Res Chem Intermed
DOI 10.1007/s11164-015-2336-3

Synthesis of Zn/Al mixed-oxide catalyst for carbonylation of glycerol with urea

Young Bok Ryu[1,2] · Ji Sun Kim[1] · Kyeong Ho Kim[1] · Yangdo Kim[2] · Man Sig Lee[1]

Received: 10 July 2015 / Accepted: 22 October 2015

Abstract Zn/Al mixed oxide was prepared by the coprecipitation or the hydrothermal method under different conditions and used as catalyst for synthesis of glycerol carbonate by carbonylation of glycerol with urea. The physical properties of the prepared Zn/Al mixed oxide particles were investigated, as well as their activity as catalyst in the mentioned synthesis. The dried Zn/Al mixed-oxide particles prepared by the coprecipitation method showed higher activity in synthesis of glycerol carbonate than those prepared by the hydrothermal method. The Zn/Al mixed oxide prepared by the coprecipitation method without $NaNO_3$ showed the highest catalytic activity in synthesis of glycerol carbonate.

Keywords Glycerol · Glycerol carbonate · Zn/Al mixed oxide · Carbonylation

Introduction

Biodiesel as defined by ASTM D6751-12 is fuel comprising monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats [1]. Use of biodiesel is increasing and becoming more common worldwide, because it is renewable, nontoxic, biodegradable, and essentially free of sulfur and aromatics. Also, addition of biodiesel to diesel can improve its lubricity, ensure complete combustion, and increase engine performance [2]. However, one major drawback of biodiesel is

---

✉ Yangdo Kim
yangdo@pusan.ac.kr

✉ Man Sig Lee
lms5440@kitech.re.kr

[1] Korea Institute of Industrial Technology (KITECH), Ulsan 681-802, Republic of Korea

[2] Department of Materials Science and Engineering, Pusan National University, Busan 609-735, Republic of Korea

byproduction of large amounts of undesired glycerol during the transesterification process, resulting in a large surplus in the current glycerol market [3]. Glycerol is normally generated at the rate of 1 mol glycerol for every 3 mol methyl ester synthesized, approximately 10 wt% of the total product. Since production of biofuels from biomass is increasing, such surplus production of glycerol is expected to continue for years to come. Utilization of glycerol as a platform chemical may partially compensate for the production costs of biodiesel, making it economically feasible as well as overcoming the problem of disposal of the surplus crude glycerol from biodiesel industries [4]. Glycerol is widely available and rich in functionalities. Recent progress in catalysis has enabled conversion of glycerol to commodity chemicals such as acrolein, 1,3-propanediol [5], docosahexaenoic acid, polyglycerols, and glycerol carbonate (GC). One important glycerol derivative is GC, which is widely used as a protic solvent (in resins and plastics), additive, and chemical intermediate [6]. Due to its low toxicity, low evaporation rate, low flammability, and moisturizing ability, GC is also used as a wetting agent in cosmetics [7] and carrier solvent for medical preparations. The main methods for preparation of GC are based on reaction of glycerol with a carbonate source (phosgene, a dialkyl carbonate [8] or an alkylene carbonate [9]), urea [10], carbon monoxide [11], carbon dioxide [12], and oxygen [13, 14]. Concerning 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 [14, 15]. As described above, the reaction between urea and glycerol has been performed using zinc sulfate ($ZnSO_4$) and zinc oxide (ZnO) catalysts. High yields are reported when using $ZnSO_4$ as catalyst [16, 17], but this salt is soluble in glycerol and the reaction takes place under homogeneous conditions with the catalyst being partially recovered after the reaction. Several catalysts have been used in carbonylation of glycerol with urea, mainly Zn-based and other metal catalysts [18–21]; For example, a high yield of glycerol carbonate (91 %) was obtained using La_2O_3 as catalyst, and the conversion of glycerol reached 98 % when using metal monoglycerolates as catalyst [18]. However, these methods suffer from the serious environmental problems of use of heavy metals and the nonrenewability and exhaustion of mineral resources.

In this study, we prepared Zn/Al mixed-oxide particles by the coprecipitation and the hydrothermal method. The physical properties of the prepared Zn/Al mixed-oxide particles were investigated. We also investigated the effect of synthesis conditions on the physical properties of the Zn/Al mixed oxide, and examined the activity of the Zn/Al mixed-oxide particles as catalyst in synthesis of glycerol carbonate.

