Catalysis Today xxx (xxxx) xxx-xxx



Contents lists available at ScienceDirect

Catalysis Today



journal homepage: www.elsevier.com/locate/cattod

Investigation of glycerolysis of urea over various ZnMeO (Me = Co, Cr, and Fe) mixed oxide catalysts

Huy Nguyen-Phu, Lien Thi Do, Eun Woo Shin*

School of Chemical Engineering, University of Ulsan, 93 Daehak-ro, Nam-gu, Ulsan 44610, South Korea

ARTICLE INFO	A B S T R A C T					
Keywords: Glycerolysis Zn-rich mixed oxide Zn-poor mixed oxide Zn NCO complex Glycerol carbonate	In this study, we investigated the glycerolysis of urea over various ZnMeO (Me = Co, Cr, and Fe) mixed oxide catalysts. ZnMeO mixed oxide catalysts were prepared by a co-precipitation method for two Zn/Me ratios, resulting in Zn-rich mixed oxide (Zn2MeO) and Zn-poor mixed oxide (ZnMe2O). In the glycerolysis of urea, the Zn2MeO catalysts exhibited higher glycerol conversion and glycerol carbonate yields than the ZnMe2O catalysts due to the predominance of homogeneous catalysis through Zn isocyanate (NCO) complexes from the Zn2MeO catalysts. Specifically, Zn2CrO was the best catalyst, with the highest yield of glycerol carbonate. Fourier transform infrared (FT-IR) and thermogravimetric analysis (TGA) results of the spent catalysts clearly demonstrated the dominant formation of a solid Zn NCO complex over the spent Zn2CrO catalyst, a unique feature indicating that the better catalytic performance of Zn2CrO was due to the additional heterogeneous reaction route through the solid Zn NCO complex.					

1. Introduction

Because glycerol is a by-product of the biodiesel and biofuel manufacturing industry which is considered as a solution for renewable fuel, the crude glycerol production capacity has rapidly increased in recent years [1]. The synthesis of glycerol carbonate (GC) has attracted great attention as a useful route for chemically converting glycerol into value-added products [2]. Among the various reaction pathways for producing GC, the glycerolysis of urea (Scheme 1) is favorable because urea is inexpensive, easily available, and recyclable from the reaction of NH₃ and CO₂ [3–13].

Various Zn-based mixed oxide catalysts have been used for the glycerolysis of urea [4–7,10,13,14]. Zn-based mixed oxide catalysts follow a dual catalytic mechanism: a homogeneous reaction route through dissolved Zn species and a heterogeneous reaction route over solid active sites. In previous studies, it was found that ZnAl mixed oxide catalysts exhibited better catalytic performance through the dual mechanism than the ZnO catalyst. The catalytic performance is related to not only the formation of Zn-containing intermediates during the reaction but also the disordered structure of the ZnAl₂O₄ spinel lattice in ZnAl mixed oxide catalysts [5,10,14]. Zn-containing intermediates are produced through Zn species dissolved from ZnAl mixed oxide catalysts, following the homogeneous reaction route in the liquid phase. The homogeneous reactivity is directly related to the amount of Zn

species dissolved in the liquid phase from ZnAl mixed oxide catalysts. Moreover, the disordered $ZnAl_2O_4$ spinel structure influences the catalytic performance *via* the surface acidity of the catalysts and the formation of a Zn-containing complex in the solid phase.

However, the investigation of dual catalysis over Zn-based mixed oxide catalysts has not been extended to Zn-based mixed oxide catalysts containing other metal components that are also favorable to the preparation of Zn-based mixed oxide catalysts [12,15–18]. In this study, we investigate the glycerolysis of urea over various ZnMeO (Me = Co, Cr, and Fe) mixed oxide catalysts with two Zn/Me ratios: a high Zn ratio (Zn2MeO) and a low Zn ratio (ZnMe2O). The Zn-rich mixed oxide catalysts (Zn2MeO) are expected to generate more Zn-containing intermediates in the liquid phase and follow both homogeneous and heterogeneous reaction routes; in contrast, the Zn-poor mixed oxide catalysts (ZnMe2O) are expected to form a spinel lattice structure with a lower level of dissolved Zn species in the liquid phase and follow a heterogeneous reaction route.

2. Experimental

2.1. Catalyst preparation

The catalysts used in this study were prepared by a co-precipitation method from metal nitrate salts $[Zn(NO_3)_2 GH_2O, Cr(NO_3)_3 GH_2O, Co$

* Corresponding author.

E-mail address: ewshin@ulsan.ac.kr (E.W. Shin).

https://doi.org/10.1016/j.cattod.2019.09.017

Received 29 June 2019; Received in revised form 30 August 2019; Accepted 11 September 2019 0920-5861/ © 2019 Elsevier B.V. All rights reserved.



Scheme 1. Glycerolysis of urea to produce GC and NH₃.

 $(NO_3)_2$ ·6H₂O, and Fe(NO₃)₃·9H₂O] [17,19,20]. All chemicals were obtained from Sigma–Aldrich Korea (Gyounggi, South Korea). Typically, an aqueous solution of Zn(NO₃)₂·6H₂O and nitrate salt of Me (Cr, Co, or Fe) with a molar ratio of 1:2 for the ZnMe2O catalysts or 2:1 for the Zn2MeO catalysts was gradually mixed with a basic solution of ammonia under constant pH and vigorous stirring. For the preparation of Zn2CoO and ZnCo2O, a hydrogen peroxide solution (H₂O₂) was continually added to the mixture to oxidize Co²⁺ to Co³⁺. After complete mixing, the suspension was filtered, and the remaining precipitate was washed with deionized water several times. Finally, the solid powder was dried at 100 °C overnight and calcined at 600 °C for 6 h.

2.2. Reaction tests

Here, 0.2 mol of glycerol was added to a 100-ml round-bottom reactor at 80 °C under stirring by a magnetic bar. The reactor was connected to a vacuum pump through an HNO_3 solution trap (to remove NH_3) and a cold trap (to protect the vacuum pump). Then, 0.2 mol of urea was added to the reactor to mix with the glycerol in the solution. When the dissolution was complete, the catalyst (5 wt% of the glycerol mass) was added to the reactor. Reaction tests were carried out under vacuum pressure (3 kPa) at 140 °C with constant stirring.

