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Effect of Cu loading on the structure evolution and catalytic activity of the Cu^{239/C9NJ06085E} Mg/ZnO catalysts for dimethyl oxalate hydrogenation

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Abstract:

The influences of Cu loading on the structure evolution and catalytic behavior in dimethyl oxalate (DMO) selective hydrogenation of the Mg²⁺ doped nano-scaled Cu-Mg/ZnO catalysts have been investigated. It is found that the accessible Cu⁰ surface area and ZnO dispersion became increased gradually with the Cu loading increasing from 10.0 wt.% to 40.0 wt.%. And the Cu and ZnO NPs size distribution shows great effect on the chemical interaction between Cu and ZnO phase, further determining the surface chemical properties of catalysts. On the other hand, the catalytic behavior of the Cu-Mg/ZnO catalyst in DMO hydrogenation is closely related to the Cu loading introduced in the system. Most of all, the 30Cu-Mg/ZnO catalyst with 30 wt.% Cu loading exhibits 100.0 % DMO conversion and 98.0 % ethylene glycol (EG) yield even under LHSV = 3.5 h^{-1} , superior to that of the other catalysts. The excellent catalytic behavior should be attributed to the strengthened Cu-Zn synergistic effect and suppressed surface strong basic sites, originating from the enhanced Cu-ZnO interface area. Additionally, the correlation between catalytic activity and Cu species distribution suggests that the DMO dissociating on the Cu⁺ sites generated on the Cu-ZnO interface is the rate-determining step in presence of enough exposed Cu⁰ sites over the Cu-Mg/ZnO catalyst.

Keywords: Cu loading, Cu-Mg/ZnO catalyst, Dimethyl oxalate, Hydrogenation, Ethylene glycol.

1. Introduction

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With the crude oil resource shrinking, the traditional and energy-intensive petroleum derived technology can not satisfy the current commercial demand for various fine chemicals [1]. Alternatively, syngas from coal and biomass has been deemed as a sustainable organic carbon resource for various chemical products, owing to the abundant feedstock, high atom economy and environmental benign [2]. Particularly, dimethyl oxalate (DMO), as an important biomass-derived intermidate for methyl glycolate (MG) [3, 4], ethylene glycol (EG) [5], ethanol [6-8], has been commercialized from syngas by coupling with nitrite esters in presence of the Pd based catalysts [9]. Among the above chemicals, EG as an important organic compound and chemical intermediate has attracted extensive interests [10]. And the optimized catalyst for DMO hydrogenation has become the pivotal issue for achieving this prospective routine.

It is well known that Cu based catalysts have been deemed as the preferred candidate in ester hydrogenation [5][11]. Because the active Cu sites show activity only in C-O/C=O bonds, but inactive in C-C bond, endowing them excellent performance [12]. Currently, application of Cu/ZnO system in ester hydrogenation to the corresponding alcohol has aroused wide concern, owing to their outstanding performance [13-16]. In general, large Cu surface area, high Cu dispersion, and synergistic interactions between Cu and ZnO phase were proposed to be essential for the catalytic activity [17-19]. For achieving improved performance, incorporating promoter or dopant has been deemed as an effective strategy to pursuit large Cu surface area, high Cu dispersion, and reasonable active sites (Cu^+ and Cu^0) distribution [20, 21]. Most of all, our previous work has revealed that doping 4.0 wt.% Mg²⁺ ions into the system can effectively rearrange the Cu/ZnO composites morphology, promote the Cu dispersion, tail the ZnO electroneutrality and interaction between Cu nanoparticles (NPs) and ZnO NPs. The strengthened Cu-ZnO interaction facilitates increased surface Cu⁺ and O²⁻ sites concentration. In this context, the synergistic effect of the Cu⁰, Cu⁺ and O²⁻ sites can boost the catalytic activity, wherein the Cu⁺ and O²⁻ sites function as electrophilic or Lewis acidic sites to polarize the C=O/C-O bond severing the resultant

