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Carbonylation of Glycerol with CO₂ to Glycerol Carbonate over Zinc Hydroxystannate

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Abstract

This study investigates the direct carbonylation of glycerol with CO₂ over zinc hydroxystannate (ZHS) catalysts for the synthesis of glycerol carbonate (GLC) under relatively milder reaction conditions. Reactions were conducted in a semi-batch reactor at 120 °C and 5 bar CO₂ for 6 h. ZHS catalysts were prepared by Zn²⁺-Sn⁴⁺ coprecipitation with NaOH (ZSCP), ZSCP by further hydrothermal treatment, or by alkaline-assisted surface treatment (CPAST), and their catalytic performances were compared. Among the catalysts examined, ZHS prepared by CPAST afforded the highest GLC yield of 17.1%, compared with 15.9% for ZSCP-derived ZHS. XPS analysis indicated that the surface basicity of ZHS is associated with partial reduction of Sn⁴⁺ to Sn²⁺ and the concomitant formation of surface oxygen vacancies. In the absence of ZHS, glycerol predominantly underwent oligomerization, whereas ZHS promoted the activation and incorporation of CO₂ into glycerol to form GLC. Notably, the GLC yield exhibited a strong linear correlation with the surface basicity of the ZHS catalysts determined by the Hammett indicator method, demonstrating that surface basicity is a key descriptor governing catalytic activity.

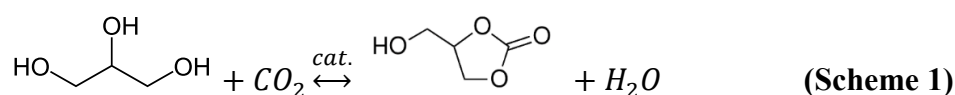
Keywords: Glycerol (GLY), Carbon dioxide (CO₂), Carbonylation, Glycerol Carbonate (GLC), Zinc Hydroxystannate (ZHS).

1. Introduction

The increasing demand for biodiesel has inevitably led to the overproduction of glycerol (GLY) as a major byproduct, resulting in a substantial decline in its market value. Consequently, the conversion of surplus glycerol (GLY) into value-added derivatives has attracted considerable interest [1]. Among the various glycerol-derived compounds, glycerol carbonate (GLC) is particularly valuable because of its multifunctional structure, which enables diverse applications and high chemical reactivity [1,2].

Meanwhile, the continuous increase in anthropogenic CO₂ emissions remains a significant environmental concern [3,4]. Consequently, extensive research and development efforts have focused on the efficient capture, utilization, and valorization of CO₂ in both academia and industry [4,5].

Interestingly, the reaction of glycerol with CO₂ has recently been investigated as a potential approach for simultaneously utilizing CO₂ and valorizing surplus glycerol [6,7]. This reaction, commonly referred to as the direct carbonylation or carboxylation of glycerol with CO₂, produces glycerol carbonate (GLC), as illustrated in Scheme 1 [6,7].



Scheme 1. Reaction scheme for direct carbonation of glycerol with carbon dioxide

Glycerol carbonate (GLC) has recently emerged as a renewable and versatile material with a wide range of applications, including as a green and low-VOC solvent for chemical processes, an

additive in personal-care and pharmaceutical products, where it can function as a humectant and emollient; and a precursor for the synthesis of chemical intermediates, polymers, coatings, and lubricants [2,6,7]. Several synthetic routes for GLC production have been reported, including phosgenation, glycerolysis of urea, transesterification, and carbonylation using carbon monoxide or carbon dioxide [1,2,6,7]. Among these approaches, the direct carbonylation of glycerol (GLY) with CO₂ is particularly attractive from an environmental perspective, although it remains technically challenging [7,8].

Historically, GLC was first produced through the transcarbonation of GLY with phosgene [2,6,7]. However, the use of highly toxic phosgene and its associated environmental and safety concerns have motivated the development of alternative synthetic routes. These approaches include the transesterification of GLY with various carbonates, glycerolysis of urea, and the direct carbonylation of GLY [2,6,7]. As mentioned above, considering the principles of environmental sustainability, the direct carbonylation of GLY with CO₂ is particularly attractive because it simultaneously utilizes CO₂ as a carbonyl source and produces water as an environmentally benign byproduct [2,6,7]. However, the reaction is thermodynamically unfavorable, which limits the formation of the desired products, GLC and water [8].

The standard chemical equilibrium constant for the reaction between GLY and CO₂ is very small under standard-state conditions [8]. Consequently, catalysts and dehydrating agents, together with elevated reaction temperatures and pressures, are commonly employed to overcome the thermodynamic limitations and enhance the formation of GLC [2,6,7,8]. For example, a GLC yield

of only 5.72% was reported for the reaction catalyzed by $n\text{-Bu}_2\text{Sn}(\text{OMe})_2$ at 453 K and 5 MPa CO_2 . In another study, a GLC yield of 35% was obtained using 1 mol% $n\text{-Bu}_2\text{SnO}$ in methanol for 4 h at 120 °C and 13.8 MPa CO_2 [8].

Li and Wang [8] calculated the chemical equilibrium constant for the direct carbonylation of GLY with CO_2 in the absence of catalysts and dehydrating agents based on the molar Gibbs free energy of reaction. At a CO_2 pressure of 5 MPa, the calculated equilibrium constants were very low, decreasing from 3.27×10^{-3} at 298.15 K to 1.506×10^{-3} at 453.15 K. At 453.15 K, the equilibrium constant decreased further with decreasing CO_2 pressure, with values of 1.11×10^{-5} at 101,325 Pa CO_2 (1 atm CO_2) and 5.55×10^{-4} at 50 atm CO_2 [8]. These results demonstrate the strong thermodynamic limitation of the direct carbonylation of GLY with CO_2 . Therefore, introducing an effective dehydrating agent and/or a suitable catalyst into the reaction system provides a potential strategy for shifting the reaction toward GLC formation and improving the overall GLC yield [2,6,7].

According to Le Chatelier's principle, continuous removal of the water produced during the reaction can shift the equilibrium toward product formation. The effects of various dehydrating agents on the yield of GLC have been investigated and reported in the literature [6,7,9]. Notably, only a limited number of dehydrating agents have been identified as suitable for the direct carbonylation of GLY with CO_2 [6,7,9].

The rational design and catalytic performance of various heterogeneous catalysts for this carbonylation reaction have also been extensively investigated and reviewed [2,6,7,10]. Notably, direct carbonylation of GLY with CO_2 has generally been conducted under relatively severe reaction

conditions, typically involving elevated CO₂ pressures and temperatures. [2,6,7,10]. For example, Sarkar et al. [11] reported a maximum GLC yield of 24.32% under optimized conditions of 150 °C, 5 MPa CO₂, 2-CP as the dehydrating agent, a Cu/In₂O₃/ZnO nanostructured catalyst, and a reaction time of 5 h. Ke *et al.* [10] achieved a GLC yield of 61.7% over a metal oxide catalyst under optimized conditions of 120 °C and 3 MPa CO₂ for 5 h. More recently, Xing *et al.* [12] reported a GLC yield of 49.3% using 0.3ZnO-CaO-SBA-15 as the catalyst under optimized conditions of 6.0 wt% catalyst loading, 110 °C, 3 MPa CO₂, and 4 h of reaction time. Li *et al.* [13] investigated hydrotalcites as solid catalysts for the direct carbonylation of glycerol with CO₂ and obtained GLC yields ranging from 9.6% to 15.1%. In their experiments, the reactor was initially charged with CO₂ at 4.0 MPa and 20 °C, subsequently heated to 170 °C, and maintained at this temperature for 12 h under magnetic stirring.

Considering the effects of dehydrating agents and heterogeneous catalysts on GLC synthesis, this study aimed to develop an effective catalyst for enhancing GLC production via the direct carbonylation of GLY with CO₂ under relatively mild reaction conditions. Recently, Sandesh et al. reported zinc hydroxystannate (ZHS) as a promising solid catalyst for GLC synthesis through the reaction of GLY with urea [14]. Therefore, ZHS was investigated in the present study for its potential application as an efficient catalyst for the direct carbonylation of GLY with CO₂ to produce GLC under mild conditions, namely 5 bar CO₂ and 120 °C.

Various methods for synthesizing ZHS have been reported in the literature [14,15]. Different synthesis routes can result in ZHS materials with distinct physicochemical properties, including surface basicity and microstructure, which may consequently influence their catalytic performance.