Experimental

Materials

Glycerol (99.5 %), urea (99 %), glycerol carbonate (99 %), zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$, 98 %], aluminum nitrate nonahydrate [$Al(NO_3)_3{\cdot}9H_2O$, 98 %], sodium nitrate ($NaNO_3$, 99 %), and tetraethylene glycol (TEG, 99 %) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, 97 %) was purchased from Daejung Chemicals and Metals. All chemicals were used directly without further purification or pretreatment.

Preparation of catalysts

Zn/Al mixed oxides were prepared by the coprecipitation and the hydrothermal method. Specifically, 25.5 g $Zn(NO_3)_2{\cdot}6H_2O$ and 13.78 g $Al(NO_3)_3{\cdot}9H_2O$ (nominal Zn:Al molar ratio 7:3) were dissolved in 100 ml deionized water at room temperature under stirring (solution A). NaOH (11.38 g) and 4.74 g $NaNO_3$ (or not included) were dissolved in 100 ml deionized water (solution B). Solution B was added dropwise to a beaker containing 100 ml solution A, resulting in a pH of 13 of the mixture. The dropping rate of solution B was under 1.0 ml/min for 2 h. Then, the mixture was aged at 50 °C for 18 h or was transferred to a 250-ml Teflon container held in a stainless-steel vessel for hydrothermal treatment at 200 °C during 3 h. After that, the precipitate was filtered and washed to eliminate alkali metals and nitrate ions until the pH of the washing water was 6–8. The particles were dried at 105 °C for 24 h and then calcined at 700 °C for 3 h.

Characterization of catalysts

Dried fine powder of synthesized Zn/Al mixed oxide was subjected to thermogravimetric–differential thermal analysis (TG–DTA, TA Instruments SDT Q600) to determine the temperature of possible decomposition and phase changes. The samples were heated at a rate of 10 °C/min from 30 to 1400 °C.

The major phase of the obtained particles was analyzed by X-ray diffraction (XRD, Philips X'Pert) using Cu K_α radiation.

The surface acidity and basicity of the catalysts were measured by temperature programmed desorption (TPD) of NH_3 and CO_2, and carred out on TPD flow system (Micromeritics AutoChem II 2920) equipped with a thermal conductivity detector (TCD). Each sample (100 mg) was preheated in He flow at 500 °C. Adsorption of NH_3 (or CO_2) was performed at 50 °C, followed by He purge to remove physisorbed NH_3 (or CO_2). The desorption process was performed at a heating rate of 10 °C/min from 50 to 800 °C.

The particle size and external morphology of the prepared particles were observed using a field-emission scanning electron microscope (FE-SEM, Hitachi, SU-8020) at accelerating voltage of 30.0 kV.

Activity test

The catalytic performance of the Zn/Al mixed oxide was evaluated in a 100-ml round-bottomed flask equipped with a vacuum pump. In a typical experiment, 0.2 mol glycerol and 0.2 mol urea were first fed to the reactor and stirred at a constant rate. After attainment of the desired temperature (140 °C), a known quantity of catalyst (5 wt% of glycerol) was added to the reactor. Then, the reaction temperature was ramped to 160 °C under vacuum to remove ammonia as a byproduct. The reaction was maintained for 5 h, then the reactants and products were analyzed using a gas chromatograph (Agilent 7890A) equipped with a flame ionization detector (FID) and a capillary column (HP-INNOWax, 30 m × 0.32 mm × 0.25 μm). Tetraethylene glycol (TEG) was used as internal standard. The conversion and selectivity were calculated based on the assumption that glycerol was the limiting reactant.

Results and discussion

Characterization of catalysts

TG–DTA

Figure 1 shows typical DTA and TGA thermodiagrams for the Zn/Al mixed-oxide particles prepared under different conditions. There are three obvious mass loss stages in the TG curve. The initial stage under 100 °C can be associated with release of superficial absorbed water. Zn/Al mixed-oxide particles showed an endothermic peak at about 100 °C [22]. It is thought that the endothermic peak is due to free adsorbed water. The minor endothermic peak at 210 °C is accompanied by weight loss of 10 %, being attributed to release of hydrate water from the Zn/Al mixed-oxide particles prepared by coprecipitation. In the temperature range of 200–500 °C, the exothermic peak at 300 °C is due to decomposition of residual nitrate in all particles.