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catalytic behavior [22]. Furthermore, the strengthened metal-support interaction (MSE)/CONJOGORSE derived from electronic transformation can inhibit the migration of Cu species, favoring the outstanding thermal stability [23]. On the other hand, previous reports identified that the Cu loading in the Cu/ZnO system shows great effect on the Cu crystallite sizes, surface active sites (Cu⁰ and Cu⁺) concentration and distribution in the Cu/ZnO systems [24, 25]. A proper Cu loading would endow a unique microstructure with adequate active sites concentration and sufficient Cu-ZnO interface area [26]. Thus, it is induced that there should be a strong interdependency of the synergistic effects on Cu loading for the activity of the Cu/ZnO systems.

In this paper, the nano-scaled Cu-Mg/ZnO catalysts for DMO hydrogenation to EG with different Cu loading were prepared by the co-precipitation method. In addition, 1 characterization techniques including N₂ adsorption-desorption, N₂O titration, X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), H₂-temperature programmed reduction (H₂-TPR), CO₂-temperature programmed desorption (CO₂-TPD) and X-ray photoelectron spectroscopy (XPS) were conducted to explore the effect of copper loading on the physicochemical properties and catalytic behavior of the as-synthesized catalysts.

2. Experimental

2.1. Catalyst Preparation

Cu-Mg/ZnO catalysts with different copper loading were prepared using the coprecipitation method. Firstly, the 200 mL solution $(15.0 \text{ g } Zn(NO_3)_2 \cdot 6H_2O, 1.5 \text{ g} Mg(NO_3)_2 \cdot 6H_2O$, and a given mass of Cu(NO_3)_2 \cdot 6H_2O) and 200 mL Na₂CO₃ solution $(1.0 \text{ mol} \cdot \text{L}^{-1})$ was prepared. Firstly, both the precursor solution and precipitator were simultaneously dropped into the reactor under constant stirring at 75 °C and constant pH value of ca. 8.0, and aged for 24 h at room temperature. Then, the precipitate was filtrated and washed using distilled water until the conductivity of the filtrate was less than 2 mS· m⁻¹. After being dried in air at 120 °C for 12 h, the precursors were calcined at 400 °C for 6 h. The calcined catalysts were denoted xCuO-Mg/ZnO, and the corresponding reduced catalysts were denoted as xCu-Mg/ZnO, wherein the x stands

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2.2. Catalyst characterization

2. 2. 1. N₂ adsorption-desorption

Textual properties of the samples were determined by a nitrogen adsorption method using a Micromeritics Tristar II 3000 Analyzer and Brunauer-Emmett-Teller method. The specific surface area was calculated according to the isotherms using the BET method, and the pore volume and pore size were calculated by BJH method according to the desorption branches of the nitrogen isotherms.

2. 2. 3. X-ray diffraction

X-ray powder diffraction (XRD) patterns of the as-prepared catalysts were collected on an advanced X-ray diffractometer (Bruker AXS D8, Germany) with monochromated Cu K α radiation, and the crystal CuO, Cu and ZnO size in the catalysts was calculated using the Scherrer equation: $D_{hkl} = \frac{K\lambda}{\beta \cdot \cos\theta}$.

2. 2. 3. N₂O chemisorption

The number of surface metallic copper sites exposed was determined by N_2O oxidation, and followed H_2 titration using the procedure described by the previous report [27].

2. 2. 4. Scanning electron microscope (SEM)

The morphology of catalysts was investigated by scanning electron microscopy (SEM) (JSM-6701F, Japan).

2. 2. 5. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) images of the catalysts were obtained by using a JEM 2010 microscope operated at 200 kV.

2. 2. 6. H₂-temperature programmed reduction (H₂-TPR)

Temperature-programmed reduction (H₂-TPR) was conducted in a conventional atmospheric quartz reactor (5 mm i.d.). 30 mg of the calcined sample was out gassed at 100 °C under Ar for 1 h. After cooling to room temperature under Ar, the gas was switched to 5% H₂/Ar, and the sample was heated to 600 °C at a ramping rate of 10 °C • min⁻¹. The amount of H₂ consumed was monitored by a thermal conductivity

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detector (TCD).