Accordingly, the synthesis parameters of ZHS were systematically investigated and optimized using the GLC yield as the primary performance indicator. Finally, the relationship between the surface basicity of the ZHS catalysts and their catalytic performance toward GLC formation was investigated and discussed.

2. Materials And Methods

2.1 Materials

Glycerol (>99%), toluene (>99%), and neutral red were purchased from Sigma-Aldrich. 2-Cyanopyridine (99%), 4-(hydroxymethyl)-1,3-dioxolan-2-one (90%; glycerol carbonate), and phenolphthalein were obtained from Acros Organics. Hydrogen peroxide (30%) was purchased from Showa, while sulfuric acid (>95%) was obtained from Honeywell. Ethanol (99%) and tin(IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 99.3%) were purchased from J.T. Baker. Zinc chloride ($\geq 98\%$), hexamethyldisilane ($\geq 98\%$), chlorotrimethylsilane ($\geq 98\%$), pyridine ($\geq 99.0\%$), and glycerol monoacetate (technical grade) were purchased from Alfa Aesar. 1-Dodecanol (98%) was obtained from VetecTM.

Unless otherwise specified, all chemicals were of analytical grade and used as received without further purification. Deionized water with a resistivity greater than $18.2 \text{ M}\Omega \cdot \text{cm}$ was produced using a Millipore Milli-Q ultrapure water purification system and used throughout the study for sample preparation.

2.2 Catalyst: Preparation and Characterization

Zinc hydroxystannate ($\text{ZnSn}(\text{OH})_6$, ZHS) was synthesized using three different methods, namely coprecipitation, hydrothermal treatment, and coprecipitation with alkali-assisted surface treatment. The prepared ZHS samples were evaluated as catalysts for the direct carbonylation of GLY with CO_2 .

2.2.1 Coprecipitation Method

Aqueous solutions of the metal precursors (50 mL) were prepared with an equimolar ratio of tin tetrachloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) to zinc chloride (ZnCl_2) of 1:1. The concentration of each metal component in the precursor solution was set at 0.1, 0.3, or 0.8 M. The precursor solutions were stirred for 1 h to ensure thorough mixing. Subsequently, 50 mL of aqueous NaOH solution was slowly added to the precursor solution. The NaOH concentration was maintained at six times the molarity of each metal component, and four NaOH amounts were investigated: the stoichiometric amount and stoichiometric excesses of 1.33, 1.66, and 1.99 times the stoichiometric amount. The resulting suspension was stirred for an additional 2 h.

After completion of the reaction, the solid product was recovered by centrifugation and filtration. The precipitate was washed six times with 50 mL of deionized water and subsequently dried at 60 °C for 24 h. The dried product was finally ground into a fine powder using a mortar and pestle.

2.2.2 Coprecipitation with Alkali-assisted Surface Treatment (CPAST)

The coprecipitation with alkali-assisted surface treatment (CPAST) method was developed by incorporating an additional alkali-assisted surface treatment step into the conventional coprecipitation procedure. An additional 2 M NaOH solution (100, 200, 300, and 450 mL) was used in CPAST treatment. The dried solid product from coprecipitation procedure was re-dispersed in these 2 M NaOH solutions and agitated well for 2 h. Afterwards, the resulting solid products were recovered, washed, dried, and ground using the same procedure described above.

2.2.3 Hydrothermal Method

The hydrothermal method was based on the coprecipitation procedure described above, with an additional hydrothermal treatment step. After the slow addition of the aqueous NaOH solution and thorough mixing, the resulting suspension was transferred to an autoclave for hydrothermal treatment. The hydrothermal treatment was conducted at different temperatures (120, 150, and 180 °C) and for different durations (6, 12, 18, 24, and 72 h). After hydrothermal treatment, the solid products were recovered, washed, dried, and ground following the same procedure described for the coprecipitation method.

2.2.4 Characterization

The physicochemical properties of the prepared catalysts were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), inductively coupled plasma optical emission spectroscopy (ICP-OES), N₂ adsorption-desorption analysis, Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron

spectroscopy (XPS). The basicity of the catalysts was further evaluated using the Hammett indicator method.

The crystalline phases of the catalysts were identified by XRD using a Rigaku Ultima IV diffractometer equipped with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV, and 20 mA). Diffraction patterns were recorded at a scanning rate of $10^\circ \text{ min}^{-1}$. The surface morphology of the catalysts was examined using a Hitachi SU8010 field-emission scanning electron microscope. Prior to SEM analysis, the samples were sputter-coated with platinum for 5 min to improve electrical conductivity.

The specific surface area and pore size distribution were determined using a Micromeritics ASAP 2020 surface area and porosity analyzer. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method, while the pore size distribution was determined using the Barrett–Joyner–Halenda (BJH) method.

The elemental composition and metal loading of the catalysts were determined by EDS and ICP-OES using a HORIBA Jobin Yvon Ultima 2000 spectrometer. Samples for ICP-OES analysis were completely digested in piranha solution prior to measurement. The surface chemical composition and oxidation states of the catalysts were analyzed by XPS using a PHI Quantera II spectrometer. The XPS spectra were corrected using Shirley background subtraction.

FTIR spectra were recorded in the range of $4000 \text{ cm}^{-1} - 400 \text{ cm}^{-1}$ with 32 scans at a resolution of 4 cm^{-1} in transmittance mode using a Varian 2000 FTIR Scimitar Series spectrometer (Varian Inc., USA). The thermal stability of the catalysts was evaluated using a TA Q50 thermogravimetric analyzer (TA Instruments, Waters Corp., USA).

The surface basicity and strength of the catalysts was initially evaluated with the Hammett indicator method using neutral red ($pK_a = 6.8$ and pH range = 6.8 – 9.0) and phenolphthalein ($pK_a = 9.5$ and pH range = 8.3 – 10.0) as indicators, following the procedures described by Tanabe and Yamaguchi [16] and elsewhere [14]. In addition, the surface basicity of the catalysts was quantitatively determined by titration of the catalyst suspension in ethanol with benzoic acid. Briefly, 0.3 g of catalyst granules was dispersed in 10 mL of ethanol containing 10 ppm neutral red or phenolphthalein as an indicator. The suspension was continuously stirred for at least 3 h to ensure a stable and homogeneous dispersion before titration with 0.01 N benzoic acid.

2.3 Carbonylation of Glycerol with CO₂ for Glycerol Carbonate

Glycerol (GLY), ethanol as the solvent, and 2-cyanopyridine (2-CP) as the dehydration agent at a molar ratio of 1:1:3 were thoroughly mixed. The resulting reaction mixture and zinc hydroxystannate (ZHS) catalyst, corresponding to 1 wt% relative to GLY, were then transferred into a stainless-steel semi-batch reactor (600 mL) equipped with a CO₂ supply. The reactor was initially purged and charged with CO₂, maintained at 80 °C for 30 min, and subsequently heated to 120 °C under a CO₂ pressure of 5 bar to initiate the direct carbonylation reaction. An Alicat pressure controller was used to maintain the reaction pressure at 5 bar. The reaction was allowed to proceed for 6 h and, subsequently, terminated rapidly by cooling the reactor to ambient temperature. Upon completion of the reaction, the products were collected and characterized mainly by Fourier-transform infrared spectroscopy (FTIR) and gas chromatography equipped with a barrier ionization

discharge detector (GC-BID). Notedly, the reaction mixture often comprising unreacted GLY and viscous glycerol oligomers has to undergo silylation prior to GC analysis [17]. The conversion of GLY as well as the yield and selectivity of glycerol carbonate (GLC) could be calculated, according to the following equations.

$$\text{Conversion of glycerol } (C_{GLY}): C_{GLY} = \left(1 - \frac{\text{Amount of Residual Glycerol}}{\text{Initial Amount of Glycerol}}\right) \times 100\% \quad (1)$$

$$\text{Yield of glycerol carbonate } (Y_{GLC}): Y_{GLC} = \frac{\text{Amount of Glycerol Carbonate}}{\text{Initial Amount of Glycerol}} \times 100\% \quad (2)$$

$$\text{Selectivity of glycerol carbonate } (Y_{GLC}): S_{GLC} = \frac{\text{Amount of Glycerol Carbonate}}{\text{Amount of Glycerol Converted}} \times 100\% \quad (3)$$

Experiments were carried out at least in triplicate ($N \geq 3$). The analysis of variance (ANOVA) was performed to evaluate the experimental results that were presented with the mean and the standard deviation (SD).

