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**Synthesis of glycerol carbonate from glycerol and urea using
zinc-containing solid catalysts: A homogeneous reaction**

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Abstract

Zinc-containing solid catalysts (zinc oxide, smectite, hydrotalcite) and several inorganic zinc salts were used to produce glycerol carbonate from glycerol and urea under solvent-free conditions at 130 °C and at a reduced pressure of 3 kPa. The leaching of Zn species was observed to occur for the solid catalysts and the carbonate yield was shown to be correlated with the amount of zinc species dissolved into the liquid phase with a single relationship in common for all the catalysts employed. The reaction was also indicated to continue in the liquid phase alone after the solid catalysts were removed from the reaction mixtures by filtration. The results obtained reveal that the reaction takes place homogeneously in the liquid phase irrespective of the parent solid catalysts used. Possible structure of active Zn species was discussed from the results of reaction runs under different conditions and Fourier transform infrared spectroscopy measurements of the liquid phase after the reaction.

Keywords: Glycerol carbonate, Glycerol, Urea, Solid zinc catalyst, Homogeneous reaction

1. Introduction

The synthesis of glycerol carbonate from glycerol and urea (Scheme 1) is currently attracting much attention from viewpoint of sustainable chemistry. This synthetic reaction has several merits: one can (a) utilize and reduce undesired CO₂ emitted from various sources, (b) utilize glycerol formed as a by-product in the manufacture of biodiesels [1], (c) produce a value added organic product of glycerol carbonate that can find practical applications [2, 3], and (d) replace a current route for the production of glycerol carbonate using such a toxic compound as phosgene [4]. Urea can be produced from CO₂ and ammonia [5] and so the synthesis of glycerol carbonate from glycerol and urea is one of indirect chemical transformations of CO₂ into organic compounds. The authors have investigated direct [6-10] and indirect utilization of CO₂ as a feedstock, including chemical reactions with urea [11, 12].

Various base catalysts have been tested for the synthesis of glycerol carbonate from glycerol and urea in the literature. Such inorganic salts as ZnSO₄ [13, 14] and MgSO₄ [15, 16] are effective homogeneous catalysts. Compared to these homogeneous ones, heterogeneous catalysts may be more useful for post-reaction procedures like easy recovery and reuse of catalysts. Several previous authors studied the performance of solid catalysts including La₂O₃ [17], Au nanoparticles [18], Co₃O₄/ZnO [19], metal

oxides (MgO, CaO) [20] and mixed metal oxides (Al/MgO_x, Al/LiO_x) prepared from hydrotalcites [20], and γ -zirconium phosphate [21]. For example, Rubio-Marcos et al. reported a conversion of about 70 % with close 100 % selectivity with a Co₃O₄/ZnO catalyst at 145 °C for 4 h [19]. Although those useful catalysts are reported, it is still a challenging task to develop new heterogeneous catalysts having a high performance as under milder conditions.

In the present work, the authors intended to apply zinc-containing mesoporous smectite-like materials as heterogeneous catalysts for the production of glycerol carbonate from glycerol and urea at a temperature of 130 °C under solvent-less conditions. Those porous catalytic materials can be prepared by a simple hydrothermal method [22, 23] and show interesting catalytic activities in direct/indirect CO₂ fixation reactions [10, 24, 25] and others [26-30]. In addition to those smectite-like catalysts, zinc oxide and a zinc-containing hydrotalcite have also been tested for comparison. It has been observed for these three catalysts that a zinc-containing species is dissolved into in the liquid phase and the product yield is well correlated with the amount of the zinc species dissolved. Therefore, the reaction should proceed homogeneously with the same active zinc species present in the liquid phase, contrary to our beginning expectation. The formation and structure of these active zinc species have been studied

by making reaction runs under different conditions and Fourier transform infrared spectroscopy (FTIR) measurements of the organic liquids after the reaction runs. It has been observed that the coexistence of glycerol and urea is required for the leaching of zinc species from the parent solid catalysts into the liquid phase. The same zinc complex coordinated with N=C=O is likely to form irrespective of the parent solid catalysts used and active for the homogeneous transformation of glycerol and urea to glycerol carbonate.

2. Experimental

2.1. Catalyst samples and characterizations

Several catalysts were used in the present work. ZnCl_2 , ZnBr_2 , ZnSO_4 , and $(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$ were purchased from Wako Pure Chemical Industries. ZnO purchased from Kanto Chemical Company was also used as a catalyst.

