatography (Agilent, 7890A) after separating the catalyst from products by centrifugation.

3. RESULTS AND DISCUSSION

3.1. Characteristic Analysis of Catalyst

We produced a mixed oxide catalyst at different molecular ratios of Zn to Al. The crystalline phase of the prepared catalyst was analyzed by XRD, and the results are shown in Figure 2. We confirmed that the crystalline of $ZnAl_2O_4$ was slowly increased with an increasing of the ratio of Al, and the crystalline of ZnO was decreased with an increasing of the ratio of Al. It is seen from the XRD patterns that the $ZnAl_2O_4$ particles at Zn/Al = 5:5 is amorphous.

The BET surface area and pore volume of the produced catalyst is listed in Table I. We confirmed that the surface area of the catalyst was slowly increased with an increasing of the ratio of Al, and the surface area was rapidly increased when the molecular ratio of Zn/Al is 5:5.

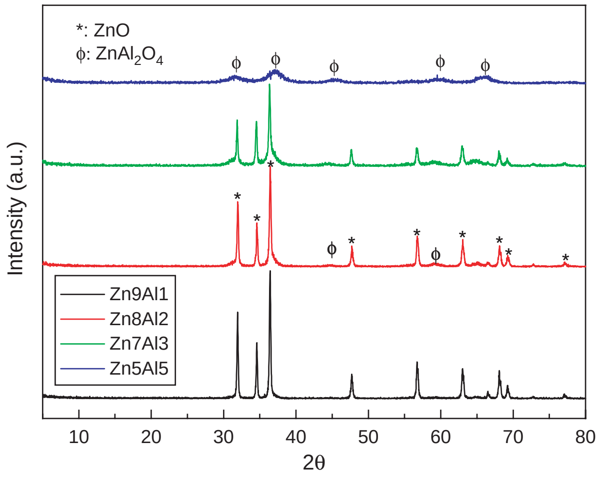

Figure 2. X-ray diffraction patterns of catalysts prepared at different Zn/Al molar ratio.

Because as shown in the results of the XRD results, crystal structure is amorphous in Zn/Al ratio = 5:5. Figure 3 shows the SEM images of the catalysts prepared by different Zn/Al ratio. The catalysts particles have 20∼30 nm size. The catalyst particles changed little according to the ratio of Zn/Al, but the needle-shaped particle was observed partly when the molecular ratio of Zn/Al was 7:3.

Figure 4 shows the NH_3 and CO_2-temperature programed desorption (TPD) of catalysts prepared at different molecular ratio of Zn/Al. The physicochemical properties of the catalysts are listed in Table II.

In NH_3-TPD results, it seems that all catalysts had the characteristics of a weak acid site in which NH_3 was desorbed at around 300 °C, and the strong acid site was increased with an increasing of the molecular ratio of Al at around 700 °C. In addition, we confirmed that the distributions of weak acid sites and strong acid sites were comparable to each other with an increasing of the number of acid sites when the molecular ratio of Zn/Al is 5:5. In NH_3-TPD results, the number of acid sites increased with an increasing of Zn–Al mixed ratio, in particular, the strong acid sites increased at around 700 °C.

In CO_2-TPD results, the prepared catalysts had the characteristics of a weak base site in which CO_2 was desorbed at around 150 °C and a strong base site existed around at 650 °C. The number of acid sites increased with an increasing of the molecular ratio of Al until Zn/Al = 7:3. When Zn/Al was 5:5 the number of base sites decreased relatively at Zn/Al = 5:5. As a result, the number of base

Table I. Physical properties of catalysts by BET.

Zn/Al molar ratio	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
9:1	20.60	0.074710	145.05
8:2	38.17	0.107202	112.33
7:3	34.73	0.057366	66.07
5:5	219.71	0.330480	60.17