3. Results and discussion

3.1 Preparation of zinc hydroxystannate (ZHS) catalyst

Zinc hydroxystannate (ZHS) is a promising solid catalyst for GLC synthesis via the reaction of GLY with urea [14]. Accordingly, ZHS was synthesized by three preparation methods and evaluated for the direct carbonylation of GLY with CO₂. Various preparation conditions were initially screened, with surface basicity used as a preliminary descriptor of ZHS quality.

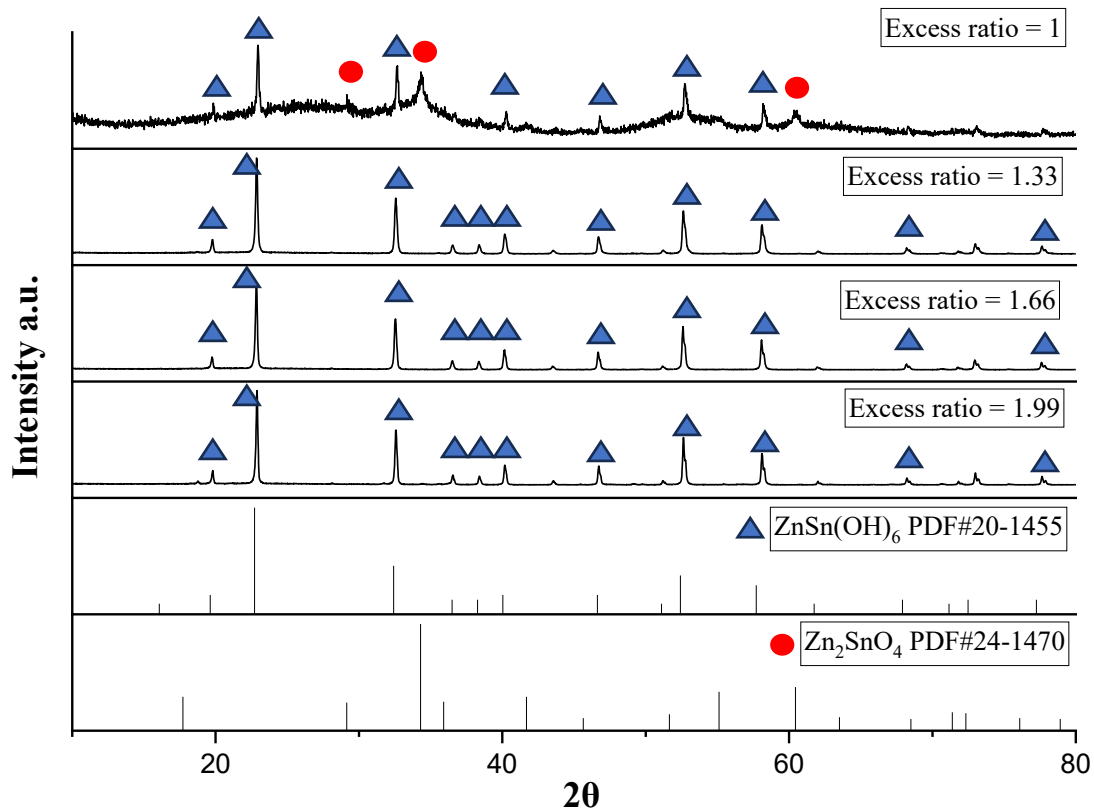


Figure 1. XRD patterns of zinc hydroxystannate (ZHS) prepared from precursor containing 0.3 M Sn^{4+} and 0.3 M Zn^{2+} with different amounts of precipitating agent, NaOH. The excess ratio was defined as the actual amount of NaOH to the stoichiometric amount of NaOH in ZHS preparation.

Under appropriate conditions, ZHS predominantly formed as microcubes. Figure 1 shows the XRD patterns of ZHS synthesized using different NaOH dosages with 0.3 M Sn^{4+} and 0.3 M Zn^{2+} precursor solutions. At the stoichiometric NaOH dosage, Zn_2SnO_4 was detected together with ZHS, indicating incomplete conversion of the precursors. Increasing the NaOH dosage promoted the formation of phase-pure cubic ZHS, characterized by a lattice parameter of 7.80 Å and space group $\text{Pn}\bar{3}$, consistent with JCPDS No. 20-1455 [14,18]. Interestingly, decreasing the Sn^{4+} and Zn^{2+} precursor concentrations from 0.3 to 0.1 M resulted in the formation of crystalline ZnO, demonstrating that precursor concentration strongly influences phase evolution during ZHS precipitation.

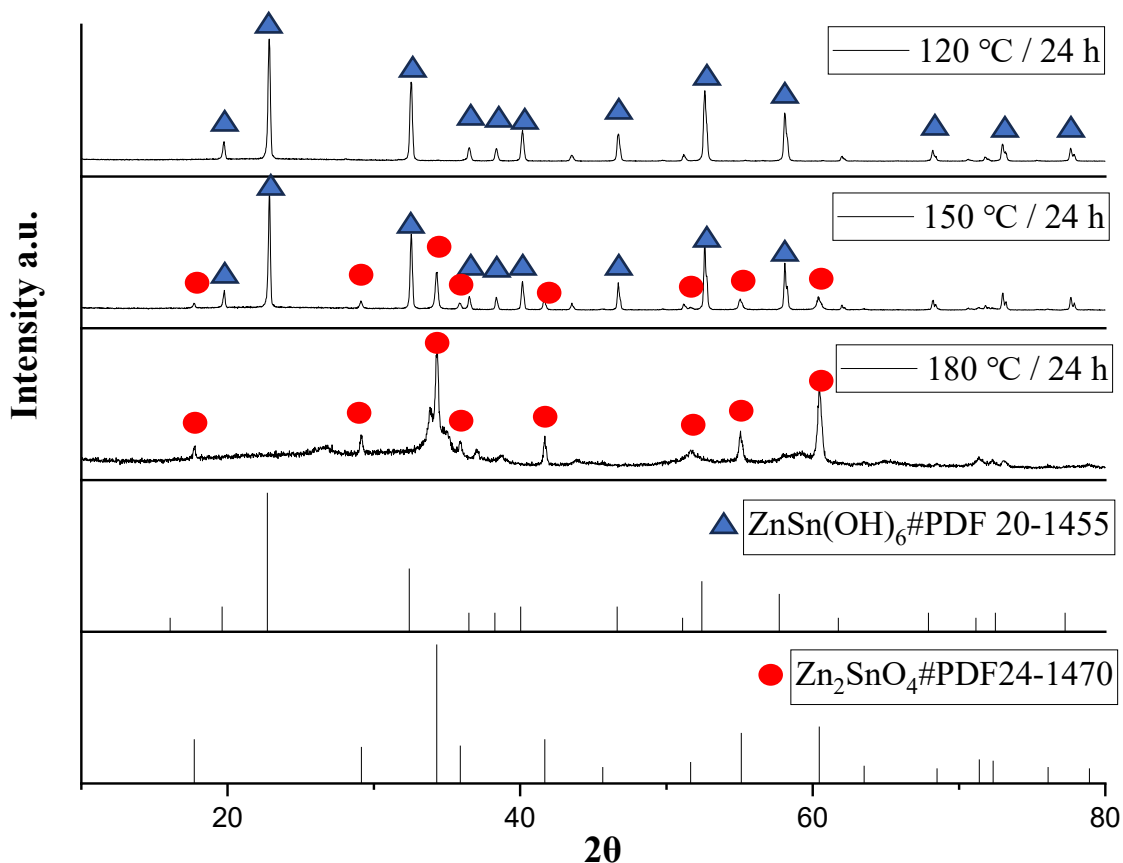


Figure 2. Effects of hydrothermal temperature on XRD patterns of ZHS microcubes prepared hydrothermally. The doses of metal salts and NaOH were the same as those in Figure 1.

Similarly, hydrothermal treatment induced temperature-dependent phase evolution in the ZHS microcubes (Figure 2). At 120 °C, ZHS remained the predominant crystalline phase, whereas increasing the hydrothermal temperature to 150 °C resulted in the formation of cubic zinc stannate (Zn_2SnO_4) alongside ZHS. The Zn_2SnO_4 phase exhibited a lattice parameter of 8.657 Å and a $\text{Fd}\bar{3}\text{m}$ space group, consistent with JCPDS No. 24-1470 [19]. Further increasing the temperature to 180 °C led to complete conversion to Zn_2SnO_4 , with no detectable ZHS remaining. Thus, ZHS and Zn_2SnO_4 were selectively obtained at 120 and 180 °C, respectively, while 150 °C yielded a mixed phase. In contrast, extending the hydrothermal duration from 6 to 24 h at 120 °C produced no detectable phase transformation, indicating that hydrothermal temperature, rather than treatment time, is the dominant

parameter governing the ZHS-to- Zn_2SnO_4 phase evolution under these conditions.