After the reaction tests, ethanol was added to the final products, and the liquid products were separated from the spent catalyst by filtration. The liquid products were quantitatively analyzed using a gas chromatography apparatus (Acme 6100 GC, YL Instrument Co., Ltd., Dongangu, Anyang, South Korea) with a flame ionization detector and a capillary column [DB-Wax ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ µm}$)]. The molar amount of each component was calculated using an internal standard method, with tetraethylene glycol as the internal standard chemical. The glycerol conversion, GC selectivity, GC yield, and by-product selectivity were calculated using the equations below.

Glycerol conversion (%)

$$= \frac{\text{Initial amount of glycerol-Residual amount of glycerol}}{\text{Initial amount of glycerol}} \times 100$$

$$\text{GC yield (\%)} = \frac{\text{Amount of GC}}{\text{Initial amount of glycerol}} \times 100$$

$$\text{GC selectivity (\%)} = \frac{\text{GC yield (\%)}}{\text{Glycerol conversion (\%)}} \times 100$$

$$\text{Byproduct (except ZnGly) selectivity (\%)}$$

$$= \frac{\text{Amount of byproduct}}{\text{Initial amount of glycerol-Residual amount of glycerol}} \times 100$$

Fourier transform infrared (FTIR) spectra of the liquid products were obtained using a Thermo Scientific[™] Nicolet[™] iS[™]5 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The levels of metal atoms (Zn, Co, Cr, and Fe) in the liquid phase were measured using an Agilent Technologies 5110 inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent, Santa Clara, CA, USA).

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns for fresh and spent catalysts were obtained using a Rigaku RAD-3C diffractometer (Rigaku Corp., Tokyo, Japan) with Cu Ka radiation ($\lambda = 1.5418$ Å) at a scattering angle (2 θ) scan rate of 2°/min, operating at 35 kV and 20 mA. The spent catalysts were analyzed by using a Thermo Scientific Nicolet iS5 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The numbers of acidic and basic sites were measured based on the temperature-programmed desorption of NH₃ and CO₂ (TPD- NH₃/CO₂) on a MicrotracBEL BELCAT-M instrument (MicrotracBEL Corp., Osaka, Japan). TPD- NH₃/CO₂ results were recorded for the temperature range of 50–600 °C by a TCD detector. The detailed procedure for the TPD analysis has been described elsewhere [5]. Thermogravimetric analysis (TGA) of the spent catalysts was measured by a TGA Q50 apparatus (TA Instruments, New Castle, DE, USA).

3. Results and discussion

3.1. Catalyst characterization: ZnO phase and ZnMe₂O₄ spinel phase

Fig. 1 shows XRD patterns of the fresh catalysts. The Zn-rich catalysts (Zn2MeO) are composed of two primary phases (ZnO and the corresponding spinel ZnMe₂O₄ phase) while only the spinel ZnMe₂O₄ phase was detected in the Zn-poor catalysts (ZnMe2O). These crystalline phases can be readily identified in the XRD patterns of the fresh catalysts (Fig. 1A). Typical XRD peaks for the ZnO phase with the P63mc space group (JCPDS No. 36-1451) are observed at 31.8°, 34.4°, 36.3°, 47.5°, 56.7°, and 62.9° in the XRD patterns of the Zn2CoO, Zn2FeO, and Zn2CrO catalysts [14]. The spinel ZnCo₂O₄ phase is detected in the XRD patterns of the Zn2CoO and ZnCo2O catalysts, with characteristic XRD peaks at 19.0°, 31.2°, 36.8°, 44.7°, 55.6°, 59.3°, and 65.1° (JCPDS No. 23-1390, Fd3m space group) [21]. Similarly, the XRD patterns of the Zn2FeO and ZnFe2O catalysts exhibit the spinel ZnFe2O4 phase, with typical peaks at 18.2°, 29.9°, 35.2°, 42.8°, 53.1°, 56.6°, and 62.2° (JCPDS No. 82-1049, Fd3m space group) [22]. Characteristic XRD peaks for the spinel ZnCr₂O₄ phase (JCPDS No. 22-1107, Fd3m space group) appear at 18.8°, 30.3°, 35.7°, 43.4°, 53.9°, 57.6°, and 63.1° in the XRD patterns of the Zn2CrO and ZnCr2O catalysts [23]. The lattice structure of all the ZnMe₂O₄ phases belongs to the spinel group. Typically, in a normal spinel $ZnMe_2O_4$ lattice, the Zn^{2+} cations occupy the tetrahedral sites and Me³⁺ cations occupy the octahedral sites. An disordered property in the spinel structure can generate a partially inversed spinel structure where some Zn^{2+} cations occupy the octahedral sites and some Me^{3+} cations occupy the tetrahedral sites [24,25].

The XRD peaks corresponding to the (311) plane of the spinel $ZnMe_2O_4$ phases are enlarged in Figs. 1.B–D to compare the lattice spacing between the Zn-rich Zn2MeO and Zn-poor ZnMe2O catalysts. For the Zn2MeO catalysts, the position of the characteristic XRD peak for the (311) plane is shifted to a lower 20 value with respect to the positions for the ZnMe2O catalysts, indicating that the lattice spacing of Zn2MeO is greater than that of ZnMe2O. This peak position shift for the Zn-rich Zn2MeO catalysts is caused by the interaction between the ZnO and spinel ZnMe₂O₄ phases in the Zn-rich mixed oxide of Zn/Me (Zn2MeO catalysts in this study), where the excess Zn (of ZnO phase)



Fig. 1. A) XRD patterns of fresh catalysts. a) Zn2CoO, b) Zn2FeO, c) Zn2CrO, d) ZnCo2O, e) ZnFe2O, and f) ZnCr2O. B, C, D) Enlarged XRD regions of the (311) peak (spinel phase ZnMe₂O₄) for the Zn-rich Zn2MeO catalyst and corresponding Zn-poor ZnMe2O catalyst.

