Activated red mud-supported Zn/Al oxide catalysts for catalytic conversion of glycerol to glycerol carbonate: FTIR analysis

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ABSTRACT

Catalytic conversion to glycerol carbonate (GC) from glycerol and urea was investigated with Zn/Al oxide catalysts supported by activated red mud (ARM), a waste material. Compared to an unsupported catalyst, ARM-supported Zn/Al oxide catalysts exhibited higher GC yields. ARM-supported Zn/Al oxide catalysts showed a volcano curve for the GC yield as a function of the Zn/Al loading. FTIR analysis revealed the ARM-supported Zn/Al oxide catalysts to be more selective, resulting in higher GC yield. The balance of active sites from ARM and Zn/Al oxide was related to rates of each reaction step in GC synthesis, which eventually influenced on the selectivity and yield of GC.

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1. Introduction

Biodiesel has received strong attention because of its potential to reduce the environmental air pollution by fossil fuel emissions and the warmer climate by greenhouse gas effect [1]. As a result, its world production capacity has increased rapidly in the last decade [2] with further production potential in the future [3]. However, a noticeable amount of glycerol, the main by-product of biodiesel industry, also has been produced and has made the crude glycerol price cheap and unstable [4]. Instead of disposal, many alternative methods to utilize glycerol have been researched, including chemical process to convert glycerol to value-added components.

A new research approach is to synthesize glycerol carbonate (GC), which has the excellent properties of high boiling point (110–115 °C at 0.1 mm Hg) [5]), low volatility (vapor pressure 0.008 bar at 177 °C [6]), low flammability (flash point 190 °C [7]), low toxicity and good biodegradability. Even though there are several methods to synthesize GC from glycerol and different carbon sources, GC glycerolysis using urea has attracted attention for the following advantages; i) no need for solvents, ii) easy removal of the by-product NH_3 (ammonia) from a reactor by vacuum or nitrogen flow and iii) heterogeneous catalysis [8–12]. Climent et al. [8] indicated that the balance between acid-base sites of calcined Zn/Al hydrotalcite catalyst acted an important role in the reaction mechanism. Based on that idea, Ryu et al. [12] investigated the optimal Zn:Al ratio and obtained a better conversion. However, there has been no report to improve the catalytic performance by

dispersing the active sites into supports. Red mud (RM) is a by-product from the manufacture of alumina by the Bayer process, specifically the solid residue of the caustic leaching of bauxite. RM has been studied as a catalyst or a support for several catalytic reactions [13–16]. Although RM has less activity than the noble metals and metal oxides, its lower price makes it more desirable economically. In this work, we introduced calcined Zn/Al active sites onto activated RM (ARM) to improve its catalytic performance in the synthesis of GC with urea. The ARM-supported Zn/Al mixed oxide catalysts showed higher GC yield than the unsupported Zn/Al catalyst.

2. Experimental

2.1. Catalyst preparation

The Zn/Al oxide catalysts with various Zn/Al molar ratio were prepared by the coprecipitation method [8,12]. An aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ was precipitated by a basic solution of NaOH and $NaNO_3$ under constant pH = 6 and vigorous stirring. The mixed solution was then filtered and washed by deionized water. The resulting solid was dried at 100 °C and finally calcined at 450 °C in 6 h. The sample was used as a control catalyst for comparison.

The ARM-supported Zn/Al oxide catalysts were prepared by the hot wet impregnation method. Typically, $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in 100 ml of deionized water, and 5 g of ARM was added. The resulted solution was mixed by stirring and the solution temperature was kept at 80 °C until all water was evaporated completely. The remaining solid was dried overnight at 110 °C and calcined at 450 °C in 6 h. The prepared catalysts were

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Table 1
Textural properties of $Zn_7Al_3O_x$ and ARM-supported Zn/Al catalysts.