As reported by Li et al. [13], higher catalyst surface basicity can promote CO_2 activation during the direct carbonylation of GLY, thereby enhancing GLC formation. Accordingly, the surface basicity of the ZHS catalysts was quantified using the Hammett indicator method, with the results summarized in Tables 1 and 2. As shown in Table 1, increasing the NaOH dosage beyond the stoichiometric amount progressively enhanced the surface basicity of ZHS, indicating that excess alkali during precipitation modifies the surface chemistry of the resulting catalyst.

Table 2. Surface Basicity of Zinc Hydroxystannate (ZHS) Measured with the Hammett method using Neutral Red ($pK_a = 6.8$) and Phenolphthalein ($pK_a = 9.5$). The concentrations of $[\text{Sn}^{4+}]$ and $[\text{Zn}^{2+}]$ in precursor (M) were 0.3 M . The excess ratio was defined as the actual amount of NaOH to its stoichiometric amount used in ZHS preparation.

Excess ratio	Neutral Red	Phenolphthalein
	Basicity ($\mu\text{mol/g}$)	Basicity ($\mu\text{mol/g}$)
1.00	260.7 ± 3.9	—
1.33	285.1 ± 6.2	—
1.66	425.0 ± 8.9	19.6 ± 0.5
1.99	420.1 ± 4.3	19.3 ± 0.4

Table 2. Surface Basicity of Zinc Hydroxystannate (ZHS) Measured with the Hammett method. The amount of precipitating agent, NaOH, used in ZHS preparation was 1.66 times the stoichiometric amount of NaOH.

$[\text{Sn}^{4+}]$ and $[\text{Zn}^{2+}]$ in precursor (M)	Neutral Red	Phenolphthalein
	Basicity ($\mu\text{mol/g}$)	Basicity ($\mu\text{mol/g}$)
0.1	269.3 ± 7.1	—
0.3	425.0 ± 8.9	19.6 ± 0.5
0.8	309.3 ± 8.7	9.8 ± 1.8

At a fixed NaOH excess ratio of 1.66, increasing the Sn^{4+} and Zn^{2+} precursor concentrations from 0.1 to 0.8 M did not produce a monotonic increase in surface basicity. As shown in Table 2, an

intermediate precursor concentration of 0.3 M afforded the highest surface basicity, suggesting that excessive metal-ion concentration is not necessarily favorable for generating basic surface sites. In contrast, increasing the hydrothermal temperature from 120 to 180 °C decreased the surface basicity from 253.6 ± 4.7 to 187.4 ± 4.4 $\mu\text{mol/g}$, which is likely associated with the progressive conversion of ZHS to Zn_2SnO_4 and the resulting decrease in the ZHS fraction of the solid product.

Alkali-assisted surface treatment produced no appreciable change in the crystalline structure of ZHS, as indicated by the nearly unchanged XRD patterns and the absence of detectable impurity phases (Figure 3). Nevertheless, the treatment substantially modified the surface basicity (Table 3), demonstrating that the alkaline treatment can alter the surface chemical properties of ZHS without measurably affecting its bulk crystal structure.

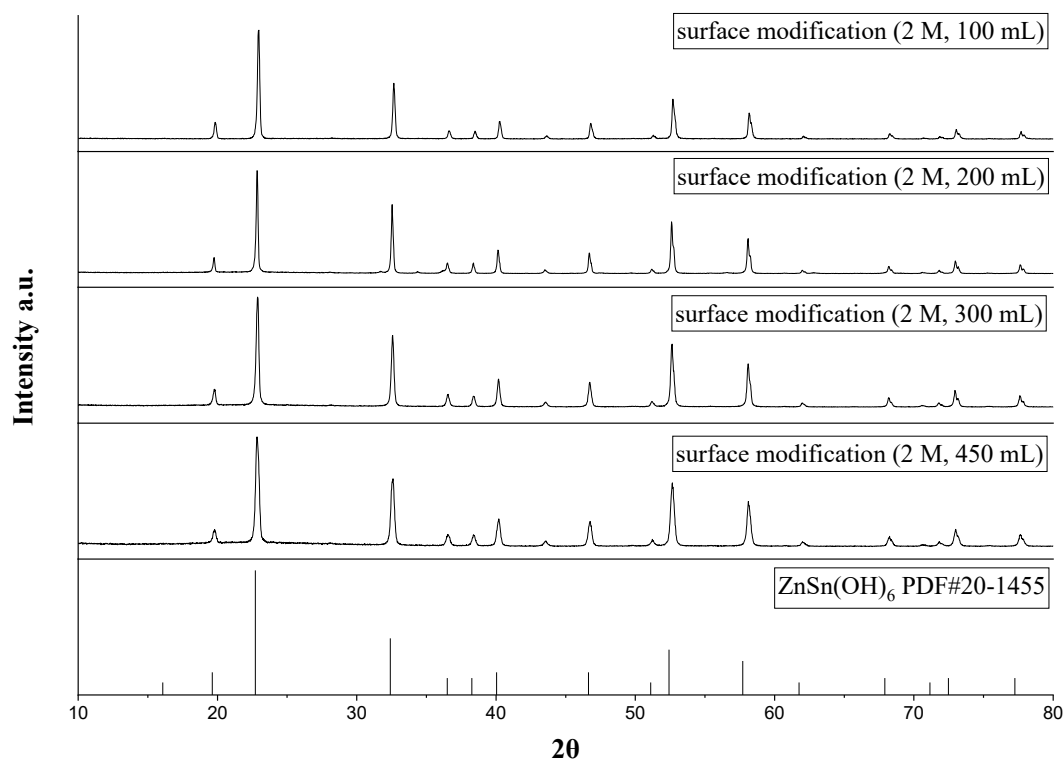


Figure 3. The XRD patterns of CFAST-treated ZHS. The doses of metal salts and NaOH were the same as those in Figure 1.

Table 3 shows that the extent of alkali-assisted treatment strongly affected the surface basicity

of ZHS. An appropriate amount of 2 M NaOH, exemplified by 200 mL, substantially increased the surface basicity, whereas excessive NaOH treatment (450 mL) caused a pronounced decrease. These results indicate that surface basicity can be optimized through controlled alkaline treatment rather than simply increased by using more NaOH. The resulting variation in surface basicity is expected to strongly influence GLC formation during the direct carbonylation of GLY with CO₂, as discussed below.

Table 3. Surface Basicity of Zinc Hydroxystannate (ZHS) after Alkali-assisted Surface Treatment. The amount of precipitating agent, NaOH, used in ZHS preparation was 1.66 times the stoichiometric amount of NaOH.

Volume of 2 M NaOH solution (mL)	Neutral Red	Phenolphthalein
	Basicity (μmol/g)	Basicity (μmol/g)
100	356.1 ± 7.9	15.2 ± 0.5
200	475.4 ± 7.4	22.8 ± 1.7
300	364.8 ± 4.5	15.3 ± 1.0
450	269.3 ± 4.6	—

Increasing the Zn²⁺ and Sn⁴⁺ concentrations in the precursor solution provides more metal ions for ZHS nucleation and crystal growth. However, excessive hydroxide concentrations can disrupt crystal formation by suppressing nucleation and promoting surface erosion or etching of the newly formed ZHS crystals. Consistent with this interpretation, increasing the alkaline solution volume during the CFAST process caused the tetradecehedral morphology to disappear and reduced the crystallinity of the ZHS granules. Therefore, the precipitant dosage must be carefully controlled to achieve complete metal-ion precipitation while minimizing hydroxide-induced disruption of ZHS

crystal growth and surface integrity.

Excessively high hydrothermal temperatures can promote the transformation of ZHS into zinc stannate, thereby altering the phase composition and potentially diminishing the surface basicity. In contrast, prolonged hydrothermal treatment generally enhanced ZHS crystallinity and produced a more uniform grain-size distribution, which may be attributed to Ostwald ripening, whereby smaller crystallites dissolve and redeposit onto larger, thermodynamically favored crystallites. Because zinc stannate exhibited lower surface basicity than ZHS, its formation is expected to adversely affect the direct carbonylation of GLY with CO₂, potentially decreasing both GLY conversion and GLC yield.