XRD

Figure 2 shows the XRD patterns of the Zn/Al mixed-oxide particles prepared under different conditions. These particles were only dried at 105 °C without any calcination. The patterns of all the Zn/Al mixed-oxide particles show strong peak reflections from hexagonal ZnO [Joint Committee on Powder Diffraction Standards (JCPDS) file no. 79-0205] as well as weak peak reflections from cubic $ZnAl_2O_4$ (JCPDS file no. 73-1961). In addition, no peak corresponding to alumina crystal phase was observed for any particles. This means that Al_2O_3 was well mixed with ZnO.

The Zn/Al mixed-oxide particles prepared by the hydrothermal method exhibited higher crystallinity than those prepared by coprecipitation. It was confirmed that the Zn/Al mixed-oxide particles prepared by the hydrothermal method could reach high crystallinity without calcination. The peak at 2θ of 29.5° is probably caused by residual $NaNO_3$ in the particles [23].

TPD

Temperature-programmed desorption (TPD) is one of the most widely used and flexible techniques for characterizing oxide surfaces. Analysis of the quantity and strength of active (acidic and basic) sites on particles is crucial to understand and predict catalyst performance. According to previous reports [18, 24], desorption peaks can be roughly divided into three regions, corresponding to weak (50–150 °C), moderate (150–400 °C), and strong (>400 °C) sites.