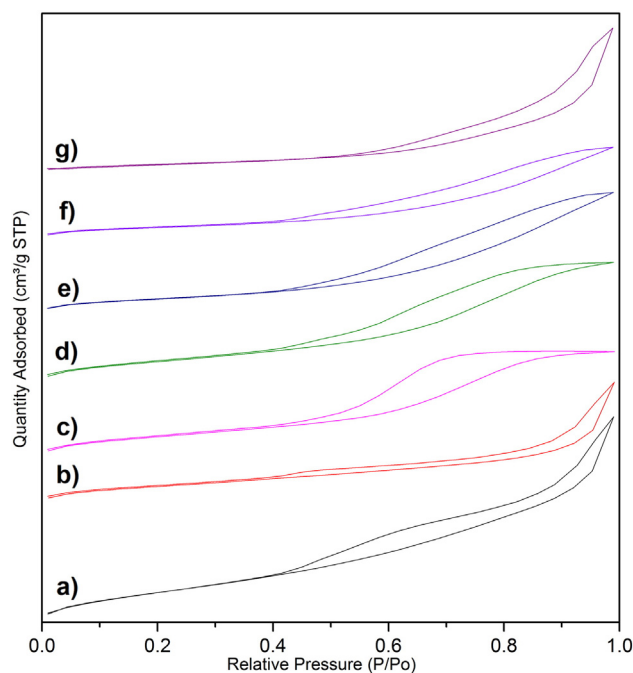| Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
$Zn_7Al_3O_x$	46	0.164	11.6
ARM	136	0.246	6.4
5%-$Zn_7Al_3O_x$/ARM	84	0.148	7.6
25%-$Zn_7Al_3O_x$/ARM	91	0.130	4.8
40%-$Zn_7Al_3O_x$/ARM	95	0.147	5.3
50%-$Zn_7Al_3O_x$/ARM	72	0.145	6.4
60%-$Zn_7Al_3O_x$/ARM	56	0.110	6.6

designated as m%-$Zn_7Al_3O_x$/ARM. The loading weight of Zn/Al (m%) changed from 5% to 60%. Detailed information on chemicals used in this study was described in Supplementary material.
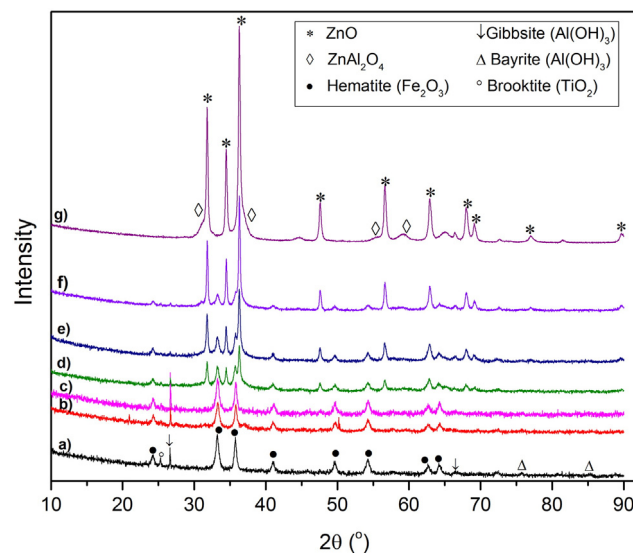
2.2. Reaction tests

The reaction was carried out in a round-bottom three-neck flask 100 ml where one neck was connected to a vacuum line through a water condenser. Typically, 0.2 mol of glycerol was added to the flask at 80 °C and the solution was mixed by a magnetic stirrer to reduce the viscosity. After 10 min, 0.2 mol of urea was added and mixed. When all the urea was dissolved completely in glycerol, a certain amount of catalyst (5% weight to the initial glycerol) was added to the flask. The reaction was performed for 5 h under vacuum pressure (3 kPa) at 140 °C with constant stirring. The products obtained from the reaction were analyzed by gas chromatography and Fourier transform infrared spectroscopy (FT-IR). Detailed procedures were described in Supplementary material.