can generate a layer of amorphous ZnO on the surface of the spinel ZnMe₂O₄ phase. The excess Zn cations in the ZnO phase can migrate into the lattice of the spinel phase to produce a non-stoichiometric spinel phase (Zn/Me ratio > 0.5), implying more Zn amount in the spinel structure [5,17,26]. In detail, the excessive Zn^{2+} cations can replace the Me³⁺ cations in the octahedral sites of the spinel lattice structure. The Zn migration and substitution cause a distortion in the spinel lattice structure, with consequent changes in the interplanar lattice spacing of the spinel phase due to the different cation radii. For the octahedral sites, the cation radii of the metal cations can be estimated as 88 pm for Zn^{2+} , 68.5 pm for Co^{3+} , 78.5 pm for Fe^{3+} , and 75.5 pm for Cr^{3+} [27]. The radius of the Zn^{2+} cation is much larger than the radii of the other Me³⁺ cations. Therefore, the migration of Zn^{2+} to the octahedral sites of the spinel $ZnMe_2O_4$ lattice structure can expand the lattice spacing of the spinel structure, with a shift in the corresponding XRD peak position to a lower value [17,26,28]. In summary, the XRD peak shift of the (311) plane indicates an interaction between the ZnO and ZnMe₂O₄ phases in the Zn-rich Zn2MeO catalysts.

FTIR spectra of the fresh catalysts are displayed in Fig. 2. Two vibration bands (ν_1 , and ν_2) of MO– bonds, related to the metal cations at



Fig. 2. FTIR spectra of fresh catalysts: a) Zn2CoO, b) ZnCo2O, c) Zn2FeO, d) ZnFe2O, e) Zn2CrO, and f) ZnCr2O.

the octahedral sites of the spinel ZnMe₂O₄ lattice, are observed in the FTIR spectra of both Zn2MeO and ZnMe2O in the range of 552–690 cm⁻¹ (ν_1) and 425–582 cm⁻¹ (ν_2) [15,29]. Because the majority of the octahedral sites in a normal spinel lattice structure are occupied by trivalent Me³⁺ cations [24], the positions of ν_1 and ν_2 may change depending on the nature of Me³⁺ cations. For the Zn2CoO and ZnCoO2 catalysts (Figs. 2a and b), the ν_1 and ν_2 modes of the spinel $ZnCo_2O_4$ lattice are found at 676 and 590 cm⁻¹, respectively. For the Zn2CrO and ZnCr2O catalysts, two bands of the spinel ZnCr₂O₄ lattice appear at 623 and 505 cm^{-1} (Figs. 2e and f). However, due to the limitation of our FTIR instrument for measurements below 400 cm⁻¹. the FTIR spectra of the Zn2FeO and ZnFe2O catalysts only show the full band of ν_1 vibration of the spinel ZnFe₂O₄ lattice at 544 cm⁻¹ (Figs. 2c and d). Beside the vibration modes ν_1 and ν_2 of the spinel phase, vibration of the ZnO lattice is detected at 434 cm⁻¹ in the FTIR spectra of all of the Zn-rich catalysts (Zn2MeO) [30], providing further evidence for the occurrence of the ZnO phase in these fresh catalysts. Therefore, the FTIR results are consistent with the XRD data. The Zn-poor ZnMe2O catalysts are composed of the pure spinel ZnMe₂O₄ phase, whereas both the ZnMe₂O₄ and ZnO phases are dominant in the Zn-rich Zn2MeO catalysts

To investigate the chemisorption properties (acidity and basicity) of these fresh catalysts, we determined the number of surface acidic sites and surface basic sites using the TPD- NH₃ and TPD – CO₂ methods, respectively. TPD- NH₃ and TPD – CO₂ profiles of the catalysts are plotted in Figs. S1 and S2 (see Supplementary Data), and the total numbers of acidic and basic sites are summarized in Table 1. Among the Zn-rich Zn2MeO catalysts, Zn2CrO has the greatest number of both acidic sites (0.186 mmol/g) and basic sites (0.157 mmol/g), and the numbers of acidic and basic sites follow the same trend: Zn2CrO > Zn2FeO. For the Zn-poor ZnMe2O catalysts, the numbers

Table 1							
Acidity and basicity of fresh catalysts.							

Sample Acidic Sites (mmol NH ₃ /g		at.) Basic Sites (mmol CO ₂ /g _{cat})				
Zn2CoO	0.144	0.113				
Zn2FeO	0.081	0.066				
Zn2CrO	0.186	0.157				
ZnCo2O	0.202	0.082				
ZnFe2O	0.225	0.084				
ZnCr2O	0.259	0.140				

H. Nguyen-Phu, et al.

Table 2

Analysis of liquid products obtained from the glycerolysis of urea over various ZnMe (Me = Co, Cr, and Fe) mixed oxide catalysts at various reaction times. (Reaction temperature = 140 °C, reaction pressure = 3 kPa, glycerol/urea ratio = 1:1). (2): 2,3-dihydroxypropyl carbamate, (4): 4-(hydroxymethyl)oxazolidin-2-one, and (5): (2-oxo-1,3-dioxolan-4-yl)methyl carbamate.