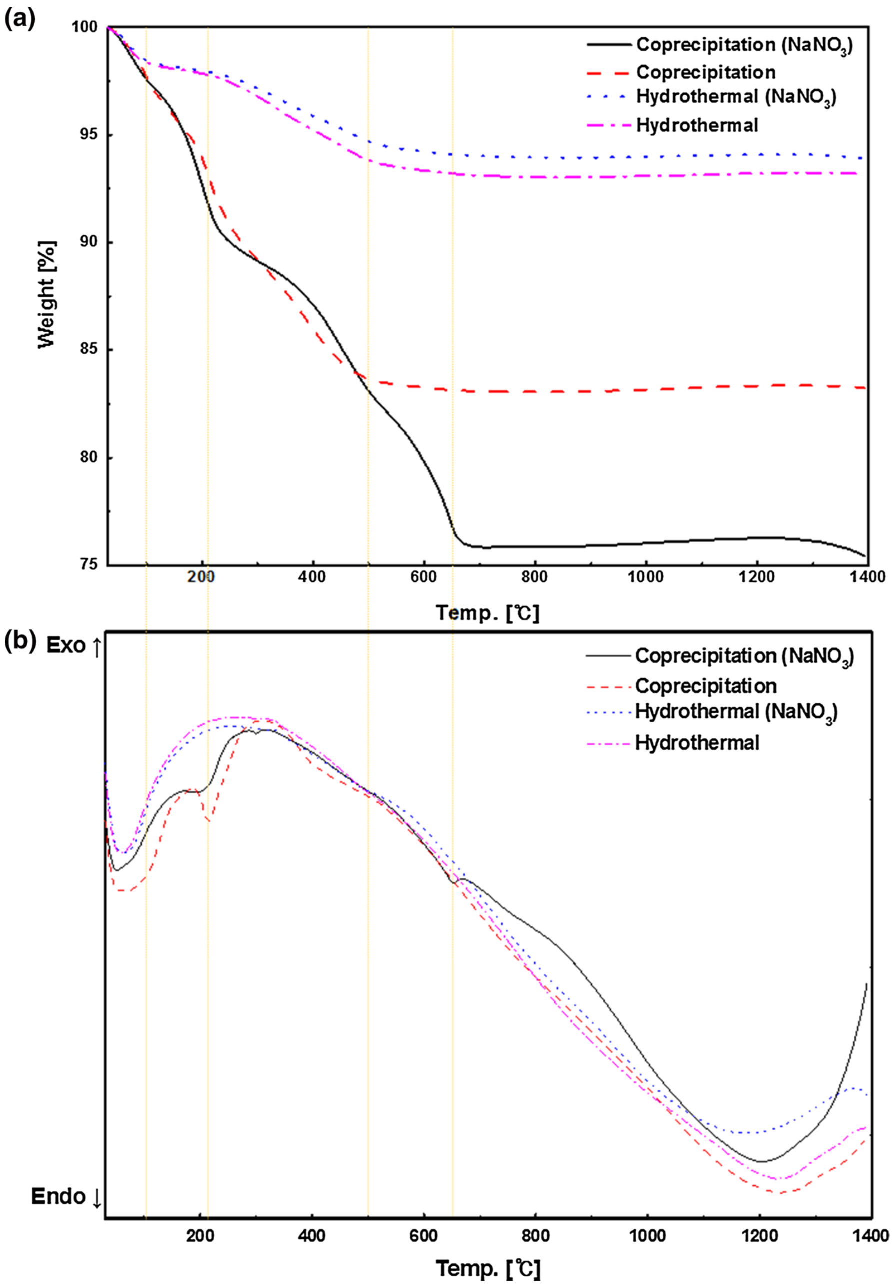

Fig. 1 TGA (**a**) and DTA (**b**) curves of Zn/Al mixed-oxide particles prepared under different conditions

Figure 3 shows the NH_3 (Fig. 3a) and CO_2 (Fig. 3b) TPD profiles for the Zn/Al mixed-oxide particles prepared under different conditions. All the profiles in Fig. 3a show weakly and moderately acidic sites. The Zn/Al mixed-oxide particles prepared

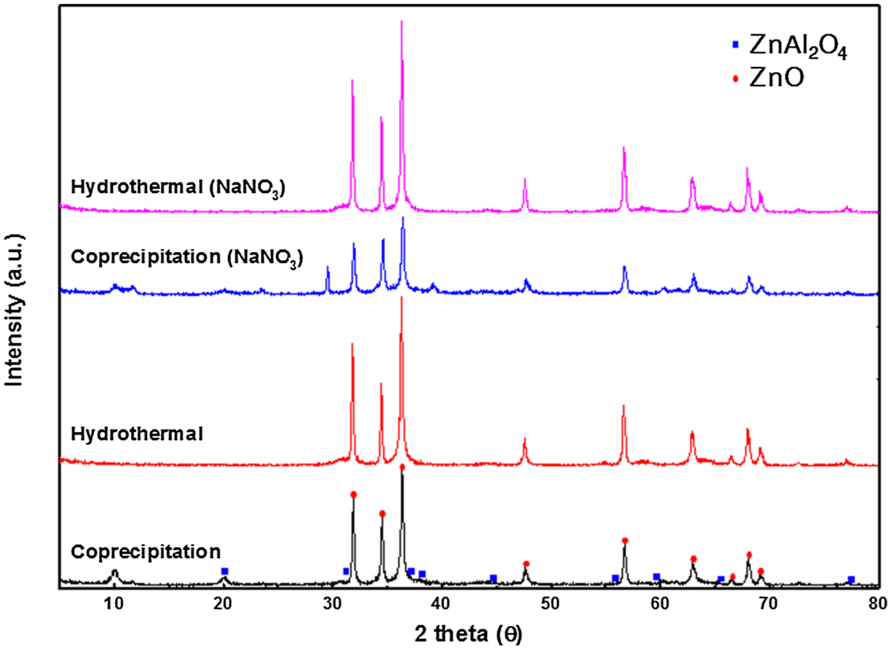

Fig. 2 XRD pattern of Zn/Al mixed-oxide particles prepared under different conditions

by coprecipitation using $NaNO_3$ showed a strong desorption peak at 600 °C (strongly acidic site).

The CO_2 desorption profiles in Fig. 3b show moderately and strongly basic sites. The total basicities of the samples follow the sequence: coprecipitation ($NaNO_3$) > coprecipitation > hydrothermal > hydrothermal ($NaNO_3$). It should also be noted that the basicity of the moderately and strongly (but not too strongly) basic sites of the samples follows the order: coprecipitation > coprecipitation ($NaNO_3$) > hydrothermal > hydrothermal ($NaNO_3$). The Zn/Al mixed-oxide particles prepared by coprecipitation using $NaNO_3$ showed a too strong desorption peak at 600 °C (too strongly basic site).