2.3. Catalyst characterization

The surface characterizations were measured by N_2 adsorption isotherm analysis on a Micromeritics ASAP 2020 (USA) apparatus. The surface area was calculated by Brunauer–Emmett–Teller method. X-ray diffraction (XRD) patterns were obtained using a Rigaku RAD-3C diffractometer (Japan) with Cu Kα radiation ($\lambda = 1.5418$ Å) at a scattering

Fig. 1. N_2 adsorption-desorption isotherms of a) ARM, b)5%-$Zn_7Al_3O_x$/ARM, c)25%-$Zn_7Al_3O_x$/ARM, d)40%-$Zn_7Al_3O_x$/ARM, e)50%-$Zn_7Al_3O_x$ARM, f)60%-$Zn_7Al_3O_x$/ARM and g) $Zn_7Al_3O_x$.

Fig. 2. XRD patterns of a) ARM, b)5%-$Zn_7Al_3O_x$/ARM, c)25%-$Zn_7Al_3O_x$/ARM, d)40%-$Zn_7Al_3O_x$/ARM, e)50%-$Zn_7Al_3O_x$ARM, f)60%-$Zn_7Al_3O_x$/ARM and g) $Zn_7Al_3O_x$.

angle (2θ) scan rate of 2°/min, operated at 35 kV and 20 mA. Surface morphology images were obtained by field- emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F, Japan).

3. Results and discussion

3.1. Catalyst characterization

The textural properties of the catalysts are summarized in Table 1. The surface area of ARM and $Zn_7Al_3O_x$ are 136 and 43 m^2/g, respectively. When Zn/Al oxide was impregnated into ARM, the surface areas of the catalysts were significantly decreased to 56 ~ 95 m^2/g, implying that the impregnation of Zn/Al oxide changed pore structure of ARM. Fig. 1 shows N_2 adsorption–desorption isotherm plots of the catalysts. All the samples belong to type IV isotherm by IUPAC classification with a hysteresis loop [17]. The catalysts can be separated into two classes according to the hysteresis loop shapes. ARM and 5%-$Zn_7Al_3O_x$/ARM samples can be grouped to type H4 hysteresis loop, implying a lack of additional phase of Zn and Al or incorporation of metal ions into ARM structure. The samples with 25% to 60% weight loading exhibit H2 hysteresis loop, representing the 'ink bottle' pores with narrow necks and wide bodies [18]. The additional patterns may be due to the existence of the new phase of ZnO and $ZnAl_2O_4$.

Fig. 2 shows XRD patterns of the catalysts. The XRD pattern of $Zn_7Al_3O_x$ has two main phases: whitezinc zincite ZnO (JCPDS No. 36-1451) and spinel $ZnAl_2O_4$ (JCPDS No. 05-0669) [19]. The high crystallinity of the ZnO phase is proven by the sharp peaks at 31.8°, 34.4°, 36.3°, 47.5°, 56.7°, and 62.9°. In contrast, the $ZnAl_2O_4$ phase has less crystalline property, proven by the broad and short peaks. At lower Zn/Al loading

Table 2
Reaction results of $Zn_7Al_3O_x$ and ARM-supported Zn/Al catalysts (Reaction conditions: Glycerol/urea molar ratio = 1, $P = 3$ kPa, $T = 140$ °C, 5 wt% catalyst (of glycerol), at 5 h of reaction time.)

Catalyst	Yield (%)	Conversion (%)	Selectivity (%)
$Zn_7Al_3O_x$	49.6 ± 0.4	62.8 ± 0.4	78.9 ± 1.3
ARM	30.9 ± 0.5	51.4 ± 0.6	60.1 ± 1.8
5%-$Zn_7Al_3O_x$/ARM	32.5 ± 0.4	48.9 ± 0.3	66.6 ± 1.7
25%-$Zn_7Al_3O_x$/ARM	50.7 ± 0.7	62.0 ± 0.8	81.8 ± 2
40%-$Zn_7Al_3O_x$/ARM	57.6 ± 0.4	64.0 ± 0.6	90.0 ± 1.3
50%-$Zn_7Al_3O_x$/ARM	58.1 ± 0.3	69.0 ± 0.7	84.2 ± 0.9
60%-$Zn_7Al_3O_x$/ARM	55.0 ± 0.6	68.3 ± 0.4	80.7 ± 1.6

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