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Synthesis of solid acid-base $ZnSn(OH)_6$ catalyts used for carbonylation of glycerol with urea into glycerol carbonate

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ABSTRACT

Zinc hydroxystannate $ZnSn(OH)_6$ a solid acid–base catalyst, was prepared by chemical co-precipitation method using zinc chloride $ZnCl_2$ and tin chloride $SnCl_4$ precursors. Structure and physical properties of $ZnSn(OH)_6$ material was characterized by X-ray diffraction (XRD), the simultaneous thermal analysis (TGA) of the after dried samples, scanning electron microscope (SEM), and acid-base strength of sites catalysts were evaluated by temperature programmed desorption (TPD). The catalyst $ZnSn(OH)_6$was used for carbonylation of glycerol with urea to glycerol carbonate. The activity testing was carried out in the carbonylation of glycerol with urea to glycerol carbonate.

Introduction

Glycerin carbonate (GLC) with high polarity and biogradability, low toxicity has various feasible applications such as polar solvents, gas-separation membrane mateirals, surfactants, especially in polycarbonates' production [1-6]. Traditional synthesis technology from reaction of glycerin and phosgene using highly toxic and corrosive phosgene have been gradually replaced by new safe and environment-friendly methods [2, 7]. There are a number of GLC manufacturing processes from various carbonyl sources such as CO_2, $CoCl_2$, CO/O_2, dialkylcarbonates and recently urea. GLC production from glycerol and urea has opened a new approach as glycerol is an available by-product of biodiesel synthesis. Glycerollysis of urea is considered as a cost-effective and safe method for storage, disposal and production of highly valuable derivatives.

Many importantly studies about glycerolysis of urea are carbonylation of glycerol under the catalysis of Co_3O_4/ZnO containing 10% Co. The converting reaction of glycerol to glycerol carbonate of Rubio-Marcos et al. (2010) obtained the high conversion and selectivity percentage of 25% and 50% before using catalyst, 69% and 97% after using catalyst [8]. The increase in percentages demonstrates the role of Co_3O_4/ZnO in speeding up the reaction. An another research of Fujita [9] used solid catalyst of zinc and its salts such as $ZnCl_2$, $ZnBr_2$ and $ZnSO_4$ to generate glycerol carbonate from glycerol and urea under the temperature of 130°C and low pressure of 3kPa. Their results show that the homogenerous reaction in the liquid phase does not depend on used solid catalyst, $ZnCl_2$ gave the highest conversion and selectivity percentage, 84% and 97% respectively, compared to other catalysts. In addition to zinc catalysts, golden [11], lanthane oxide [12] and hydrotalcite [13], mixture of tin-wolfram [14], and most recently, ionic liquids have been studied and applied in catalysis of the ureic glycerolysis [15-16].

To continue and develop catalyst systems in glycerolysis, this study aims to synthesise solid acid-base catalysing systems based on $ZnSn(OH)_6$ with different ratio of Zn/Sn =1/1, and investigate the effects of these ratios on the acid-base center of the catalyst. In this paper, we study the synthesis of $ZnSn(OH)_6$ by precipitating $ZnCl_2$ and $SnCl_2.5H_2O$ used to catalyze the conversion of glycerol to glycerol carbonate.

Experimental

1. Chemicals and method

$ZnSn(OH)_6$ was synthesized by co-precipitation using zinc clorua ($ZnCl_2$, 99 %) and tin chloride ($SnCl_2.5H_2O$, 98%) with sodas (Na_2CO_3, 99 %) acting as a precipitant

$ZnSn(OH)_6$ was prepared by chemical co-precipitation method using zinc chloride ($ZnCl_2$) and tin chloride ($SnCl_4.5H_2O$) with Na_2CO_3 as a co-precipitant. The precipitate was stirred for 2h at room temperature, then transferred into autoclave at 180°C for 20h via hydrothermal route. After that sample removed from the autoclave was filtered and dried at 80 ° C for 10 hours.

2 Physical charaterization

X-ray diffraction (XRD) patterns of $ZnSn(OH)_6$ was recorded with SIEMENS-D5000 diffractometer using monochromatic high intensity Cu Kα radiation (λ = 0.15418 nm) at the scanning rate of 0.03°/s and in the scanning range from 10 to 80°. Scanning Electron Microscope (SEM) was conducted using JSM-6500F, JEOL. The simultaneous thermal analysis (TGA) of the after dried samples was performed in a Q600 TA-Instruments apparatus under atmospheric pressure using the heating rate of 10°C/min. To investigate the acidic properties of the samples, NH_3/CO_2 Temperature Programmed Desorption (NH_3-TPD, CO_2-TPD).