The peak area can be considered to represent the amount of active sites. The acidity (acidic site density) and basicity (basic site density) of the Zn/Al mixed-oxide particles are listed in Table 1.

SEM

The surface morphology of Zn/Al mixed-oxide particles prepared under different conditions was studied by scanning electron microscopy (SEM); the images obtained are shown in Fig. 4. The Zn/Al mixed-oxide particles exhibited irregular particle shape such as rod, dumbbell, etc., thus being constructed from a net-like, porous structure. In addition, the surface of the Zn/Al mixed-oxide particles prepared using $NaNO_3$ comprised smaller aggregates with variable morphologies.

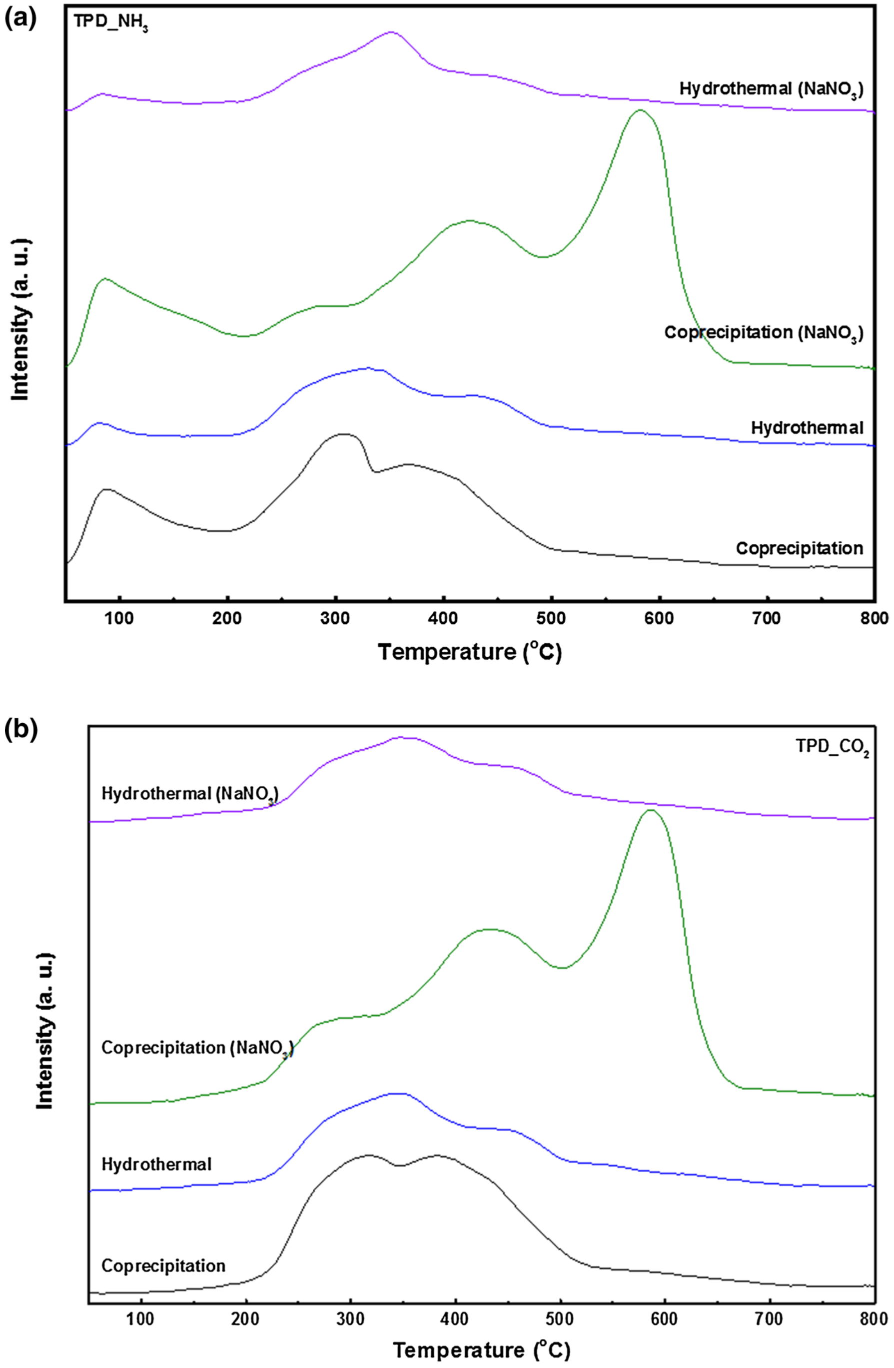

Fig. 3 **a** NH_3–TPD and **b** CO_2–TPD profiles of Zn/Al mixed-oxide particles prepared under different conditions