A Zn-containing mesoporous smectite-like material was prepared by a hydrothermal method. The detailed procedures were described elsewhere [22, 23]. In brief, an aqueous solution of ZnCl_2 was dropped to an aqueous solution of water glass (Nippon Chemical Industrial) and NaOH (Wako) while stirring. The Si:Zn molar ratio in the mixture was adjusted to 8:6. After further stirring overnight, the solid material was separated by centrifuge. The resultant solid material was mixed with distilled water and

the mixture was treated in an autoclave at 150 °C under autogeneous pressure for 5 h.

This catalyst will be abbreviated as SM(Zn) in the following.

A Zn-containing hydrotalcite material was also prepared according to the literature [20]. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Wako) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Wako) were mixed in distilled water with a Zn:Al molar ratio of 2:1. This aqueous solution was added to another solution of Na_2CO_3 (Wako) and NaOH (Wako) with a molar ratio of 3:7 while stirring and the resultant mixed solution was allowed to stand at 65 °C for 18 h. Then, the precipitate obtained was separated by centrifuge and washed with distilled water; this was repeated four times and the solid material obtained was dried at 110 °C for 12 h. It was then used as a catalyst for the title reaction. This sample will be referred to as HT(Zn) hereinafter.

The structural features of solid catalysts of ZnO, SM(Zn), and HT(Zn) used were examined by X-ray diffraction (XRD) and nitrogen adsorption using JOEL JDX-8020 and Quantachrome NOVA 1000, respectively.

2.2. Reaction runs and leaching tests

A 100 cm³ pear shape flask with a condenser was loaded with glycerol (Wako) in 50 mmol (4.6 g), urea (Wako) in 50 mmol (3.0 g), and solid catalyst in 0.25 g. After the pressure was reduced to 3 kPa by an aspirator, the reaction mixture was heated in an

oil bath to 80 °C and kept at this temperature for 30 min while stirring by a magnetic stirrer. Then, the reaction mixture was further heated and kept at 130 °C for 180 min. After the reaction, the solid catalyst was separated by filtration and the liquid phase was diluted by ethanol (Wako) and analyzed by a gas chromatography with a flame ionization detector (Shimadzu GC-14B with ZB-50 column). Anisole (Wako) was used as an internal standard.

As described in the following, the leaching of Zn from the Zn-containing solid catalysts was observed to occur. The amount of Zn species dissolved into the liquid phase after the reaction was measured by chelatometry. The liquid phase was separated from the solid materials by filtration. A small quantity of an indicator of blue tetrazolium (Aldrich) was added to this liquid sample. A 0.01 M ethylenediamine-tetraacetic acid (EDTA, Aldrich) solution was dropped to the liquid to find an end point when the liquid changed in color from red to blue. The leaching of Zn was then determined from the amount of EDTA used. The liquid phase after the reaction was also examined by FTIR (JASCO FTIR-620). It was separated from the catalysts by filtration and then subjected to FTIR measurement under ambient conditions.

3. Results and discussion

The three different solid catalysts of ZnO, SM(Zn), and HT(Zn) used in the

present work indicated Brunauer-Emmett-Teller (BET) surface areas of 3.5, 248, and 45.7 m² g⁻¹. Before the detailed results with the three solid catalysts are presented, the activities of several heterogeneous and homogeneous catalysts are compared (Table 1). The selectivity to glycerol carbonate was < 100 %, mainly due to the oligomerization of the product. It was found that ZnCl₂, ZnBr₂, and ZnSO₄ gave conversion values > 80 % and selectivity levels > 90 % (entries 4 – 6) but (CH₃COO)₂Zn·2H₂O was less active and selective (entry 7). After the reaction with ZnBr₂, the reaction solution was colored, indicating the decomposition of the catalyst and the formation of Br₂. Compared with zinc halides and sulfate, ZnO and SM(Zn) showed smaller activity and selectivity values (entries 1, 2); the activity of HT(Zn) was good but the selectivity was not so high (entry 3). However, Table 1 indicates that the differences in the performance among those heterogeneous and homogeneous catalysts examined are not large, and so there is still room to further examine the performance of those solid catalysts.

Fig. 1 gives XRD patterns of the three solid catalysts before and after a reaction run. Surprisingly, the XRD measurements of ZnO showed that, on the reaction run, ZnO changed almost completely to a certain species, which is zinc glycerolate, C₃H₆O₃Zn, according to the literature XRD data [31]. It was further observed that the catalyst weight increased after the reaction. The XRD patterns of SM(Zn) were almost the same

before and after one reaction run, but the XRD peaks of SM(Zn) gradually became broader and weaker after repeating several reaction runs (not shown), strongly suggesting that its crystallinity became lowered. No peak was observed in the XRD pattern of HT(Zn) after the reaction. Thus, XRD results did not indicate the formation of zinc glycerolate for these two mesoporous catalyst samples, but some structural changes occurred in the course of reaction. The absence of the formation of zinc glycerolate might result from the presence of Si and Al atoms in their layer structures.