Sample	Reaction time (h)	Glycerol conv. (%)	GC yield (%)	Selectivity (%)			Metallic content in liquid phase (mmol) ^a				
				GC	(2)	(4)	(5)	Со	Fe	Cr	Zn
Zn2CoO	1	50	34	67	24	7	2	-	_	-	1.50
	3	74	52	71	9	7	14	-	-	-	0.66
Zn2FeO	1	57	41	72	17	10	1	-	-	-	1.43
	3	74	52	70	7	15	8	-	-	-	0.75
Zn2CrO	1	50	38	75	16	7	1	-	-	0.02	2.07
	3	76	57	74	5	13	8	-	-	-	0.99
ZnCo2O	3	50	29	57	28	10	4	0.09	-	-	0.38
	5	63	40	63	17	6	13	0.13	-	-	0.41
ZnFe2O	3	34	18	53	32	11	4	-	-	-	-
	5	47	27	57	20	8	15	-	-	-	-
ZnCr2O	3	37	21	56	32	7	4	-	-	0.02	-
	5	53	33	62	21	4	13	_	_	0.03	_

^a Amounts of metals dissolved in the liquid phase as measured by the ICP-OES method.

of both acidic and basic sites follow the order of ZnCr2O > ZnFe2O > ZnCo2O, and the highest values (acidic site amount = 0.259 mmol/g, and basic site amount = 0.140 mmol/g) are observed for ZnCr2O. In the literature, high amounts of acidic and basic sites in ZnO/ZnAl₂O₄ mixed oxides are attributed to the disordered structure of a partially inversed spinel lattice prepared by the polystyrene-template method [10,14] or citrate complex method [5]. In this study, all catalysts were prepared by the co-precipitation method, where the structure of the prepared spinel phase is less disordered. As a result, the amounts of acidic and basic sites are lower than those of catalysts prepared by other methods. The TPD profiles were deconvoluted to check the relative distributions of acidic sites and basic sites for each catalyst (Figs. S1 and S2, see the Supplementary Data). The strength of deconvoluted acidic and basic sites can be classified as follows: weak strength sites (< 300 °C), medium strength sites (300–550 °C) and strong strength sites (> 550 °C) [31–33]. The distributions of individual acidic and basic sites on each fresh catalyst are summarized in Table S1 (see the Supplementary Data).

3.2. Glycerolysis of urea over various ZnMeO catalysts: the formation of Zn isocyanate complex in the liquid phase and on the solid catalysts

The reaction results for the glycerolysis of urea over various ZnMe mixed oxide catalysts are summarized in Table 2. The Zn-rich Zn2MeO catalysts were tested at reaction times of 1 and 3 h while the Zn-poor ZnMe2O catalysts were investigated at longer reaction times (3 and 5 h) since the ZnMe2O catalysts exhibit lower catalytic reaction rates than the Zn2MeO catalysts. The relationship between the glycerol conversion and GC yield for each catalyst is depicted in Fig. 3. Clearly, the data for the Zn2MeO catalysts correspond to higher positions with a higher glycerol conversion compared to the results for the ZnMe2O catalysts. In Fig. 3, data points at a higher position indicate that a higher GC yield or selectivity can be achieved at a given glycerol conversion. For all of the Zn2MeO catalysts, the highest glycerol conversion and GC yield (glycerol conversion = 76%, GC yield = 57%) was observed for Zn2CrO at a reaction time of 3 h; meanwhile, the results for the Zn2CoO and Zn2FeO catalysts are similar, with glycerol conversion = 74% and GC yield = 52% at a reaction time of 3 h. Among the ZnMe2O catalysts, the glycerol conversion and GC yield follow the order of ZnFe2O < ZnCr2O < ZnCo2O; the best reaction performance was observed for the ZnCr2O catalyst at a reaction time of 5 h, with glycerol conversion = 63% and GC yield = 40%.

According to Fujita et al. [13] and Turney et al. [9], in the glycerolysis of urea over Zn-containing catalysts, Zn atoms can leach from the ZnO phase into the liquid phase through a reaction with urea to



Fig. 3. Relationship between glycerol conversion (%) and GC yield (%) in the glycerolysis of urea over various ZnMe (Me = Co, Cr, and Fe) mixed oxide catalysts.

generate an isocyanate (NCO) complex of Zn, which is an active site for the reaction. This phenomenon was also confirmed in our previous studies [5,10,14]. Furthermore, we found that the NCO complexes adsorbed on the surface acidic sites of the catalyst (ZnAl₂O₄ phase) act as additional active sites to catalyze the reaction. For this reason, we measured the metal cation levels using an ICP-OES instrument (Table 2) and collected FTIR spectra of both the liquid products (Fig. 4) and the spent catalysts (Fig. 5) to identify the existence of an NCO functional vibration.

The ICP results in Table 2 show that Zn atoms are detected in the liquid products for all of the Zn-rich Zn2MeO catalysts. After a reaction time of 1 h, high levels of Zn are detected: 2.07 mmol for Zn2CrO, 1.50 mmol for Zn2CoO, and 1.43 mmol for Zn2FeO. After a reaction time of 3 h, the level of Zn in the liquid phase for the Zn-rich Zn2MeO catalysts is lower, resulting from the formation of zinc glycerolate. However, no Fe or Co atoms are detected in the liquid phases of the Zn2CoO or Zn2FeO catalysts. Moreover, a negligible amount of Cr (0.02 mmol) is observed in the liquid product of the Zn2CrO catalyst after a reaction time of 1 h. The level of Cr in the liquid is 100-fold times smaller than the corresponding level of Zn (2.07 mmol) in the liquid and falls to zero after a reaction time of 3 h. The FTIR spectra of the liquid products obtained from the Zn2MeO catalysts (Fig. 4A) are in good agreement with the ICP results. The peak at 2210 cm⁻¹ can be



Fig. 4. FTIR spectra of liquid products obtained from the glycerolysis of urea over different catalysts at various reaction times. A): a) Zn2CoO-1 h, b) Zn2CoO-3 h, c) Zn2FeO-1 h, d) Zn2FeO-3 h, e) Zn2CrO-1 h, and f) Zn2CrO-3 h. B): a) ZnCo2O-3 h, b) ZnCo2O-5 h, c) ZnFe2O-3 h, d) ZnFe2O-5 h, e) ZnCr2O-3 h, and f) ZnCr2O-5 h.

assigned to the NCO vibration [13,34]. The intensities of the NCO peaks in Fig. 4A follow the same trend as the amount of Zn in the liquid products for the Zn2MeO catalysts. A peak at 2210 cm^{-1} is clearly present in the FTIR spectra after a reaction time of 1 h and almost disappears after a reaction time of 3 h. Therefore, we can conclude that for the Zn2MeO catalysts, the Zn NCO complex exists in the liquid phase for at least 1 h of reaction time.