2. 2. 7. CO₂-temperature programmed desorption (CO₂-TPD)

The basicity of the catalyst was measured by CO_2 temperature programmed desorption (CO_2 -TPD). The catalyst was firstly reduced at 300 °C in H₂ flow of 30 mL • min⁻¹ for 2 h. After cooling to room temperature, the catalyst was saturated with pure CO_2 (30 mL •min⁻¹) at 50 °C for 60 min and then flushed with Ar flow (40 mL •min⁻¹) to remove all physical adsorbed molecules. Afterward, the TPD experiment was started with a heating rate of 15 °C • min⁻¹ under Ar, and the desorbed CO_2 was detected by an AMETEK mass spectrometer.

2. 2. 8. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) were carried out on a Quantum 2000 Scanning ESCA Microprob instrument (Physical Electronics) equipped with an Al Ka X-ray radiation source (hm = 1486.6 eV).

2.3. Catalytic behavior test

The catalytic behaviors were assessed using a fixed-bed tubular reactor (the tube's inner diameter of 10 mm). Before the test, the calcined samples were firstly activated in 5% H₂/95% N₂ (volume ratio) atmosphere at 300 °C for 6 h with a ramping rate of 2 °C • min⁻¹. After that, 12.5 wt.% DMO (purity 99.9%) in methanol and H₂ was fed into the reactor under the reaction conditions: 2.5 MPa, 220 °C, H₂: DMO (mole ratio) of 100: 1. The products were analyzed with a GC-920 gas chromatograph fitted with a DB-FFAP capillary column (30.00 m×0.45 mm×0.85 µm) and a flame ionization detector with relative standard deviation less than 2.0 %.

3. Results and discussion

3.1. Structure evolution of catalysts

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Table 1 Physicochemical characteristic of the as-prepared samples.						DOI: 10.1039/C9NJ06085E	
Catalysts	SBET	V_p	D _p (nm)	D ^a Cu	D ^a ZnO	${ m S}_{ m Cu}{}^{0}{ m b}$	b
	$(m^2 \cdot g^{-1})$	$(m^2 \cdot g^{-1})$ $(cm^3 \cdot g^{-1})$		(nm)	(nm)	$(\ m^2 \cdot \ g^{\text{-}1})$	
10Cu-Mg/ZnO	72.9	0.34	4.7	7.3	15.8	0.73	
20Cu-Mg/ZnO	93.1	0.26	6.4	7.9	14.3	1.84	
30Cu-Mg/ZnO	93.0	0.26	9.1	9.7	12.9	2.16	
40Cu-Mg/ZnO	93.1	0.26	11.4	11.1	11.6	2.42	

Table 1 Physicochemical characteristic of the as-prepared samples.

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59 60 a D_{Cu} and D_{ZnO} were calculated from the reflections of Cu and ZnO planes in the activated catalysts using the Scherrer equation. b S_{Cu}⁰ and copper dispersion (D _{Cu}) were measured by N₂O adsorption.



Fig. 1 N₂ adsorption-desorption isotherms (A) and pore size distribution curves (B) calculated by BJH equation in desorption branch of the Cu-Mg/ZnO catalysts: (a) 40Cu-Mg/ZnO, (b) 30Cu-Mg/ZnO, (c) 20Cu-Mg/ZnO and (d) 10Cu-Mg/ZnO.

The textural properties of the as-prepared catalysts with different Cu loading are collected in the Table 1 and Fig. 1. The 10Cu-Mg/ZnO catalyst was found to possess the S_{BET} of 72.9 m² \cdot g⁻¹ and pore volume of 0.34 cm³ \cdot g⁻¹. Notably, the Cu loading higher than 10.0 wt.% promotes the S_{BET} increased up to 93.1 m^2 \cdot g^-1, but decreased Vp of 0.26 cm³ \cdot g⁻¹. The type IV with a H4-type hysteresis loop in the Fig. 1(A) show a typical large-pore mesoporous material with a 1D cylindrical channel in these catalysts [28]. From the Fig. 1(B), it is found that the 10Cu-Mg/ZnO catalyst displays the highest double peak intensity at about 2.8 nm and 12.1 nm. When the Cu loading increased from 10.0 wt.% to 30.0 wt.%, the pore size became reduced gradually, suggesting that more Cu species intend to facilitate micropore structure. However, excessive 40.0 wt.% Cu loading destructs the New Journal of Chemistry