Fig. 2 shows the changes in the yield of glycerol carbonate using the three solid catalysts by varying the catalyst amount. The increases of the yield were marginal above certain amounts of the catalysts used. Thus, the yield of glycerol carbonate was not simply determined by the catalyst amount. Zhao et al. used ZnO for the reaction of urea and methanol to produce dimethyl carbonate and showed that ZnO was converted to a zinc complex of $(\text{NH}_3)_2\text{Zn}(\text{NCO})_2$, in which two molecules of ammonia were weakly coordinated to Zn atom [32]. This Zn complex was proposed to be the active species for the dimethyl carbonate synthesis from methanol and urea. These results strongly suggest that similar Zn complexes were also produced in the present reaction system and participated in the reaction. So, the possibility of leaching of Zn species from these solid catalysts was studied. The reaction runs were conducted with different amounts of

catalysts while keeping the other reaction conditions unchanged. The amounts of Zn species dissolved into the organic liquid phase were also measured. The amount of dissolved Zn species is plotted against the initial amount of Zn included in the catalysts used in Fig. 3a. The amount of dissolved Zn species increased significantly with the amount of catalyst used when it was small (< 1 mmol). But, when the catalyst amount was further increased (> 1 mmol), the amount of dissolved Zn species did not change so much. Fig. 3b shows the yield of glycerol carbonate formed against the amount of dissolved Zn species. A single relationship can be seen in common for ZnO, SM(Zn) and HT(Zn) catalysts. Fig. 3b also gives the glycerol carbonate yield obtained with the homogeneous catalysts against the amount of Zn in the reaction mixture. It should be noted that the relationship for the solid catalysts can also well correlate the glycerol carbonate yields obtained with the homogeneous catalysts. Those results strongly suggest that the synthesis of glycerol carbonate is catalyzed by Zn species dissolved in the liquid phase and such active Zn species have the same structure (thus the same specific performance) irrespective of the parent Zn-containing solid and homogeneous catalysts used.

The homogeneous nature of the present glycerol carbonate synthesis was further studied with the liquid phase alone after the solid – liquid reaction. Table 2 gives

the results with the three solid catalysts, with which a reaction run was conducted for 1 h, the catalyst was separated from the reaction mixture by filtration, and the liquid phase was further kept to stand for 6 h under the same reaction conditions. The conversion and selectivity obtained with the filtrates were the same as in the reactions carried out for 7 h in the presence of catalysts. These results also indicate that the reaction proceeds homogeneously with the Zn species dissolved in the liquid phase. Table 2 gives another interesting fact that the amount of Zn dissolved in 7 h was smaller than that in 1 h for the three solid catalysts. This indicates a possibility that the dissolved Zn species may re-deposit on the parent catalysts and/or precipitate separately in a long reaction time (at a higher conversion). The Zn leaching occurs for the three Zn-containing solid catalysts but the extent of leaching and the extent of re-deposition/precipitation depend on the catalysts used.

The present results demonstrate that the production of glycerol carbonate from glycerol and urea is catalyzed by a certain Zn species dissolved from the solid catalysts into the organic liquid phase. FTIR measurements were made for the liquid phase after the reaction runs to examine structural features of the dissolved Zn species present therein. Fig. 4a and 4b show FTIR spectra for the liquid phases of glycerol and urea in the absence and presence of ZnO, respectively, after the same thermal history as in the

reaction runs. Additional absorption bands were observed to exist at 2216, 1791, 1713, 1186, and 778 cm^{-1} in the presence of ZnO. These absorption bands can be assigned to such functional groups according to the literature: 2216 cm^{-1} to NCO [32], 1791, 1186 and 778 cm^{-1} to glycerol carbonate [33], 1713 cm^{-1} to intermediate carbamate species [33]. The same FTIR measurements were also made for the liquid phases containing homogeneous catalysts of ZnCl_2 , $(\text{CH}_3\text{COO})_2\text{Zn}$, and ZnSO_4 . Fig. 5 shows FTIR spectra obtained, indicating that new absorption bands appeared at very similar frequencies in the presence of the homogeneous catalysts as observed with the Zn-containing solid ones (Fig. 4). Therefore, the same Zn-containing complex should also exist in the liquid phases with the homogeneous catalysts and it should be an active species irrespective of the parent heterogeneous and homogeneous catalysts used.