Based on the surface-basicity screening, three representative ZHS samples were selected for further FTIR, TGA, BET, EDS, and XPS characterization. The reference ZHS was prepared by coprecipitation using 0.3 M Sn⁴⁺ and 0.3 M Zn²⁺ precursor solutions (50 mL each) with 1.66 times the stoichiometric NaOH dosage (0.5 M, 50 mL). For CFAST, the resulting solid was subsequently treated with 200 mL of 2 M NaOH_(aq), whereas the hydrothermally treated sample was obtained by treating the same precursor-derived solid at 120 °C for 24 h. Under these selected conditions, all three treatments yielded phase-pure ZHS, providing a consistent basis for subsequent structural and surface-property characterization.

Figure 4 presents the FTIR spectra of ZHS prepared by the three synthesis methods. The broad bands at 3229 and 3105 cm⁻¹ are assigned to O–H stretching and intramolecular hydrogen-bonded hydroxyl groups, respectively. The sharp band at 1174 cm⁻¹ is attributed to Sn–OH bending, while the bands at 855 and 775 cm⁻¹ are associated with surface carbonate species formed through CO₂/H₂O

adsorption and hydrogen-bonded water, respectively [15]. The band at 541 cm^{-1} corresponds to Zn–O stretching [20]. Notably, the three ZHS samples exhibited nearly identical FTIR profiles, with no significant differences in their characteristic vibrational bands. These spectra were also highly consistent with those reported for hydrothermally synthesized ZHS [20], indicating that the different preparation treatments did not substantially alter the chemical functionalities of the ZHS surface.

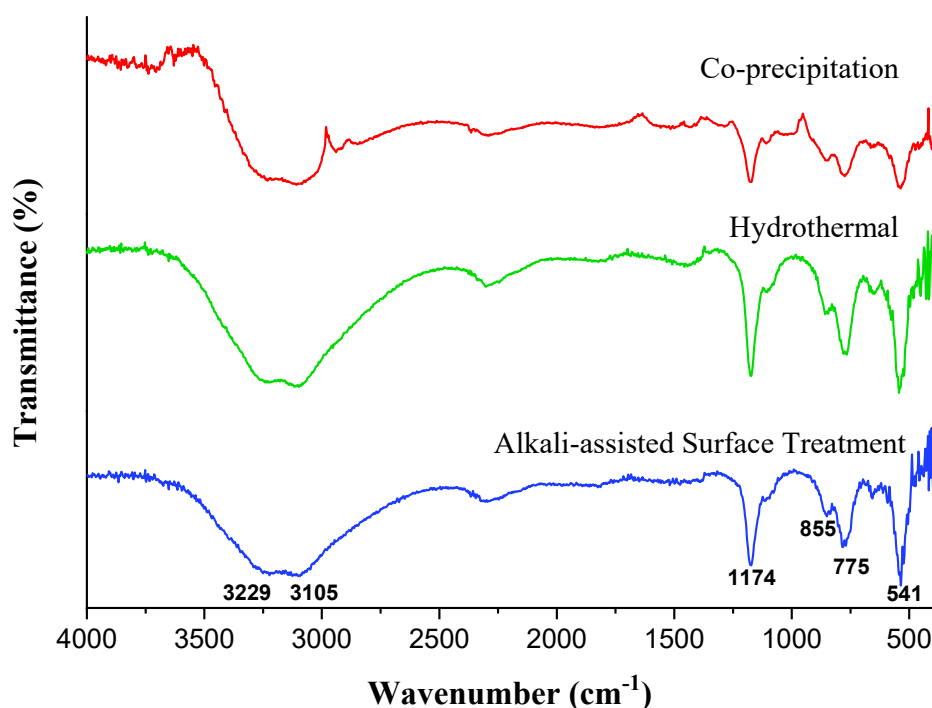
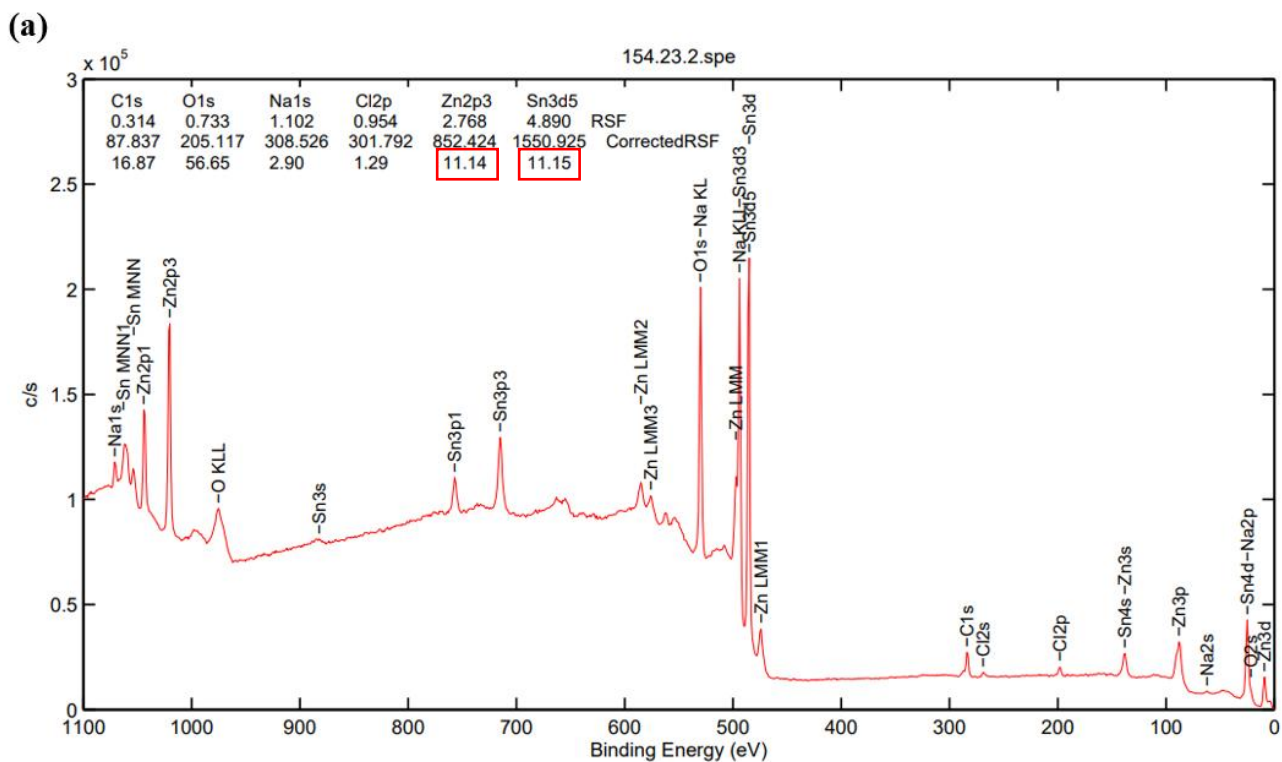


Figure 4. FTIR Spectra of ZHS synthesized via different routes.

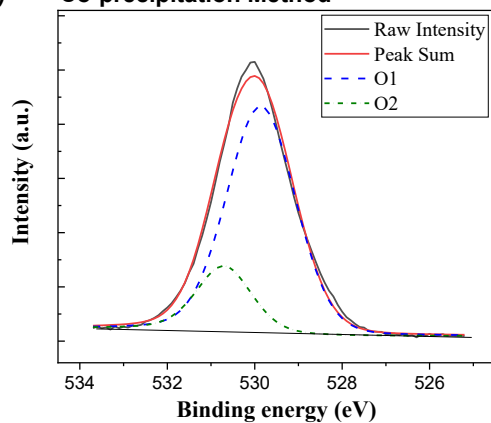
The morphology and elemental composition of the ZHS samples were examined by SEM and EDS. All three samples exhibited tetradecahedral microcubes with a hollow interior. The Sn/Zn atomic ratios determined by EDS were close to the theoretical 1:1 stoichiometry of ZHS, consistent with the nearly equimolar Sn and Zn contents obtained by ICP-OES. Combined with the XRD results, these analyses confirm the formation of $\text{ZnSn}(\text{OH})_6$ with the expected composition and crystalline structure.