Fig. 5A displays the FTIR spectra of the spent Zn2MeO catalysts. All of the typical FTIR peaks of M–O bonding in the spinel ZnMe₂O₄ lattice are detected in the range of $400-680 \text{ cm}^{-1}$. However, the typical peak of Zn-O bonding in the ZnO lattice almost disappears due to the Zn dissolution. Additionally, characteristic peaks for zinc glycerolate appear at 1950 cm⁻¹ (C–O stretching modes with oxygen in hydrogen bonding), 655 cm^{-1} , and 514 cm^{-1} (Zn-O stretching mode) [35], confirming the formation of zinc glycerolate. Interestingly, the vibration peak of an NCO functional group is detected only in the FTIR spectrum of the spent ZnCr2O catalyst at 2220 cm⁻¹, which is assigned to the NCO complex adsorbed on the solid surface. These results are consistent with our previous reports on the reaction over ZnO/ZnAl₂O₄ mixed oxides [5,10,14]. Zn atoms from the ZnO phase can dissolve and react with urea to produce a Zn NCO complex in the liquid phase, providing an active site for a homogeneous reaction route in the glycerolysis of urea. Furthermore, the Zn NCO complex can be adsorbed on



Fig. 5. FTIR spectra of spent catalysts. A): a) Zn2CoO-1 h-spent, b) Zn2CoO-3 h-spent, c) Zn2FeO-1 h-spent, d) Zn2FeO-3 h-spent, e) Zn2CrO-1 h-spent, and f) Zn2CrO-3 h-spent. B): a) ZnCo2O-3 h-spent, b) ZnCo2O-5 h-spent, c) ZnFe2O-3 h-spent, d) ZnFe2O-5 h-spent, e) ZnCr2O-3 h-spent, and f) ZnCr2O-5 h-spent.

the surface acidic sites of the catalyst to form a Zn NCO complex on the surface, which generates another heterogeneous reaction route for the glycerolysis of urea. This interpretation explains the reaction behavior of the Zn-rich Zn2MeO catalysts (ZnO/ZnMe₂O₄ mixed oxide). The existence of a Zn NCO complex in the liquid phase for all Zn2MeO catalysts leads to a homogeneous reaction occurs only over Zn2CrO *via* the formation of the Zn NCO complex on the solid because the acidity of Zn2CrO is higher than that of the other Zn2MeO catalysts (Table 1), and a high surface acidity is necessary for adsorption of the Zn NCO complex on the catalyst surface.

The FTIR spectra of the liquid products from the Zn-poor catalysts (ZnMe2O) are displayed in Fig. 4B. A vibration band for the NCO functional group at 2210 cm⁻¹ is detected only for the ZnCo2O catalyst after reaction times of 3 and 5 h. Meanwhile, there is no evidence of an NCO functional group in the FTIR spectra of the liquid products from the ZnFe2O and ZnCr2O catalysts. The ICP results in Table 2 reveal an interesting appearance of both Zn and Co atoms in the liquid phase of ZnCo2O. While the Zn level in the liquid phase of the Zn2MeO catalysts decreases for longer reaction times, the levels of Zn and Co in the liquid phase of the ZnCo2O catalyst increase slightly with increasing reaction time. In detail, after a reaction time of 3 h, the levels of Zn and Co in the liquid phase of ZnCo2O are 0.09 and 0.38 mmol, respectively, and increase to 0.13 and 0.41 mmol for a 5 h reaction time, respectively. In

H. Nguyen-Phu, et al.

the liquid phase of the ZnFe2O catalyst, there is no evidence of Zn or Fe atoms in the ICP measurements. For the ZnCr2O catalyst, only a trace level of Cr atoms is measured in the liquid phase (0.02 mmol at 3 h and $0.03 \,\mathrm{mmol}$ at 5 h).

Based on the ICP and FTIR results for the liquid products, the ZnFe2O catalyst does not induce the generation of an NCO complex in the liquid phase. In contrast, for the ZnCo2O catalyst, both NCO functional groups and Zn/Co atoms are present in the liquid phase, implying NCO complexes of Co and Zn in the liquid phase. In previous works, NCO complexes of Co²⁺ and Co³⁺ have been reported as intermediates of the reduction reaction [36,37] or glycerolysis reaction [9]. Herein, the Co NCO complex can form in the liquid phase in the case of the ZnCo2O catalyst but not in the case of the Zn2CoO catalyst because no Co atoms are found in the liquid phase of the Zn2CoO catalyst due to the difference in the structures of ZnCo2O and Zn2CoO. As previously mentioned, the ZnCo2O catalyst is composed of a pure normal spinel phase of ZnCo₂O₄ with a predominance of Co³⁺ cations on the outset surface layer. According to the model by Wachs and Routray [38], other layers of Co^{3+} and Zn^{2+} cations can be found below the outset surface layer. In the reaction process over ZnCo2O, the outer layer of Co³⁺ cations can react with urea and dissolve to the liquid phase, resulting in the further dissolution of Co^{3+} and Zn^{2+} cations in the lower layers. This process renders the ZnCo2O catalyst unstable and causes Zn (or Co) NCO complex to appear in the liquid phase. In contrast, the structure of the Zn2CoO catalyst includes an amorphous layer of ZnO above the spinel phase of ZnCo₂O₄, which can prevent the Co³⁺ cations from leaching into the liquid phase.