The leaching of Zn species from ZnO by either glycerol or urea at a reaction temperature of 130 $^\circ\text{C}$ was examined. Only a small amount of Zn species was found to leach into the liquid phase, and so the coexistence of glycerol and urea was required for the Zn leaching. Furthermore, ZnO changed to zinc glycerolate after a reaction run (Fig. 1). These results and those obtained by FTIR led us to propose reaction mechanisms as depicted in Scheme 2. ZnO reacts with isocyanic acid produced from urea, transforming to a zinc complex **1** to which two ammonia molecules are weakly coordinated [32]. One

of the coordinated ammonia molecules would be exchanged with one glycerol molecule, resulting in the formation of a complex **2** to which the glycerol molecule interacts with the Zn center through its oxygen atom. Then, the interacting hydroxyl group of glycerol captures the neighboring isocyanate group, producing a carbamate complex **3**. The coordinated carbamate group is further converted to glycerol carbonate via intra-cyclization, releasing ammonia and regenerating the complex **1**. Probably, the weak coordination of the glycerol (complex **2**) and the carbamate group (complex **3**) to the Zn center through their hydroxyl oxygen atoms makes them more active, and zinc glycerolate is produced from the complex **2** thorough the formation of a complex **4**.

Some fraction of the dissolved Zn species might precipitate and/or re-deposit on the remaining parent solid catalyst when the amounts of glycerol and urea become small at high conversion levels. This may explain the smaller quantity of the dissolved Zn species at a high conversion (Table 2). The precipitation/re-deposition of active species at the later stage of reaction is phenomenally similar to the results of Heck coupling reactions with conventional supported Pd catalysts. The supported metal is leaching to the organic liquid phase and the reaction is homogeneously catalyzed by the dissolved Pd species; at close 100 % conversion, however, those Pd species will return onto the surface of the parent supported catalysts [34, 35].

4. Conclusion

The synthesis of glycerol carbonate from glycerol and urea using Zn-containing solid catalysts (zinc oxide, smectite, hydrotalcite) under solvent-free conditions at 130 °C and at 3 kPa proceeds homogeneously but not heterogeneously. The constituent Zn species may dissolve into the liquid phase by an action of both glycerol and urea. The dissolved Zn species are active ones for the reaction, which has the same structure irrespective of the parent solid catalysts used. The active species could be a complex of a Zn atom coordinated with N=C=O. For homogeneous catalysts such as ZnCl₂, (CH₃COO)₂Zn, and ZnSO₄, the same Zn complex is likely to form and be an active species for the transformation of glycerol and urea to glycerol carbonate.

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Captions for Figures, Tables, and Schemes

Fig. 1. XRD patterns of Zn-containing solid catalyst samples used: (a) ZnO, (b) smectite, and (c) hydrotalcite before and after activity measurements in glycerol carbonate synthesis

Fig. 2 The yield of glycerol carbonate as a function of the amount of Zn included in the catalyst used. (○) ZnO, (□) SM(Zn), and (●) HT(Zn).

Fig. 3. (a) Relationship between the amount of Zn species dissolved and the initial amount of Zn included in the parent catalysts. (b) Relationship between the yield of glycerol carbonate (GC) and the amount of Zn species dissolved in the liquid phase. (○) ZnO, (□) SM(Zn), (●) HT(Zn) and (■) zinc salts.

Fig. 4. FTIR spectra collected in the presence and absence of Zn-containing solid catalysts. (a) glycerol + urea, (b) glycerol + urea + ZnO, (c) glycerol + urea + SM(Zn), (d) glycerol + urea + HT(Zn)

Fig. 5. FTIR spectra collected in the presence and absence of Zn-containing homogeneous catalysts. (a) glycerol + urea, (b) glycerol + urea + ZnCl₂, (c) glycerol + urea + (CH₃COO)₂Zn, and (d) glycerol + urea + ZnSO₄.

Table 1 Comparison of the performance among several heterogeneous and homogeneous catalysts for the synthesis of glycerol carbonate from glycerol and urea

Table 2 Results in the presence and absence (filtrate) of solid catalysts in synthesis of glycerol carbonate from glycerol and urea

Scheme 1 Synthesis of glycerol carbonate from glycerol and urea

Scheme 2 Reaction mechanisms proposed for the synthesis of glycerol carbonate from glycerol and urea with Zn-containing catalyst

Table 1

Comparison of the performance among several heterogeneous and homogeneous catalysts for the synthesis of glycerol carbonate from glycerol and urea^a

Entry	Catalyst	Conversion (%)	Selectivity (%)	TOF ^b (h ⁻¹)
1	ZnO	61	69	2.3
2	SM(Zn)	65	75	5.3
3	HT(Zn/Al)	82	80	6.2
4	ZnCl ₂	84	97	7.5
5	ZnBr ₂	82	96	12
6	ZnSO ₄	81	92	8.0
7	(CH ₃ COO) ₂ Zn·2H ₂ O	65	80	7.7

^a Reaction conditions: Catalyst 0.25 g, Glycerol 50 mmol, Urea 50 mmol, Temperature 130 °C, Pressure 3 KPa, Time 3 h.