Figure 5 presents the XPS spectra of ZHS prepared by the three methods. The survey spectra (Figure 5a) showed only Zn, Sn, and O as the major surface elements, with a Zn/Sn atomic ratio consistent with the 1:1 stoichiometry determined by EDS and ICP-OES. The high-resolution Zn $2p$ spectrum exhibited two peaks at 1021.8 and 1044.9 eV, assigned to Zn $2p_{3/2}$ and Zn $2p_{1/2}$, respectively. Their characteristic 2:1 peak-area ratio confirms that Zn predominantly exists as Zn^{2+} in ZHS.

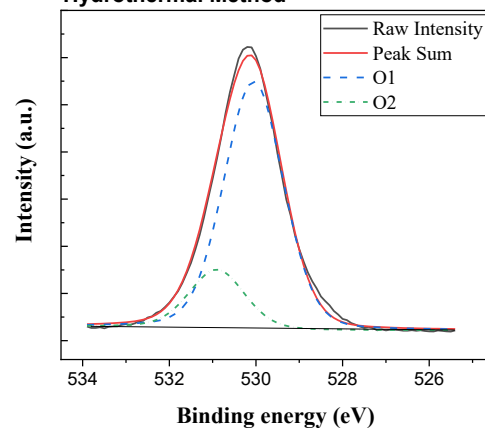
The high-resolution Sn $3d$ spectra exhibited Sn $3d_{5/2}$ and Sn $3d_{3/2}$ signals at 485.4–485.8 and 493.9–494.3 eV, respectively. Among the three samples, the CFAST-derived ZHS showed the largest shift toward lower binding energies, followed by the coprecipitated ZHS, whereas the hydrothermally treated ZHS exhibited the highest binding energies. These systematic shifts suggest differences in the local electronic environment of surface Sn species, which can be associated with oxygen-vacancy formation. Although Sn predominantly exists as Sn^{4+} in ZHS, oxygen vacancies can induce partial reduction of neighboring Sn^{4+} to Sn^{2+} , resulting in a shift of the Sn $3d$ signals toward lower binding energies [21]. The greater low-binding-energy shift observed for the CFAST sample therefore suggests a higher concentration of reduced Sn species and associated oxygen vacancies.



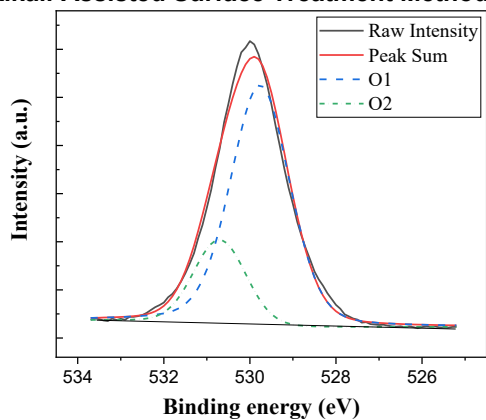
(b) Co-precipitation Method



Hydrothermal Method



Alkali-Assisted Surface Treatment Method



O1: Lattice oxygen
O2: Oxygen vacancy

Figure 5. XPS Analyses of Zinc Hydroxystannate: (a) Survey Scan, and (b) O *1s* Spectra.

The high-resolution O 1s spectra (Figure 5b) contained contributions from lattice oxygen (O1) and oxygen-vacancy-related species (O2). The chemical shifts between Sn²⁺ and Sn⁴⁺ species (e.g. Sn²⁺:SnO and Sn⁴⁺:SnO₂) in the Sn 3d and O 1s spectra were reported to be approximately 1.0 and 0.87 eV, respectively [20], supporting the assignment of the lower-binding-energy components to oxygen-vacancy-associated environments. The calculated oxygen-vacancy fractions were 19.23%, 18.00%, and 21.25% for the coprecipitated, hydrothermally treated, and CFAST-derived ZHS, respectively. Thus, the CFAST sample possessed the highest oxygen-vacancy concentration, consistent with its greater low-binding-energy shift in the Sn 3d spectrum.

Table 4. N₂ adsorption-desorption analyses of ZHS catalysts

Preparation Method of ZHS catalysts	BET Surface Area (m ² /g)	Pore Volume (mm ³ /g)	Pore Size (nm)
Co-precipitation	3.402	12	15.78
Hydrothermal	2.244	6	13.83
Coprecipitation with Alkali-Assisted Surface Treatment (CFAST)	8.029	23	17.11

The textural properties of the ZHS samples were further examined by N₂ adsorption–desorption analysis (Table 4). All samples exhibited very low BET surface areas, indicating limited porosity. Notably, alkali-assisted surface treatment increased the BET surface area from 3.402 to 8.029 m²/g and nearly doubled the pore volume from 12 to 23 mm³/g. In contrast, hydrothermal treatment produced more compact ZHS microcubes with limited development of porosity. Given the low overall

surface areas, the catalytic activity of these ZHS samples is therefore expected to depend predominantly on their accessible surface chemical properties, particularly surface basicity and oxygen-vacancy-associated sites, rather than on extensive pore structure.

3.2 Catalytic carbonylation reaction

The products from GLY carbonylation were qualitatively analyzed by GC–MS and quantitatively determined by GC-BID. After reaction, the mixture was rapidly silylated prior to GC analysis. GC–MS identified GLC as the principal product, together with unreacted GLY, residual 2-cyanopyridine (2-CP) used as the dehydrating agent, and several by-products. The major by-products included glycerol monoacetate, glycerol diacetate, and oligomeric species derived from GLY and 2-CP. In addition, 2-pyridinecarboxylic acid ethyl ester, formed through the reaction of 2-CP with water, was detected, providing evidence of the dehydration activity of 2-CP under the reaction conditions. Notably, the formation of glycerol- and 2-CP-derived oligomers substantially increased the reaction-mixture viscosity, which hindered subsequent product–catalyst separation and purification.

The ZHS synthesis parameters were optimized to enhance catalytic performance in the direct carbonylation of GLY with CO₂. Accordingly, GLC yield, rather than GLY conversion alone, was used as the primary criterion for catalyst evaluation. GLC was quantified by GC-BID using 1-dodecanol as the internal standard. Figure 6 compares the GLY conversion, GLC yield, and selectivity obtained with ZHS catalysts prepared by the three synthesis methods.

Interestingly, the presence of ZHS did not increase GLY conversion. GLY conversion over the

ZHS catalysts remained at 20–30%, compared with 36% for the blank reaction without catalyst. However, ZHS markedly redirected the converted GLY toward GLC. The GLC selectivity increased from only 12.3% in the blank reaction to 75.7%, 84.2%, and 25.0% over the coprecipitated, CPAST, and hydrothermally treated ZHS catalysts, respectively. Consequently, the CPAST-derived ZHS afforded the highest GLC yield of 17.1%, followed by the coprecipitated ZHS (15.9%) and hydrothermally treated ZHS (7.6%). In the absence of ZHS, only 4.5% of the GLY was converted to GLC, whereas diglycerols and triglycerols were the predominant products. These results demonstrate that ZHS primarily promotes the selective conversion of GLY to GLC rather than overall GLY conversion, with the CPAST treatment providing the most favorable catalytic surface.

The GLC yields obtained with the coprecipitated and CPAST-derived ZHS catalysts (15.9% and 17.1%, respectively) are comparable to those reported for hydrotalcite-derived mixed oxides (9.6–15.1%) by Li *et al* [13]. Notably, the present reaction was conducted under substantially milder conditions, using 5 bar CO₂ and 120 °C, compared with 40 bar CO₂ and 170 °C in the study of Li *et al* [13].

Direct GLY carbonylation with CO₂ has generally been investigated under relatively severe conditions, typically requiring CO₂ pressures of 40–100 bar and temperatures above 150 °C [2,6,10]. Studies at lower CO₂ pressures remain comparatively scarce. Hu *et al.* [9] reported GLC formation at 7 bar CO₂ and 150 °C for 15 h using a 5La/ZIF-8 catalyst, achieving a GLC yield of approximately 35.3%. Lee *et al.* [22] reported a good GLC yield near 69.4% from the reaction at 15 bar CO₂ and 100°C with iodide-containing ammonium ionic liquid as catalyst and with propylene oxide as a

coupling agent to inhibit and bypass water generation during the reaction. Thus, although the present ZHS system gives a lower product yield, it operates at a substantially lower temperature (120 °C) and shorter reaction time (6 h), demonstrating the potential of ZHS for GLY carbonylation under comparatively mild conditions.