2.3 Performance evaluation

The products were analyzed by gas chromatography, FID detector (PerkinElmer Claus 680) and FFAP capillary column (30 m in length, 0.25 mm of the diameter). The temperature of the system was programmed as follows: hold for 5 mins at 35°C, then heat 10°C/min from 35 °C to 60 °C and keep 1 min at 60°C, then heat 15°C/min from 60°C to 230 °C and hold for 10 mins at 230 °C.

$$\textbf{Conversion(\%)} = \frac{\text{Glycerol}_{initial} - \text{Glycerol}_{residual}}{\text{Glycerol}_{initial}} \times 100 \quad \textbf{(1)}$$

Yield (%) = Conversion x Selectivity (2)

$$\textbf{Selectivity (\%)} = \frac{Glycerol\,Carbonate}{\Sigma Product} \times 100 \quad \textbf{(3)}$$

Results and discussion

$ZnSn(OH)_6$ was characterized by using various techniques like XRD, TGA, SEM, TEM. The XRD pattern of the as-prepared $ZnSn(OH)_6$ is shown in Fig. 1. All of the diffraction peaks can be assigned to the cubic phase of $ZnSn(OH)_6$ (JCPDS 20-1455). No extra peaks due to the impurity phase are found in the patterns. For $ZnSn(OH)_6$ catalyst, the hkl values were indexed and the major diffraction peaks at 2θ values of 22.6, 32.5, 40.1, 46.7, 52.4, 57.8 °. This result proves that our synthesis method is consistent

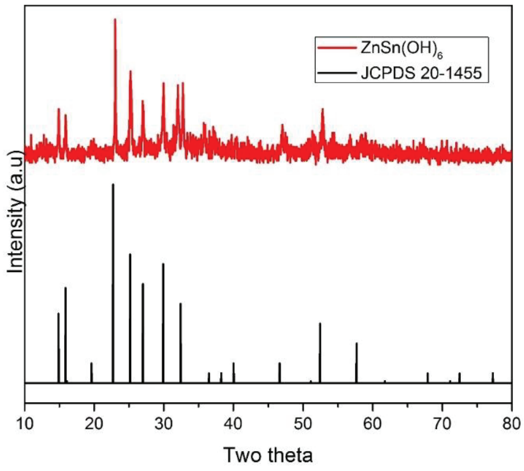

Fig 1. XRD pattern of $ZnSn(OH)_6$ catalyst

Figure 2 showed TGA analysis result of the samples $ZnSn(OH)_6$ catalyst. The result showed a major weight loss of about 30 % in the range of 0 – 300°C. The first stage of 0 and 250°C, the mass was lost 18% due to hydration in $ZnSn(OH)_6$. In the second stage, after 250 °C, the oxide was formed due to the removal of hydroxyl groups. As a result, the weight loss of $ZnSn(OH)_6$

occurred, which is the same as study of Swetha Sandesh and co-workers [17].

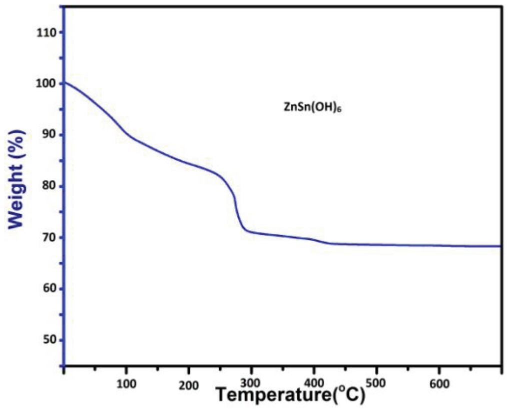

Fig 2. Thermal analysis of $ZnSn(OH)_6$ catalyst

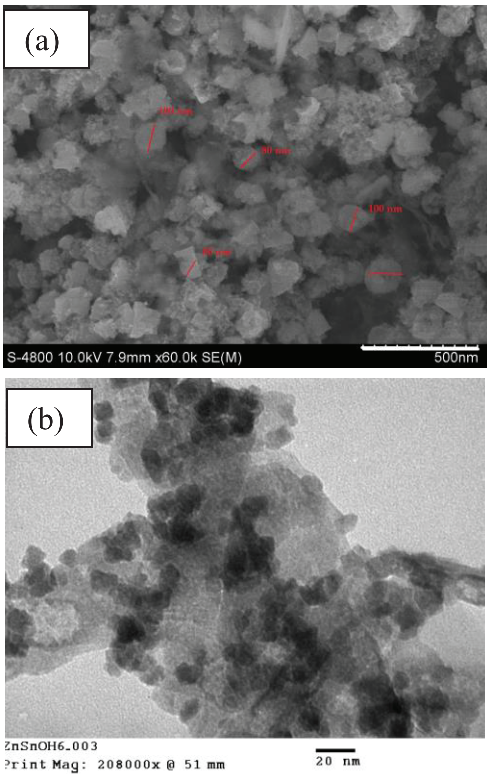

Fig 3. (a) SEM image and (b) TEM of the as-prepared $ZnSn(OH)_6$.