^b Apparent turnover frequency = (moles of glycerol carbonate formed) / ((moles of Zn used)·(reaction time)).

Table 2

Results in the presence and absence (filtrate) of solid catalysts in synthesis of glycerol carbonate from glycerol and urea^a

Catalyst	Time (h)	Conversion (%)	Selectivity (%)	Dissolved Zn (mmol)
(a) ZnO	1	52	58	0.39
	7 ^b	78	74	
	7 ^c	81	74	0.18
(b) SM(Zn)	1	33	61	0.36
	7 ^b	87	86	
	7 ^c	87	86	0.23
(c) HT(Zn)	1	43	60	0.41
	7 ^b	92	80	
	7 ^c	88	82	0.24

^a Reaction conditions: Catalyst 0.25 g, Glycerol 50 mmol, Urea 50 mmol, Temperature 130 °C, Pressure 3 KPa, Time 3 h.

^b The reaction was conducted in the presence of catalyst for 1 h, it was separated by filtration, and then the filtrate was kept to stand under the reaction conditions for 6 h, total 7 h.

^c The reaction was conducted in the presence of catalyst for 7 h.

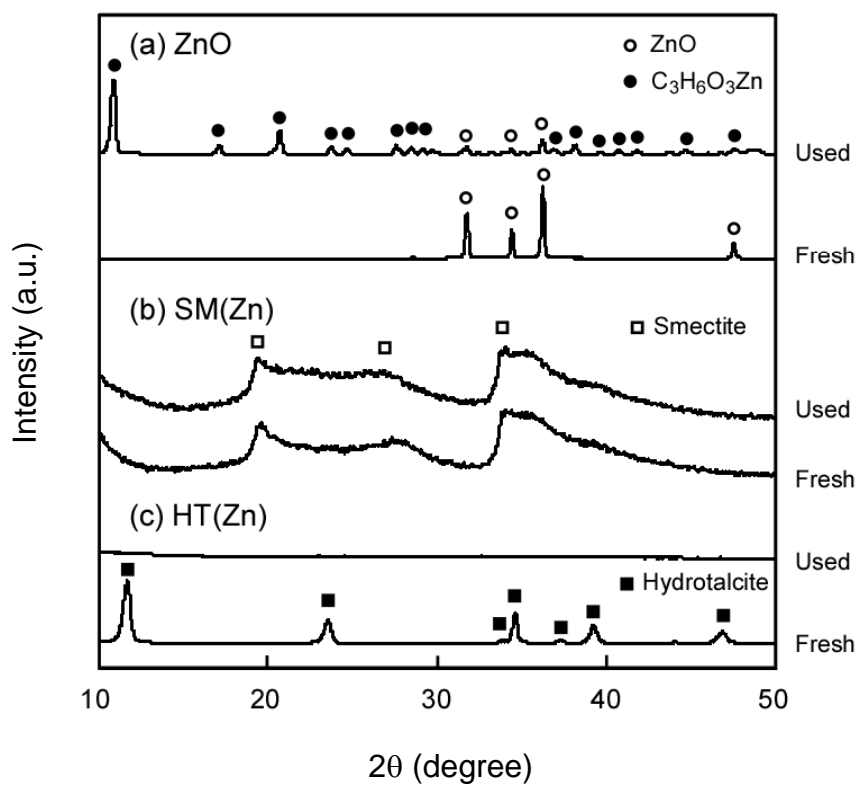


Fig. 1. XRD patterns of Zn-containing solid catalyst samples used: (a) ZnO, (b) smectite, and (c) hydrotalcite before and after activity measurements in glycerol carbonate synthesis