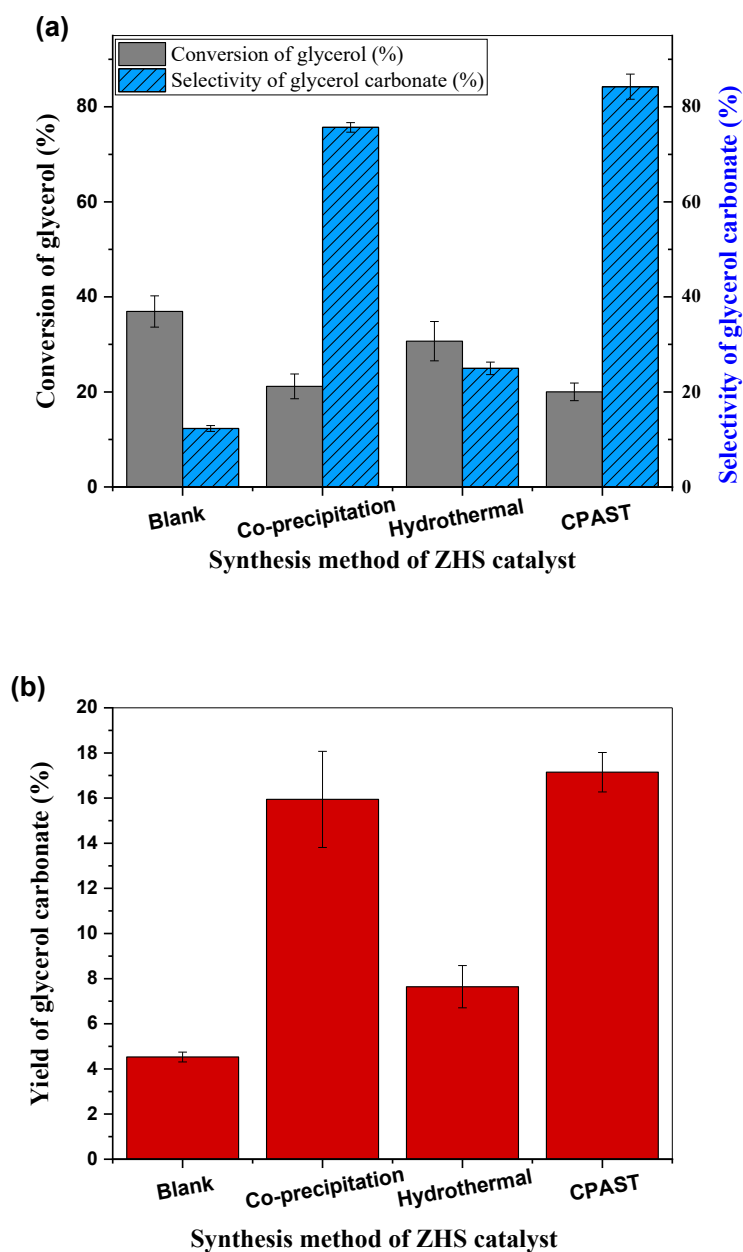


Figure 6. Effect of ZHS preparation methods on (a) the conversion of glycerol and the selectivity of glycerol carbonate, as well as (b) the yield of glycerol carbonate.

The CFAST-derived ZHS exhibited higher surface basicity, a greater concentration of oxygen vacancies, and a larger BET surface area than ZHS prepared by the other two methods. To examine whether surface basicity was associated with catalytic performance, the GLC yield was plotted against the surface basicity of the ZHS catalysts (Figure 7). A positive linear correlation was obtained and described by the following equation,

$$y = 0.03475 \cdot x - 0.57573, \quad (R^2_{adj.} = 0.8369) \quad (4)$$

with an adjusted R^2 of 0.8369, where y is the GLC yield (%) and x is the surface basicity of ZHS ($\mu\text{mol/g}$). The relatively high adjusted R^2 indicates that surface basicity is a strong descriptor of GLC formation under the investigated conditions. This relationship can be rationalized by the role of basic surface sites in CO_2 adsorption and activation, which may facilitate subsequent carbonylation of GLY. Nevertheless, the correlation should not be interpreted as definitive evidence of causality because the alkali-assisted treatment simultaneously modified the surface area, morphology, and oxygen-vacancy concentration. Thus, the enhanced catalytic performance of CFAST-derived ZHS likely reflects the combined effects of increased surface basicity and associated changes in surface structure and accessibility.

Within the investigated catalyst and reaction conditions, Eq. (4) provides a useful empirical relationship for estimating the catalytic performance of ZHS in the direct carbonylation of GLY with CO_2 . Accordingly, surface basicity can serve as a practical screening descriptor for adjusting ZHS synthesis parameters and developing catalysts with enhanced activity for CO_2 utilization with GLY.

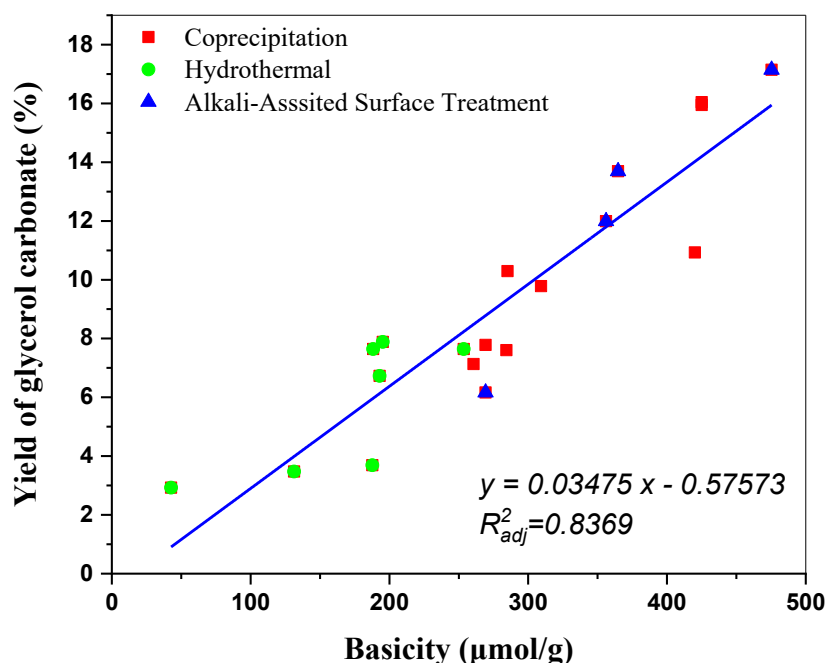


Figure 7 Correlation between Surface Basicity of Zinc Hydroxystannate and the Yield of Glycerol Carbonate.

4. Conclusion

Zinc hydroxystannate (ZHS) catalysts were successfully synthesized by coprecipitation of Zn^{2+} and Sn^{4+} with NaOH, yielding a Zn/Sn atomic ratio consistent with the 1:1 stoichiometry of ZHS as confirmed by EDS, XPS, and ICP-OES. Subsequent hydrothermal or alkali-assisted surface treatment preserved the tetradecehedral morphology and crystallographic structure of the ZHS, as evidenced by XRD. All ZHS catalysts exhibited measurable surface basicity, and XPS analysis indicated that this basicity was primarily associated with oxygen vacancies arising from changes in the oxidation state of surface Sn species. Direct GLY carbonylation with CO_2 was conducted in a semi-batch reactor at 120 °C and 5 bar CO_2 for 6 h. In the absence of ZHS, GLY conversion was relatively high, but the reaction predominantly produced diglycerols and triglycerols, resulting in the lowest GLC yield. In

contrast, the ZHS catalyst prepared by the CPAST method afforded the highest GLC yield of 17.1%. Notably, GLC yield exhibited a strong linear correlation with the surface basicity of the ZHS catalysts, identifying surface basicity as a key descriptor of catalytic performance. This structure–basicity–activity relationship provides a practical basis for rationally designing ZHS catalysts for the direct conversion of GLY and CO₂ to GLC. Notedly, zinc stannate would not catalyze effectively the direct carbonylation of GLY with CO₂ and, consequently, should be avoided during the ZHS synthesis.

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CRedit authorship contribution statement:

1. H-L Chen: Data curation, Methodology, Visualization, Writing – original draft.
2. W-I Chen: Data curation, Writing – original draft.
3. Y-C Yu: Data curation, Writing – original draft.
4. B-H Chen: Conceptualization, Data curation, Methodology, Funding acquisition, Supervision, Writing – review & editing.

Declarations of interest:

The authors declare that they have no known competing financial interests or personal

relationships that could have appeared to influence the work reported in this paper.

Data Availability

The data that support the findings of this study are available on request from the corresponding author, BH Chen.