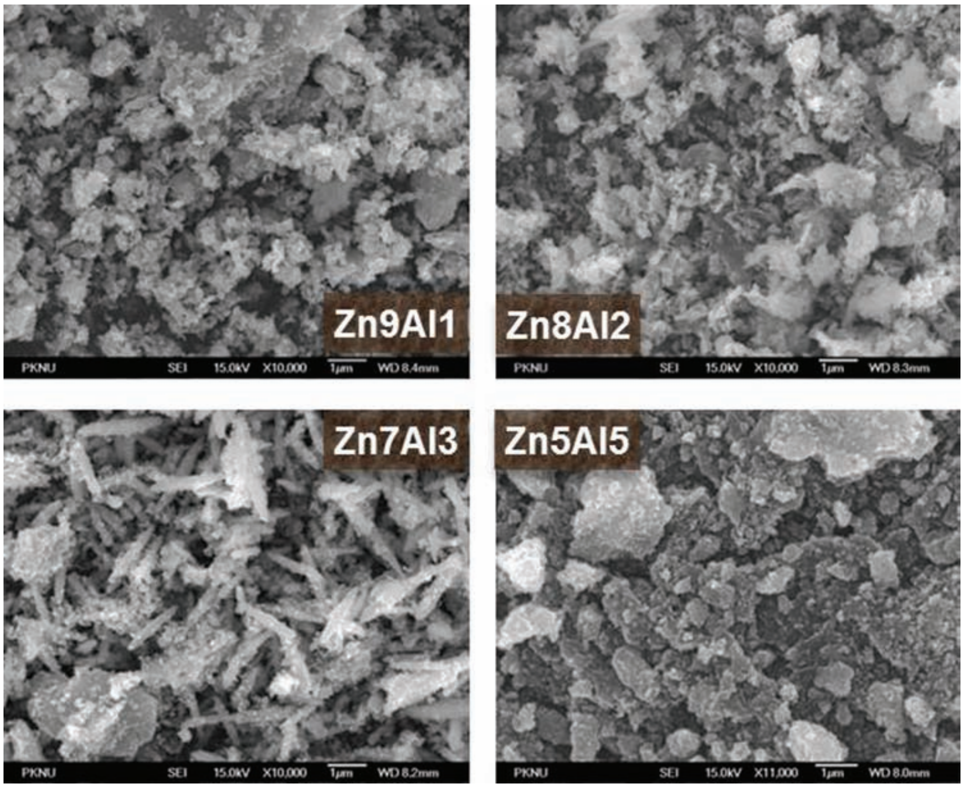

Figure 3. SEM image of catalysts prepared at different Zn/Al molar ratio.

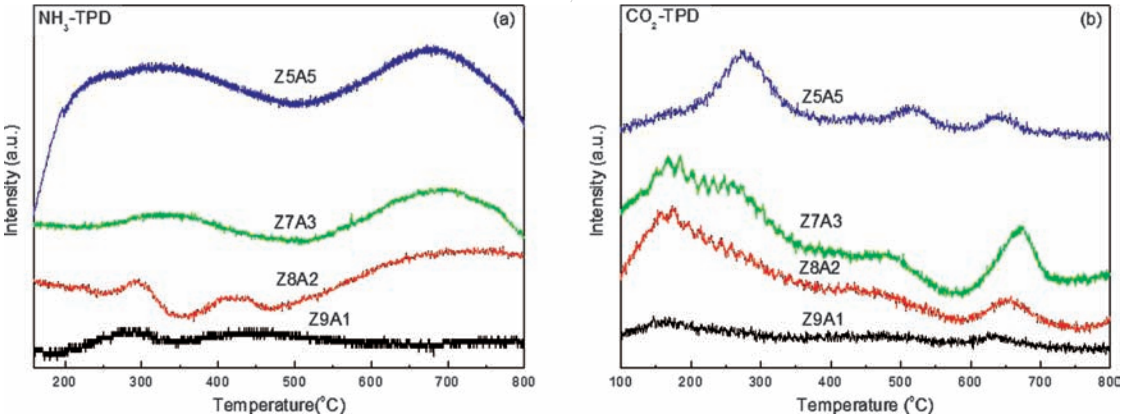

Figure 4. NH_3 and CO_2-TPD spectra of Zn–Al mixed oxides [(a) NH_3-TPD, (b) CO_2-TPD].

site increased with an increasing of molecular of Al, but the number of base site decreased at Zn/Al = 5:5.

3.2. Relation Between Characteristic of Catalyst Surface and Reaction Activity

The accepted mechanism for the reaction of urea with alcohols involves two steps, and in the specific case of glycerol it is as follows.[15] The first step is the carbamoylation of glycerol to glycerol carbamate liberating a mole of ammonia. This step occurs at a higher reaction rate than the second step, which is the carbonylation of glycerol

Table II. Physicochemical properties of catalysts.

Zn/Al molar ratio	Surface area (m^2/g)	Acid site density[a] (μmol/g)	Base site density[b] (μmol/g)	Acid/base ratio
9:1	20.60	7.61	1.86	4.09
8:2	38.17	9.93	5.41	1.84
7:3	34.73	6.24	7.15	0.87
5:5	219.71	12.03	2.92	4.12

Notes: [a]by TPD of NH_3; [b]by TPD of CO_2.

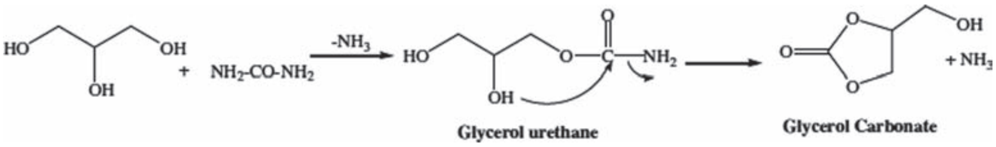

Figure 5. The accepted mechanism for the reaction of urea with glycerol.

urethane to glycerol carbonate, with the elimination of a second mole of ammonia (Fig. 5).