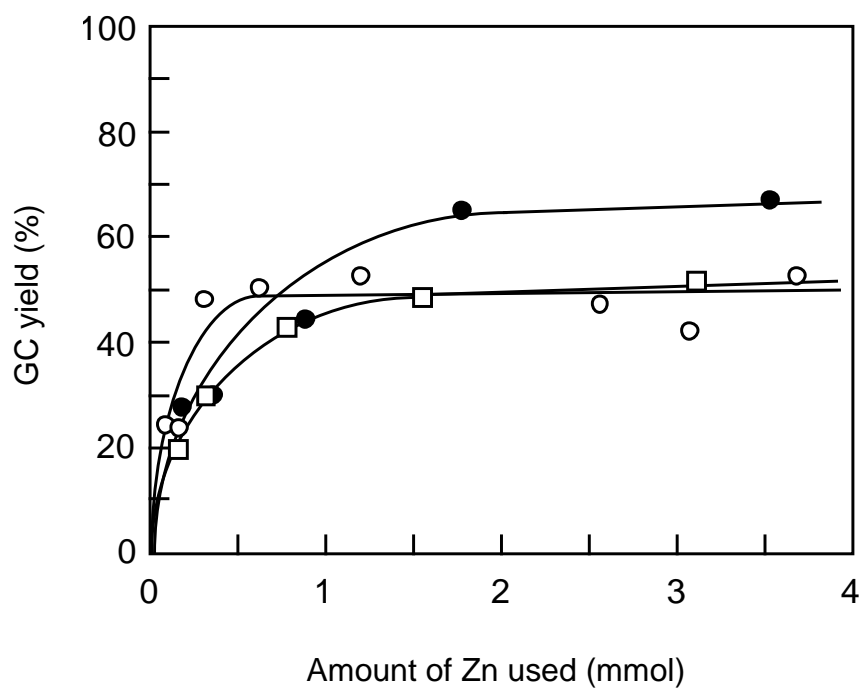


Fig. 2 The yield of glycerol carbonate as a function of the amount of Zn included in the catalyst used. (○) ZnO, (□) SM(Zn), and (●) HT(Zn).

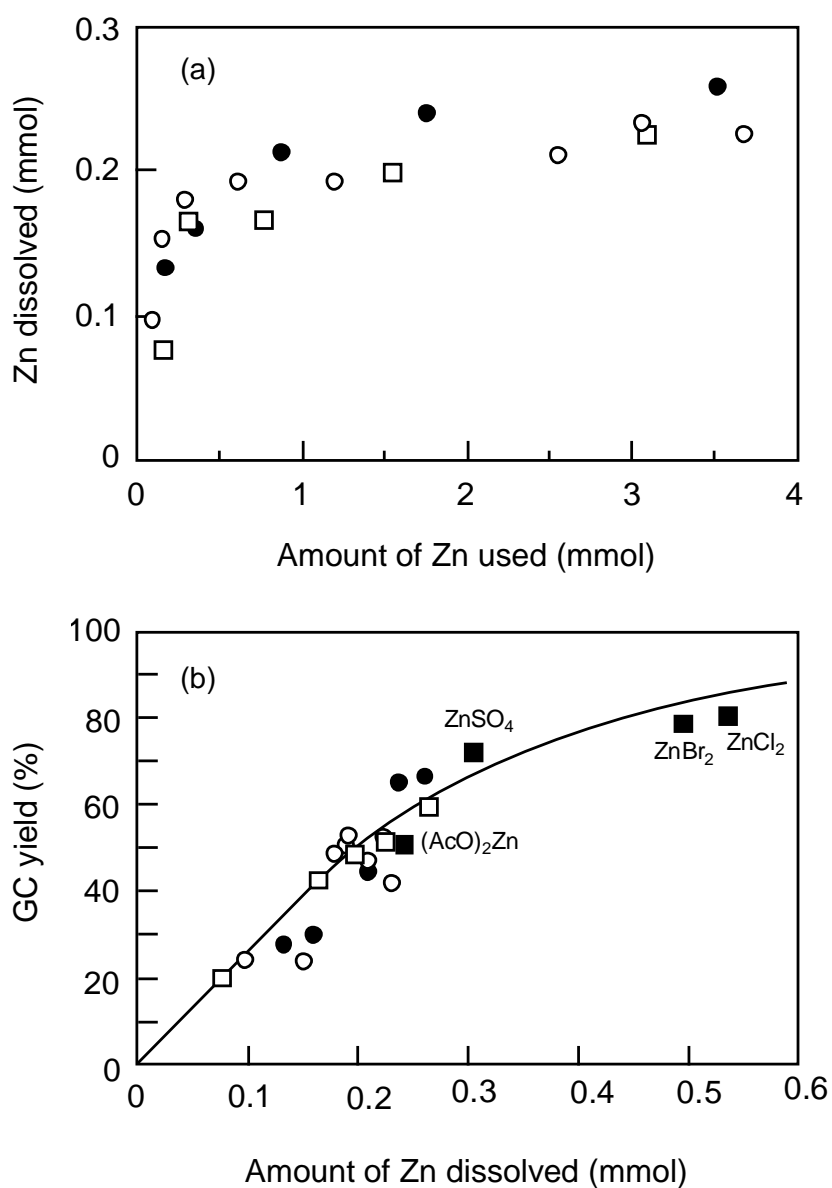


Fig. 3. (a) Relationship between the amount of Zn species dissolved and the initial amount of Zn included in the parent catalysts. (b) Relationship between the yield of glycerol carbonate (GC) and the amount of Zn species dissolved in the liquid phase. (○) ZnO, (□) SM(Zn), (●) HT(Zn) and (■) zinc salts.