References

- [1] C. Rosmini, Y. Mitrev, M. Dimitrov, 2026. The Crude Glycerol Challenge: Purification Technologies and Possible Valorization Pathways in the Biodiesel Industry. *Molecules*. 31, 1841. <https://doi.org/10.3390/molecules31111841>.
- [2] M. O. Sonnati, S. Amigoni, E.P.T. de Givenchy, T. Darmanin, O. Choulet, F. Guittard. Glycerol carbonate as a versatile building block for tomorrow: synthesis, reactivity, properties and applications. *Green Chem.* 15 (2013) 283–306. <https://doi.org/10.1039/c2gc36525a>
- [3] C. Choe, M. Kim, C. Quintana, H. Lim. Integrated overview of solvents and materials for reactive carbon capture and utilization. *J. Mater. Chem. A* 14 (2026) 18450–18496. <https://doi.org/10.1039/d5ta10129h>.
- [4] S. Thiruketheeswaranathan, B.F. Wang, E.J. Anthony, A.K. Vuppaladadiyam, M. Zhao, 2026. Integrated CO₂ capture and conversion (ICCC): Advancing dual-function materials with techno-economic perspectives for sustainable fuels. *Prog. Energy Combust. Sci.* 116–117, 101303. <https://doi.org/10.1016/j.pecs.2026.101303>.
- [5] K. Mori, 2026. Architected metal catalysts for carbon-neutral hydrogen energy conversion. *Bull. Chem. Soc. Jpn.* 99, uoag106. <https://doi.org/10.1093/bulcsj/uoag106>.
- [6] P. Inirai, J. Keogh, A. Centeno-Pedrazo, N. Artioli, H. Manyar, 2024. Recent advances in processes and catalysts for glycerol carbonate production via direct and indirect use of CO₂. *J. CO₂ Utilization*. 80, 102693. <https://doi.org/10.1016/j.jcou.2024.102693>.
- [7] S. Chaowamalee, C. Ngamcharussrivichai. Exploring the direct carbonylation of glycerol with CO₂ for sustainable glycerol carbonate production: Current development, challenges and future perspectives. *J. Ind. Eng. Chem.* 156 (2026) 192–209. <https://doi.org/10.1016/j.jiec.2025.09.017>.
- [8] J. Li, T. Wang. Chemical equilibrium of glycerol carbonate synthesis from glycerol. *J. Chem.*

Thermodyn. 43 (2011) 731–736. <https://doi.org/10.1016/j.jct.2010.12.013>.

- [9] C.C. Hu, C.-W. Chang, M. Yoshida, K.-H. Wang. Lanthanum nanocluster/ZIF-8 for boosting catalytic CO₂/glycerol conversion using MgCO₃ as a dehydrating agent. *J. Mater. Chem. A* 9 (2021) 7048–7058. <https://doi.org/10.1039/d0ta12413c>.
- [10] Y.-H. Ke, H. Xu, X. Wang, H. Liu, H. Yuan, 2024. Production of glycerol carbonate by coupling glycerol and CO₂ over various metal oxide catalyst. *J. CO₂ Utilization*. 83, 102813. <https://doi.org/10.1016/j.jcou.2024.102813>.
- [11] A. Sarkar, T. Tyagi, S. Sharma, V. Joshi, P. Gogoi, A. Puzari, B. Paul, 2025. Synthesis of glycerol carbonate from glycerol and CO₂ over Cu/In₂O₃/ZnO nanostructured catalyst. *Catalysis Today*. 448, 115164. <https://doi.org/10.1016/j.cattod.2024.115164>.
- [12] N. Xing, Y. Zhang, W. Jian, Y. Zhang, S. Li. Production of glycerol carbonate from carboxylation of glycerol with CO₂ using 0.3ZnO-CaO-SBA-15 as catalyst. *Chem. Eng. Res. Des.* 25 (2026) 74 – 84. <https://doi.org/10.1016/j.cherd.2025.11.033>.
- [13] H. Li, X. Jiao, L. Li, N. Zhao, F. Xiao, W. Wei, Y. Sun, B. Zhang. Synthesis of glycerol carbonate by direct carbonylation of glycerol with CO₂ over solid catalysts derived from Zn/Al/La and Zn/Al/La/M (M= Li, Mg and Zr) hydrotalcites. *Catal. Sci. Technol.* 5(2) (2015) 989–1005. <https://doi.org/10.1039/c4cy01237b>.
- [14] S. Sandesh, G.V. Shanbhag, A.B. Halgeri. Zinc hydroxystannate: a promising solid acid–base bifunctional catalyst, *RSC Advances*, 4(2) (2014) 974-977. <https://doi.org/10.1039/c3ra44370a>.
- [15] X. Fu, D. Huang, Y. Qin, L. Li, X. Jiang, S. Chen, S. Effects of preparation method on the microstructure and photocatalytic performance of ZnSn(OH)₆. *Applied Catalysis B: Environmental*, 148 (2014) 532–542. <https://doi.org/10.1016/j.apcatb.2013.11.039>.
- [16] K. Tanabe, T. Yamaguchi. Basicity and Acidity of Solid Surfaces, *Journal of the Research*

Institute for Catalysis Hokkaido University, 11(3) (1964) 179 – 184.

<https://eprints.lib.hokudai.ac.jp/repo/huscap/all/24771/>.

- [17] C.C. Sweeley, R. Bentley, M. Mekita, W.W. Wells. Gas-Liquid Chromatography of Trimethylsilyl Derivatives of Sugars and Related Substances. *J. Amer. Chem. Soc.*, 85 (1963) 2497–2507. <https://doi.org/10.1021/ja00899a032>.
- [18] Y. Zhang, M. Guo, M. Zhang, C. Yang, T. Ma, X. Wang. Hydrothermal synthesis and characterization of single-crystalline zinc hydroxystannate microcubes. *Journal of Crystal Growth*, 308(1) (2007) 99-104. <https://doi.org/10.1016/j.jcrysgro.2007.07.030>
- [19] A. A. Bhat, I. Assadullah, A. Farooq, K. A. Malik, J. H. Malik, R. Tomar, I. Islam. A. M. Ali, S. A. Khandy, 2023. Band-gap alteration of Zn_2SnO_4 nanostructures for optical and photo-luminescent applications. *Materials Chemistry and Physics*. 306, 127993. <https://doi.org/10.1016/j.matchemphys.2023.127993>.
- [20] M. Jose, G. Nithya, R. Robert, S. M. B. Dhas. Formation and optical characterization of unique zinc hydroxy stannate nanostructures by a simple hydrothermal method. *J Mater Sci: Mater Electron*. 29 (2018) 2628–2637. <https://doi.org/10.1007/s10854-017-8188-4>.
- [21] W.K. Choi, H.J. Jung, S.K. Koh. Chemical shifts and optical properties of tin oxide films grown by a reactive ion assisted deposition. *J. Vac. Sci. Technol. A* 14 (1996) 359–366. <https://doi.org/10.1116/1.579901>.
- [22] Y.-L. Lee, Y.-C. Kao, H.-X. Xu, S. Tsunekawa, M. Yoshida, Y.-P. Li, C.C. Hu, 2026. Green synthesis of glycerol carbonate from glycerol and CO_2 using a polymeric ionic liquid catalyst: An experimental and theoretical study. *J. Clean. Prod.* 560, 148344. <https://doi.org/10.1016/j.jclepro.2026.148344>.

Figure Captions:

Figure 1. XRD patterns of zinc hydroxystannate (ZHS) prepared from precursor containing 0.3 M Zn^{2+} and 0.3 M Sn^{4+} with different amounts of precipitating agent, NaOH. The excess ratio was defined as the actual amount of NaOH to the stoichiometric amount of NaOH in ZHS preparation.

Figure 2. Effects of hydrothermal temperature on XRD patterns of ZHS microcubes prepared hydrothermally. The doses of metal salts and NaOH were the same as those in Figure 1.

Figure 3. The XRD patterns of CFAST-treated ZHS. The doses of metal salts and NaOH were the same as those in Figure 1.

Figure 4. FTIR Spectra of ZHS synthesized via different routes.

Figure 5. XPS Analyses of Zinc Hydroxystannate: (a) Survey Scan, and (b) O 1s Spectra.

Figure 6. Effect of ZHS preparation methods on (a) the conversion of glycerol and the selectivity of glycerol carbonate, as well as (b) the yield of glycerol carbonate

Figure 7. Correlation between Surface Basicity of Zinc Hydroxystannate and the Yield of Glycerol Carbonate.