The FTIR spectra of the spent Zn-poor ZnMe2O catalysts are displayed in Fig. 5B. For all three catalysts, the typical vibration peaks of M–O bonding in the spinel ZnMe₂O₄ are unaltered compared to those of the fresh catalysts (even for spent ZnCo2O, where Zn^{2+} and Co^{3+} cations are dissolved in the liquid phase). However, in the FTIR spectra of spent Zn2CoO, a small additional vibration band for the NCO functional group is observed at 2192 cm⁻¹, which is redshifted in comparison to the vibration for the spent Zn2MeO catalysts (2220 cm^{-1}). Turney et al. [9] found that the FTIR vibration of NCO functional groups related to the Co NCO complex occurred at a lower position compared to that of the NCO functional group related to the Zn NCO complex. Because the NCO functional group of the spent ZnCo2O catalyst is related to the NCO complexes of both Zn and Co, its vibrational wavenumber is lower than that of Zn2MeO (NCO functional group of only the Zn NCO complex). In the FTIR spectrum of the spent ZnCr2O catalyst, a small additional vibration band for the NCO functional group appears at 2211 cm⁻¹, which may be associated with a Cr NCO complex. A reaction between Cr³⁺ and urea to generate an insoluble Cr NCO complex has been previously reported [39,40].

The XRD patterns of the spent catalysts after a reaction time of 3 h are displayed in Fig. 6. For the spent Zn-rich Zn2MeO catalysts, the characteristic peaks for the ZnO phase almost disappear while the peaks for the spinel phase ZnMe₂O₄ remain unchanged. Moreover, typical peaks for the zinc glycerolate phase (JCPDS No. 23-1975, P21/c space group) are clearly detected in the XRD patterns of the spent Zn2MeO catalysts at 10.9°, 17.1°, 20.5°, 23.8°, 24.7°, 27.6°, 27.7°, 36.4°, and 38.2° [41]. Conversely, the XRD patterns of the spent Zn-poor ZnMe2O catalysts are almost identical to those of the fresh ZnMe2O catalysts; only typical peaks for the spinel phase ZnMe₂O₄ are detected, without any other phases. The XRD results of the spent catalysts are in good agreement with the FTIR results. That is, the ZnO phase of the Zn2MeO catalysts disappears with the additional formation of the zinc glycerolate phase after the reaction, whereas the spinel ZnMe₂O₄ phase of the ZnMe2O catalysts remains unchanged. For the spent ZnCo2O catalyst, metal glycerolate is not found due to the different oxidation states of the Co cations: Co³⁺ cations in the ZnMe₂O₄ lattice and Co NCO complex and Co^{2+} cations in cobalt glycerolate [42,43].



Catalysis Today xxx (xxxx) xxx-xxx



Fig. 6. XRD patterns of spent catalysts: a) Zn2CoO-3 h-spent, b) Zn2FeO-3 hspent, c) Zn2CrO-3 h-spent, d) ZnCo2O-3 h-spent, e) ZnFe2O-3 h-spent, and f) ZnCr2O-3 h-spent.

Based on the TGA analysis, DTGA profiles of the spent catalysts are plotted in Fig. S3 (see Supplementary Data). The DTGA results for the spent catalysts match the XRD and FTIR results. Decomposition peaks of zinc glycerolate are observed in the range of 350-400 °C for the spent Zn2MeO catalysts [44], and decomposition peaks of metal NCO complex in the range of 200-350 °C are detected for the spent Zn2CrO, ZnCr2O, and ZnCo2O catalysts [5].

3.3. Catalytic reaction routes through different NCO complexes

We can summarize the catalytic performance of the various ZnMe mixed oxide catalysts in the glycerolysis of urea in terms of the formation of the NCO complex. Different types of NCO complexes are detected in the liquid phase and on the solid surface of the catalysts, except for the ZnFe2O catalyst, for which no NCO complex is formed because no metal cations dissolve from the catalyst. In the reaction over the ZnCr2O catalyst, there is a small amount of Cr NCO complex on the solid phase. For the ZnCo2O catalyst, NCO complexes of Zn and Co are found in the liquid phase, with a low amount of complexes on the solid surface of the spent catalyst. In contrast, for all of the Zn-rich catalysts, a high level of Zn NCO complexes is clearly detected in the liquid phase for a reaction time of 1 h, indicating Zn dissolution from the ZnO phase in the Zn2FeO, Zn2CoO, and Zn2CrO catalysts. Interestingly, a higher level of Zn NCO complexes is observed on the solid surface only for the Zn2CrO catalyst, due to its higher surface acidity/basicity and the occurrence of ZnO phases.

Based on the reaction mechanism of urea glycerolysis, which has been described elsewhere [5,10,14], we illustrate three primary catalytic reaction routes $(r_1, r_2, and r_3)$ in Scheme 2.

i) r_1 is a heterogeneous reaction route *via* the adsorption of glycerol and urea on the surface acidic and basic sites of the catalysts [4]. This reaction is the slowest reaction route, resulting in the lowest catalytic performance.

adsorbed glycerol + adsorbed urea \rightarrow GC (r₁)

i) r₂ is a homogeneous reaction route via NCO complexes of Zn or Co in the liquid phase [5,13]. This homogenous reaction occurs more rapidly than r₁; however, the formation of zinc glycerolate as a byproduct from the reaction between the Zn NCO complex and

H. Nguyen-Phu, et al.

Catalysis Today xxx (xxxx) xxx-xxx



Scheme 2. Catalytic reaction routes for urea glycerolysis over various ZnMe (Me = Co, Cr, and Fe) mixed oxide catalysts.

glycerol in the liquid phase reduces the number of Zn NCO active sites and the GC selectivity.

Me NCO complex (liquid) + glycerol \rightarrow GC (r₂) Zn NCO complex (liquid) + glycerol \rightarrow zinc glycerolate

i) r_3 is another heterogeneous reaction route *via* NCO complexes adsorbed on the surface acidic sites of the catalysts [5,14]. This reaction route can enhance the catalytic reaction performance because there is no formation of zinc glycerolate.

Me NCO complex (solid) + glycerol \rightarrow GC (r₃)

The reaction performance of the catalysts can be evaluated on the basis of GC yields, which follow the order of ZnFe2O < ZnCr2O < ZnCo2O < Zn2FeO < Zn2CoO < Zn2CrO in this study. Depending on the NCO complex, different catalytic reaction routes occur for each catalyst. Scheme 2 presents the performance of the catalysts in terms of the catalytic reaction routes (r_1 , r_2 , and r_3) as follows:

- ZnFe2O (glycerol conversion = 34%, GC yield = 18%): r₁ route only.
- ZnCr2O (glycerol conversion = 37%, GC yield = 21%): r₁ (main route) + r_3 (minor route).
- ZnCo2O (glycerol conversion = 50%, GC yield = 28%): r_1 (main route) + r_2 + r_3 (minor route).
- Zn2FeO and Zn2CrO (glycerol conversion = 74%, GC yield = 52%): r_1 (minor route) + r_2 (main route).
- Zn2CrO (glycerol conversion = 76%, GC yield = 57%): r_1 (minor route) + r_2 (main route) + r_3 .