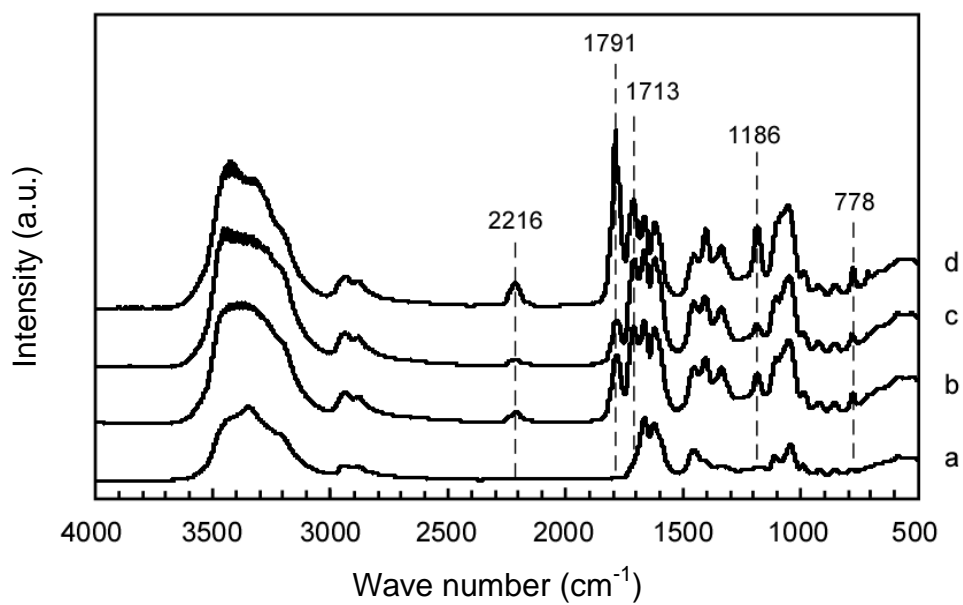


Fig. 4. FTIR spectra collected in the presence and absence of Zn-containing solid catalysts. (a) glycerol + urea, (b) glycerol + urea + ZnO, (c) glycerol + urea + SM(Zn), and (d) glycerol + urea + HT(Zn).