Table 1. Catalytic activities of catalyst

Entry		Total (mmol/g)	B/A
1	TPD-NH_3	1.23	2.97
2	TPD-CO_2	3.66	

B/A: base/acid ratio

The overall morphology of $ZnSn(OH)_6$ particles was examined using SEM and TEM. A large quantity of crystal cubes with a length of about 150 nm can be observed in Fig. 3a. It is also clearly seen from Fig. 3b that the dimension of crystal cubes is approximately 20 nm. This indicates that combination of co-precipitation with hydrothermal method can produce small dimension products, from 20 nm to 150 nm.

The acidic and basic properties of the $ZnSn(OH)_6$ catalyst were evaluated by the temperature programmed desorption (TPD) of NH_3 and CO_2, respectively. The results of the TPD characterization of the catalysts are summarized in Table 1. Figure 4 illustrates the CO_2-TPD, NH_3-TPD profiles of the ZHS catalyst. This result proves that the amount of base is more than the amount of acid in ZHS catalyst about 2.97, which is suitable for carbonylation of glycerol and urea because the acid sites activate the carbonyl group of urea and base sites activate the hydroxyl groups of glycerol [9].

The reactions were performed in the absence of solvent, under inert atmosphere with a molar glycerol/urea ratio of 1, at 145°C and 5 wt% of $ZnSn(OH)_6$ catalyst. The results obtained are summarized in Table 2. A preliminary experiment observed that the trans-esterification is a slow reaction in the absence of catalyst. Particularly, the catalysis of ZHS under these conditions above gave 77% yield of glycerol carbonate and 88.5% glycerol conversion after 5 h of reaction time.

Table 2: Results of carbonylation of glycerol and urea in the presence of solid catalyst

Entry	Catalyst	Glycerol conversion (%)	GC yield (%)	GC selectivity (%)
1	Blank	15.6	16.6	10.8
2	$ZnSn(OH)_6$	88.5	77.0	86.9

Reaction conditions: Glycerol/urea molar ratio = 1/1, 145°C, 5 wt% catalyst at 5 h of reaction time

The reaction time was increased while the temperature, glycerol/urea molar ratio, the amount of catalyst were kept unchanged. Table 3 shows that, glycerol conversion efficiency and product selectivity increases. After 5 hours of reaction time, GLC yield and GLC selectivity did not increase significantly. Therefore, for time-consuming and economic proposes, 5 hours is the most suitable time for this reaction.

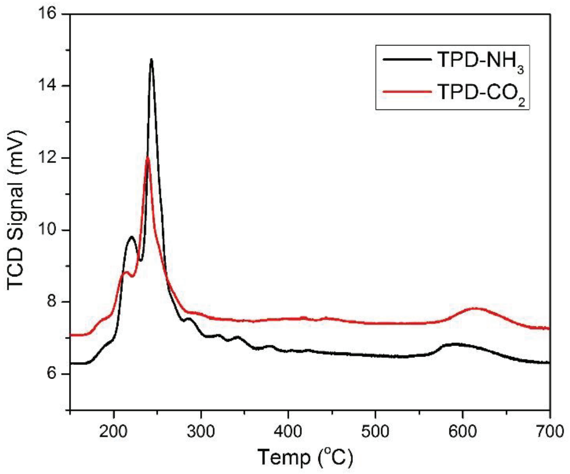

Fig 4. Temperature Programmed Desorption of $ZnSn(OH)_6$

Table 3. Results of carbonylation of glycerol and urea in the presence of solid catalyst at different times

Entry	Reaction time (h)	Glycerol conversion (%)	GC yield (%)	GC selectivity (%)
1	3	50.5	16	65.9
2	5	88.5	77.0	86.9
3	7	90.0	79.2	88.1

Reaction conditions: Glycerol/urea molar ratio = 1/1, 145°C, 5 wt% catalyst at 3, 5, 7 h of reaction time

Conclusion

In this study, the $ZnSn(OH)_6$ catalyst was synthesized by co-precipitation combining with hydrothermal method at 180°C. Catalytic activity of $ZnSn(OH)_6$ was evaluated in the carbonylation reaction of glycerol and urea. The presence of Lewis acidic zinc in the catalyst facilitates the reaction to give a high product yield. It showed excellent glycerol conversion of 88.5% with almost 86.9% glycerol carbonate selectivity under these suitable following condtions: molar ratio of glycerol:urea = 1:1, 145°C, 5 wt% catalyst within 5 hours

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