4. Conclusion

Various Zn-containing mixed oxide catalysts with different secondary metals (Me = Cr, Co, Fe) were successfully prepared by the coprecipitation method with two Zn/Me ratios, resulting in Zn-rich and Zn-poor catalysts. Depending on the Zn content and the nature of the metal ions, the structures of the Zn-containing phases differed, resulting in various types of NCO complexes in the liquid phase and on the solid surface. The formation of the NCO complex strongly influenced the catalytic route in urea glycerolysis. The Zn2CrO catalyst achieved the best catalytic reaction performance because of the high level of NCO complex in the liquid phase and the unique formation of the adsorbed NCO complex due to the high surface acidity.

Acknowledgments

This work was financially supported by the Research Fund of the University of Ulsan.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2019.09.017.

References

- C.A.G. Quispe, C.J.R. Coronado, J.A. Carvalho Jr., Glycerol: production, consumption, prices, characterization and new trends in combustion, Renewable Sustainable Energy Rev. 27 (2013) 475–493.
- [2] M.O. Sonnati, S. Amigoni, E.P. Taffin 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.
- [3] M. Aresta, A. Dibenedetto, F. Nocito, C. Ferragina, Valorization of bio-glycerol: new catalytic materials for the synthesis of glycerol carbonate via glycerolysis of urea, J. Catal. 268 (2009) 106–114.
- [4] M.J. Climent, A. Corma, P. De Frutos, S. Iborra, M. Noy, A. Velty, P. Concepción, Chemicals from biomass: synthesis of glycerol carbonate by transesterification and carbonylation with urea with hydrotalcite catalysts. The role of acid-base pairs, J. Catal. 269 (2010) 140–149.
- [5] H. Nguyen-Phu, E.W. Shin, Disordered structure of ZnAl₂O₄ phase and the formation of a Zn NCO complex in ZnAl mixed oxide catalysts for glycerol carbonylation with urea, J. Catal. 373 (2019) 147–160.
- [6] J.-H. Park, J.S. Choi, S.K. Woo, S.D. Lee, M. Cheong, H.S. Kim, H. Lee, Isolation and characterization of intermediate catalytic species in the Zn-catalyzed glycerolysis of urea, Appl. Catal. A Gen. 433–434 (2012) 35–40.
- [7] H. Nguyen-Phu, C. Park, E.W. Shin, Activated red mud-supported Zn/Al oxide catalysts for catalytic conversion of glycerol to glycerol carbonate: FTIR analysis, Catal. Commun. 85 (2016) 52–56.
- [8] C. Hammond, J.A. Lopez-Sanchez, M. Hasbi Ab, N. Rahim, R.L. Dimitratos, A.F. Jenkins, Q. Carley, C.J. He, D.W. Kiely, G.J. Knight, Hutchings, Synthesis of glycerol carbonate from glycerol and urea with gold-based catalysts, Dalton Trans. 40 (2011) 3927.
- [9] T.W. Turney, A. Patti, W. Gates, U. Shaheen, S. Kulasegaram, Formation of glycerol carbonate from glycerol and urea catalysed by metal monoglycerolates, Green Chem. 15 (2013) 1925.
- [10] H. Nguyen-Phu, C. Park, E.W. Shin, Dual catalysis over ZnAl mixed oxides in the

H. Nguyen-Phu, et al.

glycerolysis of urea: homogeneous and heterogeneous reaction routes, Appl. Catal. A Gen. 552 (2018) 1–10.