Table 1 Physical properties of Zn/Al mixed oxide particles prepared under different conditions

	Coprecipitation		Hydrothermal		Coprecipitation ($NaNO_3$)		Hydrothermal ($NaNO_3$)	
Results of XRF analysis	Zn(O)	Al($_2O_3$)	Zn(O)	Al($_2O_3$)	Zn(O)	Al($_2O_3$)	Zn(O)	Al($_2O_3$)
Element (%)	83.1	16.9	82.3	17.7	82.7	17.3	82.8	17.2
Oxide (%)	75.2	24.8	74.0	26.0	74.7	25.3	74.7	25.3
Results of TPD analysis								
Acidic site density (mmol/g)	3.43		1.91		5.86		2	
Basic site density (mmol/g)	2.76		1.56		4.44		1.44	
Acidic site density (mmol/g)	1.24		1.22		1.32		1.39	
Intensity (XRD)	559		818		381		925	
GC yield	82.4 %		73.3 %		78.6 %		55.5 %	

XRF X-ray fluorescence

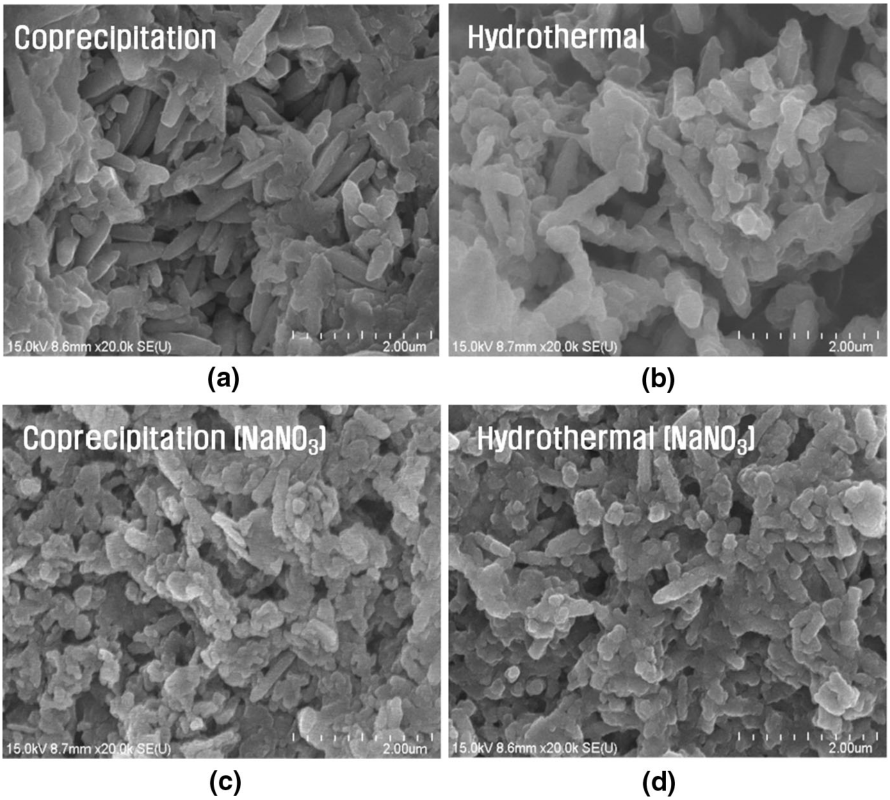

Fig. 4 SEM images of Zn/Al mixed-oxide particles prepared under different conditions: **a** coprecipitation, **b** hydrothermal, **c** coprecipitation ($NaNO_3$), and **d** hydrothermal ($NaNO_3$)

Activity of catalysts

Figure 5 shows the catalytic activity of the Zn/Al mixed-oxide particles in terms of glycerol conversion, glycerol carbonate selectivity, and yield. The yield of glycerol carbonate obtained through the catalyzed reaction was significantly higher compared with the uncatalyzed homogeneous reaction. In the blank test in the absence of catalyst, a GC yield of 22.2 % was obtained with glycerol conversion of 22.2 %. It is apparent that the important role of the catalyst increased the conversion of glycerol under our reaction conditions.