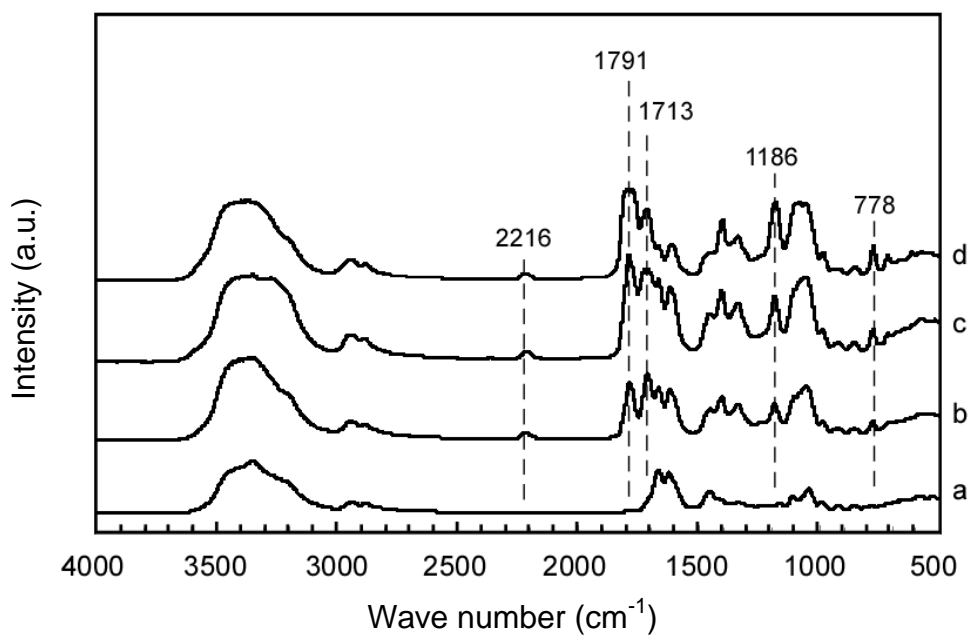
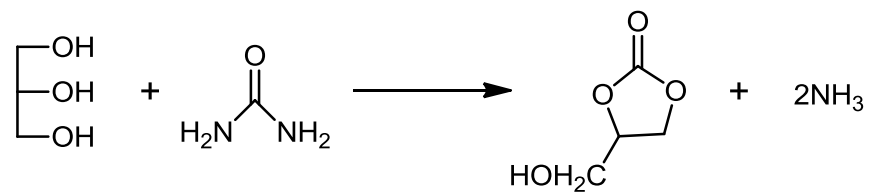
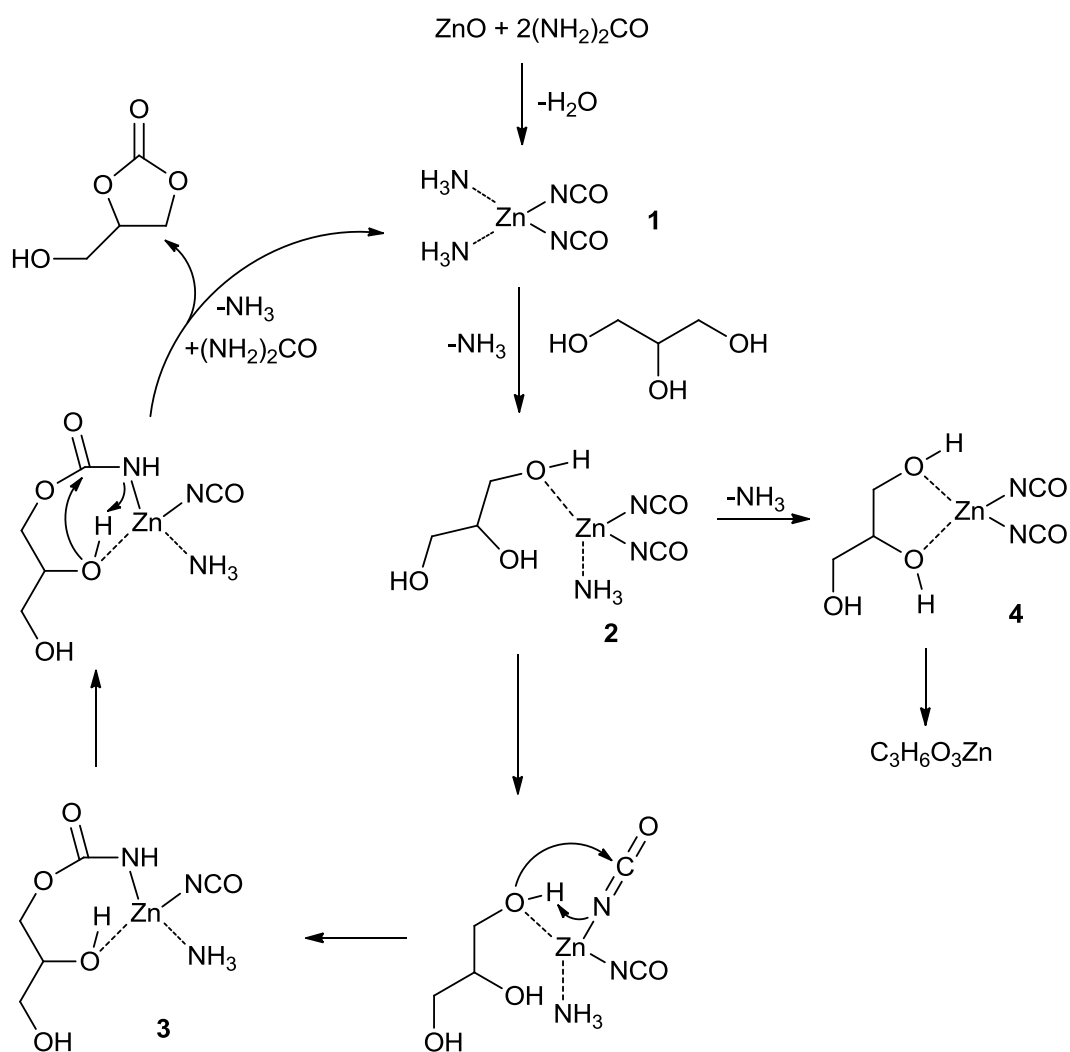


Fig. 5. FTIR spectra collected in the presence and absence of Zn-containing homogeneous catalysts. (a) glycerol + urea, (b) glycerol + urea + ZnCl₂, (c) glycerol + urea + (CH₃COO)₂Zn, and (d) glycerol + urea + ZnSO₄.



Scheme 1 Synthesis of glycerol carbonate from glycerol and urea



Scheme 2 Possible reaction mechanisms proposed for the synthesis of glycerol carbonate from glycerol and urea with Zn-containing catalyst