In this study, the result of the reaction test in the synthesis of the glycerol carbonate with glycerol and urea shown in Figure 6. The Acid/Base ratio of catalysts is a very important parameter in conversion, selectivity and yield of products and the results were summarized in Table III. We obtained that the conversion was 34.9% and the yield was 30.4% using only ZnO catalyst. In addition, it was found that by-products were created besides the final product, glycerol carbonate in the reaction. The conversion of the glycerol decreased and the yield of the glycerol carbonate also decreased because by-product created. It is supposed that the additional by-product was created because the reaction time between the reaction intermediate and ammonia gas, which was created in the course of reaction, was faster than the time available for the ammonia gas to escape. The conversion and yield were increased with an increasing of molecular ratio of Al, and has a maximum point when Zn/Al molecular ratio was 7:3. In the maximum point, the conversion of the glycerol was 82.7% and the yield of the glycerol carbonate was 82.3%. However, it was found that the conversion and the yield decreased with a molecular ratio of 5:5.

The change of the yield of the glycerol carbonate and the acid/base ratio of the catalysts are shown in Figure 6. When the yield has maximum point (Zn/Al = 7:3), acid/base ratio was 0.87. From this result, the yield of the glycerol carbonate increases with an increasing of acid and base site density of catalysts and the highest catalytic activity was obtained when acid/base ratio was approx. 1. Taking into account all the above-mentioned features, a mechanism can be proposed in which Lewis acid sites are able to activate the carbonyl group, making it more prone to the nucleophilic attack of the glycerol adsorbed on the Lewis basic site (Fig. 7).[16] It considered that the acid/base site in the synthesis of the glycerol carbonate with glycerol and urea is the active site of the catalyst when they react on the surface of catalyst. In the reaction between glycerol and urea, the acid/base ratio of the catalyst should be equal. We may conclude that the acid and base site density and ratio were very important parameters in the synthesis of glycerol carbonate from urea and glycerol.

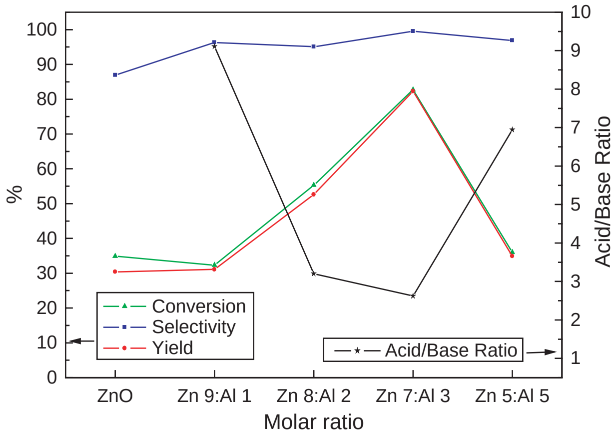

Figure 6. Effect of acid/base ratio on the conversion, selectivity and yield of products.

Table III. Conversion, selectivity and yield of prepared at different Zn/Al molar ratio.

Zn/Al molar ratio	Conversion (%)	Selectivity (%)	Yield (%)	Acid/base ratio
10:0	34.9	86.9	30.4	–
9:1	32.3	96.3	31.1	4.09
8:2	55.3	95.1	52.6	1.84
7:3	82.7	99.5	82.3	0.87
5:5	36.0	96.9	34.9	4.12

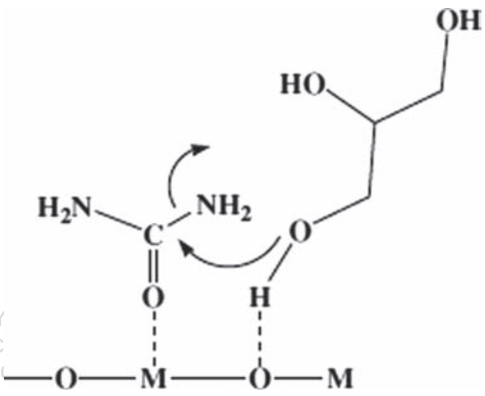

Figure 7. Reaction mechanism on catalyst surface.

4. CONCLUSION

In this paper, the glycerol carbonate was synthesized by glycerol and urea using metal oxide catalysts. The physical properties of the prepared metal oxide catalysts were investigated by XRD, BET, FE-SEM, and TPD. In addition, we confirmed the conversion of the glycerol and the yield of the glycerol carbonate according to different molecular ratio of Zn/Al. From XRD results, the crystalline of prepared $ZnAl_2O_4$ was slowly increased with an increasing of the ratio of Al. When the molecular ratio was Zn/Al = 7:3, the conversion of the glycerol was 82.7% and the yield of the glycerol carbonate was 82.3%. The conversion of the glycerol and the yield of the glycerol carbonate can be obtained higher when acid/base ratio is approx. 1. From this result, we may conclude that the acid and base site density and ratio of catalysts were very important parameters in the synthesis of glycerol carbonate from urea and glycerol.

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