The conversion of glycerol increased with increasing basicity of the catalyst (Table 2). A possible reason for this variation in catalytic activity may derive from the various surface acid–base properties, as measured by CO_2–TPD. The catalytic activity can be roughly correlated with the order of basicity, suggesting that the basicity (expect for too strongly basic) plays an important role in the superior activity. A possible reason for the lower activity achieved after coprecipitation with $NaNO_3$ than coprecipitation is the too strong basicity, thus resulting in strong interaction with the reactants and blocking of active sites [25].

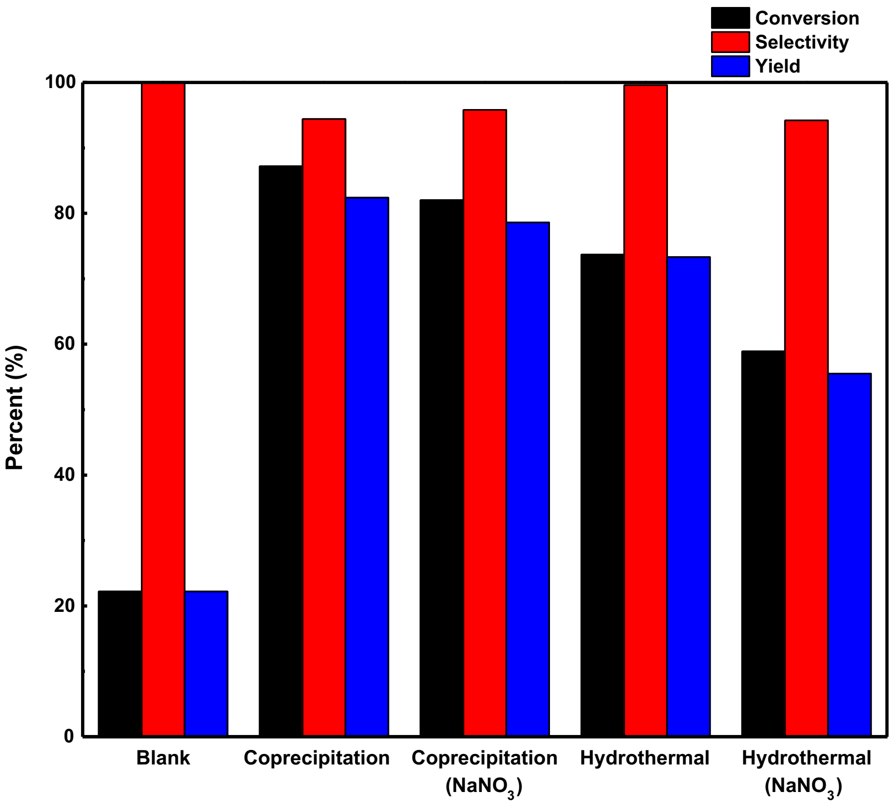

Fig. 5 Activities of different catalysts for synthesis of GC

Table 2 Catalytic activity and physical properties of Zn/Al mixed-oxide particles prepared under different conditions

Conditions	Conversion (%)	Selectivity (%)	Yield (%)	Basic site density (mmol/g)	Intensity (XRD)
Blank	22.2	100	22.2	–	–
Coprecipitation	87.2	94.4	82.4	2.76	559
Coprecipitation ($NaNO_3$)	82.0	95.8	78.6	4.44 (1.92, excluding too strongly basic site)	381
Hydrothermal	73.7	99.6	73.3	1.56	818
Hydrothermal ($NaNO_3$)	58.9	94.2	55.5	1.44	925

The selectivity for GC increased with increasing diffraction peak intensity. The Zn/Al mixed-oxide particles prepared using $NaNO_3$ exhibited lower conversion of glycerol than those prepared without $NaNO_3$. This suggests that the effect of the synthesis temperature in the preparation of Zn/Al mixed oxides in these systems by the hydrothermal method is worthy of study in future work.