- [11] L. Wang, Y. Ma, Y. Wang, S. Liu, Y. Deng, Efficient synthesis of glycerol carbonate from glycerol and urea with lanthanum oxide as a solid base catalyst, Catal. Commun. 12 (2011) 1458–1462.
- [12] F. Rubio-Marcos, V. Calvino-Casilda, M.A. Bañares, J.F. Fernandez, Novel hierarchical Co₃O₄/ZnO mixtures by dry nanodispersion and their catalytic application in the carbonylation of glycerol, J. Catal. 275 (2010) 288–293.
- [13] S.I. Fujita, Y. Yamanishi, M. Arai, Synthesis of glycerol carbonate from glycerol and urea using zinc-containing solid catalysts: a homogeneous reaction, J. Catal. 297 (2013) 137–141.
- [14] H. Nguyen-Phu, E.W. Shin, Investigating time-dependent Zn species over Zn-based catalysts in glycerol carbonylation with urea and their roles in the reaction mechanism, Appl. Catal. A Gen. 561 (2018) 28–40.
- [15] G.N. Kustova, E.B. Burgina, G.G. Volkova, T.M. Yurieva, L.M. Plyasova, IR spectroscopic investigation of cation distribution in Zn–Co oxide catalysts with spinel type structure, J. Mol. Catal. A Chem. 158 (2000) 293–296.
- [16] D. Sibera, J. Kaszewski, D. Moszyński, E. Borowiak-Paleń, W. Łojkowski, U. Narkiewicz, ZnFe₂O₄/ZnO nanoparticles obtained by coprecipitation route, XPS and TEM study, Phys. Status Solidi 7 (2010) 1420–1423.
- [17] H. Song, D. Laudenschleger, J.J. Carey, H. Ruland, M. Nolan, M. Muhler, Spinelstructured ZnCr₂O₄ with excess Zn is the active ZnO/Cr₂O₃ catalyst for high-temperature methanol synthesis, ACS Catal. 7 (2017) 7610–7622.
- [18] S. Chen, Y. Wu, P. Cui, W. Chu, X. Chen, Z. Wu, Cation distribution in ZnCr₂O₄ nanocrystals investigated by X-ray absorption fine structure spectroscopy, J. Phys. Chem. C. 117 (2013) 25019–25025.
- [19] C. Xiangfeng, L. Xingqin, M. Guangyao, Preparation and gas sensitivity properties of ZnFe₂O₄ semiconductors, Sensors Actuators B Chem. 55 (1999) 19–22.
- [20] X. Song, Q. Ru, B. Zhang, S. Hu, B. An, Flake-by-flake ZnCo₂O₄ as a high capacity anode material for lithium-ion battery, J. Alloys. Compd. 585 (2014) 518–522.
- [21] Y. Sharma, N. Sharma, G.V. Subba Rao, B.V.R. Chowdari, Nanophase ZnCo₂O₄ as a high performance anode material for Li-Ion batteries, Adv. Funct. Mater. 17 (2007) 2855–2861.
- [22] F. Liu, X. Chu, Y. Dong, W. Zhang, W. Sun, L. Shen, Acetone gas sensors based on graphene-ZnFe₂O₄ composite prepared by solvothermal method, Sensors Actuators B Chem. 188 (2013) 469–474.
- [23] J.-H. Kim, H.-M. Jeong, C.W. Na, J.-W. Yoon, F. Abdel-Hady, A.A. Wazzan, J.-H. Lee, Highly selective and sensitive xylene sensors using Cr₂O₃-ZnCr₂O₄ heteronanostructures prepared by galvanic replacement, Sensors Actuators B Chem. 235 (2016) 498–506.
- [24] K.E. Sickafus, J.M. Wills, N.W. Grimes, Structure of spinel, J. Am. Ceram. Soc. 82 (2004) 3279–3292.
- [25] J.K. Burdett, G.D. Price, S.L. Price, Role of the crystal-field theory in determining the structures of spinels, J. Am. Chem. Soc. 104 (1982) 92–95.
- [26] D. Makovec, A. Kodre, I. Arčon, M. Drofenik, The structure of compositionally constrained zinc-ferrite spinel nanoparticles, J. Nanopart. Res. 13 (2011) 1781–1790.
- [27] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic

distances in halides and chalcogenides, Acta Crystallogr. Sect. A. 32 (1976) 751–767.

- [28] G. Del Piero, F. Trifiro, A. Vaccari, Non-stoicheiometric Zn–Cr spinel as active phase in the catalytic synthesis of methanol, J. Chem. Soc. Chem. Commun. 0 (1984) 656–658.
- [29] J. Preudhomme, P. Tarte, Infrared studies of spinels-III. The normal II-III spinels, Spectrochim, Acta Part A Mol. Spectrosc. 27 (1971) 1817–1835.
- [30] M. Samadi, H.A. Shivaee, M. Zanetti, A. Pourjavadi, A. Moshfegh, Visible light photocatalytic activity of novel MWCNT-doped ZnO electrospun nanofibers, J. Mol. Catal. A Chem. 359 (2012) 42–48.
- [31] Š. Hajduk, V.D.B.C. Dasireddy, B. Likozar, G. Dražić, Z.C. Orel, COx-free hydrogen production via decomposition of ammonia over Cu–Zn-based heterogeneous catalysts and their activity/stability, Appl. Catal. B Environ. 211 (2017) 57–67.
- [32] M. Chen, J. Xu, F.-Z. Su, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, Dehydrogenation of propane over spinel-type gallia–alumina solid solution catalysts, J. Catal. 256 (2008) 293–300.
- [33] J.C. Lavalley, Infrared spectrometric studies of the surface basicity of metal oxides and zeolites using adsorbed probe molecules, Catal. Today 27 (1996) 377–401.
- [34] W. Zhao, W. Peng, D. Wang, N. Zhao, J. Li, F. Xiao, W. Wei, Y. Sun, Zinc oxide as the precursor of homogenous catalyst for synthesis of dialkyl carbonate from urea and alcohols, Catal. Commun. 10 (2009) 655–658.
- [35] J. Das, D. Khushalani, Nonhydrolytic route for synthesis of ZnO and its use as a recyclable photocatalyst, J. Phys. Chem. C. 114 (2010) 2544–2550.
- [36] T. Sun, M.D. Fokema, J.Y. Ying, Mechanistic study of NO reduction with methane over Co²⁺ modified ZSM-5 catalysts, Catal. Today 33 (1997) 251–261.
- [37] T. Montanari, O. Marie, M. Daturi, G. Busca, Searching for the active sites of Co-H-MFI catalyst for the selective catalytic reduction of NO by methane: a FT-IR in situ and operando study, Appl. Catal. B Environ. 71 (2007) 216–222.
- [38] I.E. Wachs, K. Routray, Catalysis science of bulk mixed oxides, ACS Catal. 2 (2012) 1235–1246.
- [39] H. -H Schmidtke, T. Schönherr, Darstellung von Isocyanatopentamminchromat(III) mittels thermischer Zersetzung von Harnstoff, ZAAC -, J. Inorg. Gen. Chem. 443 (1978) 225–230.
- [40] T. Schönherr, The cyanate ion as bridging ligand: synthesis, spectroscopic characterization, and magnetic properties of (μ-Cyanato)bis(pentaamminechromium (III)) chloride, Inorg. Chem. 25 (1986) 171–175.
- [41] L. Pan, S. Wang, W. Mi, J. Song, J.-J. Zou, L. Wang, X. Zhang, Undoped ZnO abundant with metal vacancies, Nano Energy 9 (2014) 71–79.
- [43] E. Radoslovich, M. Raupach, P. Slade, R. Taylor, Crystalline cobalt, zinc, manganese, and iron alkoxides of glycerol, Aust. J. Chem. 23 (1970) 1963.
- [44] D.M. Reinoso, D.E. Damiani, G.M. Tonetto, Zinc glycerolate as a novel heterogeneous catalyst for the synthesis of fatty acid methyl esters, Appl. Catal. B Environ. 144 (2014) 308–316.