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Fig. 2 XRD patterns of the calcined CuO-Mg/ZnO catalysts (A) and reduced Cu-xMg/ZnO catalysts (B) with different Cu loading.

Fig. 2 shows the XRD patterns of the calcined catalysts (A) and reduced catalysts (B). From the Fig. 2(A), it is found that there is a series of diffraction peaks index well to CuO (JCPDS 48-1548) and ZnO (JCPDS 36-1451), suggesting that typical two well-crystallized phases of CuO and ZnO were synthesized in the samples. And a slight shift and increased FWHM of XRD peaks demonstrates that partial Cu²⁺ species were actually doped into the Zn-O lattice during the preparation process, then affecting the

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View Article Online subsequent nucleation rate and growth rate [29-31]. Upon reduction, the XRD patterns/C9NJ06085E [Fig. 2(B)] of the reduced catalysts exhibits diffraction peaks assigned to ZnO (JCPDS 36-1451) and metallic Cu (JCPDS 15-0836), implying that CuO species completely transform to the metallic state. And the Cu characteristic diffraction peaks intensity grew gradually, indicating of aggravated agglomeration of Cu species via the Cu loading increasing. In contrast, the ZnO NPs sizes calculated using the Scherrer's equation (Fig. 2 and Table 1) display a monotonously opposite trend (from 15.8 nm for 10Cu-Mg/ZnO down to 11.6 nm for a sample with 40.0 wt.% Cu loading) with the Cu concentration increasing, suggesting that more Cu species intend to hinder the ZnO crystals growth. Additionally, the overlap of Cu and ZnO reflection peaks in the Fig. 2(B) implies of a well-dispersed mixture of Cu and ZnO NPs, which can impede the motion of ZnO grain during the thermal process [32]. A small shift and broadening in XRD peaks further confirmed that both the Cu and ZnO dispersion depends critically on the Cu loading [33]. Accordingly, sufficient Cu species intend to generate more S_{Cu}^{0} exposed and promote ZnO dispersion, further modulating the textual feature and Cu-ZnO interaction.

3.2 Crystalline morphology



Fig. 3 SEM images of the prepared precursors and catalysts: (A, B) 10Cu-Mg/ZnO, (C, D) 20Cu-Mg/ZnO, (E, F) 30Cu-Mg/ZnO, (G, H) 40Cu-Mg/ZnO.

The morphologies of the as-synthesized catalysts were analyzed by scanning electron microscopy (SEM). The Fig. 3 shows that the catalysts were mainly consisted of the dense mushroom-shaped agglomerate with relatively uniform size distribution.

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 Notable, the 10Cu-Mg/ZnO catalyst are mainly constructed by many interconnected/C9NJ06085E and congregated nanosheets as " petals " with developed porous structure, as shown in the Fig. 3(A-F). With the Cu loading increasing up to 30.0 wt.%, the nanosheets size became enlarged, but the crystals accumulation became more intensive. However, excessive 40.0 wt.% Cu loading caused crystal morphology transformed into nanorodes, producing enlarged pore structure, as shown in the Fig. 3(G-H).



Fig. 4 TEM and HR-TEM images of the pre-reduced samples: (A) 10Cu-Mg/ZnO, (B) 20Cu-Mg/ZnO, (C, D) 30Cu-Mg/ZnO and (E, F) 40Cu-Mg/ZnO.