Conclusions

We prepared Zn/Al mixed oxides by the coprecipitation and the hydrothermal method. The physical properties of the prepared Zn/Al mixed oxides were investigated, as well as their activity as catalyst for synthesis of glycerol carbonate by carbonylation of glycerol with urea. The Zn/Al mixed oxides prepared by the coprecipitation method without $NaNO_3$ showed the highest catalytic activity in synthesis of glycerol carbonate. The conversion of glycerol increased with increasing catalyst basicity, and the selectivity for GC increased with increasing diffraction peak intensity.

Acknowledgments This research was financially supported by the Technology Innovation Development Program (Code No. SE140001) of the Small & Business Administration (SMBA) and also by the Project of Research and Development for Regional Industry (Code No. R0003028) through the Ministry of Trade, Industry, & Energy (MOTIE) and Korea Institute for Advancement of Technology (KIAT).

References

1. ASTM D6751:12
2. M.R. Jakeria, M.A. Fazal, A.S.M.A. Haseeb, Renew. Sustain. Energy Rev. **30**, 154 (2014)
3. C.H.C. Zhou, J.N. Beltramini, Y.X. Fan, G.Q.M. Lu, Chem. Soc. Rev. **37**, 527 (2008)
4. N. Nguyen, Y. Demirel, J. Sustain. Bioenergy Syst. **3**, 209 (2013)
5. M.A. Dasari, P.P. Kiatsimkul, W.R. Sutterlin, G.J. Suppes, Appl. Catal. A **281**, 225 (2005)
6. M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, Angew. Chem. Int. Ed. **46**, 4434 (2007)
7. Y. Sun, J. Liu and E. Kimbleton, US Patent 5,993,787 (1999)
8. M. Aresta, A. Dibenedetto, F. Nocito, C. Pastore, J. Mol. Catal. A Chem. **257**, 149 (2006)
9. A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner, Green Chem. **10**, 13 (2008)
10. Q. Li, W. Zhang, N. Zhao, W. Wei, Y. Sun, Catal. Today **115**, 111 (2006)
11. J. Li, T. Wang, Chem. Eng. Process. **49**, 530 (2010)
12. C. Vieville, J.W. Yoo, S. Pelet, Z. Mouloungui, Catal. Lett. **56**, 245 (1998)
13. S. Claud, Z. Moulougui, J.W. Yoo, A. Gaset, US Patent 6,025,504 (2000)
14. M. Okutsu, T. Kitsuki, US Patent 6,495,703 (2002)
15. M. Okutsu, T. Kitsuki, EP 11,566,042 (2001)
16. J.W. Yoo, Z. Mouloungui, Stud. Surf. Sci. Catal. **146**, 757 (2003)
17. P. Ball, H. Fullmann, W. Heitz, Angew. Chem. Int. Ed. Engl. **19**, 718 (1980)
18. L. Wang, Y. Ma, Y. Wang, S. Liu, Y. Deng, Catal. Commun. **12**, 1458 (2011)
19. T.W. Turney, A. Patti, W. Gates, U. Shaheen, S. Kulasegaram, Green Chem. **15**, 1925 (2013)
20. M.H.A. Rahim, Q. He, J.A. Lopez-Sanchez, C. Hammond, N. Dimitratos, M. Sankar, A.F. Carley, C.J. Kiely, D.W. Knight, G.J. Hutchings, Catal. Sci. Technol. **2**, 1914 (2012)
21. K. Jagadeeswaraiah, C.R. Kumar, P.S.S. Prasad, S. Loridant, N. Lingaiah, Appl. Catal. A **469**, 165 (2014)
22. A.A. Da Silva, A. de Souza Gonçalves, M.R. Davolos, J. Sol Gel Sci. Technol. **49**, 101 (2009)
23. J.M. Fraile, N. García, J.A. Mayoral, E. Pires, L. Roldán, Appl. Catal. A **387**, 67 (2010)
24. M.G. Álvarez, M. Plíšková, A.M. Segarra, F. Medina, F. Figueras, Appl. Catal. B Environ. **113–114**, 212 (2012)
25. M.J. Climent, A. Corma, P. De Frutos, S. Iborra, M. Noy, A. Velty, P. Concepción, J. Catal. **269**, 140 (2010)