TEM images of the Cu-Mg/ZnO catalysts are given in the Fig. 4. The Fig. 4(A) shows that the 10Cu-Mg/ZnO catalysts are mainly consisted of light gray spherical ZnO NPs along with Cu NPs, indicating that the surplus Cu species beyond partial dissolved into ZnO phase aggregate into Cu NPs locating on the ZnO substrate. And the Cu agglomeration became more serious gradually with the Cu loading increasing, as shown in the Fig. 4(B-F). Notable, the Cu and ZnO phase are not quite separately, but the Cu NPs are partially submerged in the ZnO phase. From a microstructural perspective, one important role of ZnO is to act as dispersant and stabilizer avoiding agglomeration $\mathcal{O}^{\text{VewArticle Online}}$ Cu particles. Nonetheless, the thinner and sheet like platelets ZnO phase cause Cu NPs partially embedded into or encased by ZnO phase, fabricating Cu/ZnO interface area by depriving S_{Cu}^{0} exposed, as shown in the Table 1. The change of crystalline morphology of the catalysts should depend critically on the doped Cu species, which is closely related to the Cu loading.

3.3 Reduction behavior

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Fig. 5 H₂-TPR curves of the as-prepared catalysts with various Cu loading.

Fig. 5 shows the H₂-TPR curves of the of the as-prepared xCuO-Mg/ZnO catalysts with various Cu loading. Notable, the 40CuO-Mg/ZnO catalyst features an overlapped asymmetric peak, including a main reduction peak at 248 °C and a shoulder peak at 230 °C. These two hydrogen consumption peaks are assigned to highly dispersed CuO phases and CuO NPs located in the support structure reducing, respectively [34]. When the Cu loading decreased from 40.0 wt.% to 10.0 wt.%, the main reduction peaks shifted to the higher temperature gradually, due to a growing MSI [35, 36]. Besides, the CuO species in the 10Cu-Mg/ZnO blocked by the excess ZnO phase maybe another reason for the retarded reduction [37]. On the other hand, increased intensity of the main peak with the weakened shoulder peak, even disappeared, can be discovered with the Cu loading decreasing. It proves that low Cu content promotes the Cu-ZnO interaction. Whereas, excessive Cu loading leads to reduced interaction between CuO and support through aggravating Cu species agglomeration and hinder Cu species migrating to

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59 60 support surface. Additionally, the hydrogen consumption area variation displayed/C9NJ06085E consistent trend with the Cu content change in the catalysts. A clear conclusion emerging from the H₂-TPR curves is that not only the Cu dispersion but also the Cu-ZnO interaction depends critically on the Cu loading.

3.4 Surface chemical properties of catalysts



Fig. 6 CO₂-TPD profiles of the reduced xCu-Mg/ZnO catalysts.

Temperature programmed desorption of CO₂ (CO₂-TPD) was adopted to explore the relation between surface basic sites and Cu loading of the catalysts. As shown in the Fig. 6, the 40Cu-Mg/ZnO catalyst exhibits a low temperature peak (LT Peak) at around 240 °C together with a high temperature peak (HT Peak) locating in the 400-700 °C range. The LT peak should be corresponding to weak basic surface site assigned to surface hydroxyl groups [38], and the HT peak from the adsorption on the medium strong basic sites associated with low coordinated oxygen atoms [39]. Compared to the 40Cu-Mg/ZnO, decreasing Cu loading to 30.0 wt.% caused the intensity of the HT peak weakened, while further reducing Cu loading leaded to the HT peak increased adversely. Most of all, the 30Cu-Mg/ZnO features the weakest HT peak, implying of the suppressed medium strong basic sites in presence of the Cu-ZnO interface area [40]. Moreover, it is identified that the Cu loading introduced in the Cu-Mg/ZnO catalysts shows great effect on the Cu and ZnO NPs dispersion, further influencing the interaction between each component. Then the surface basicity be related to the electronic effect can be tailed by the Cu loading [41]. Additionally, the LT peaks exhibit

the similar intensity trend with that of the HT peaks, indicating of the least surface/C9NJ06085E hydroxyl groups concentration. Thus, it is deduced that the Cu loading in the Cu/ZnO systems can regulate both the density and strength of the surface basic sites of the Cu-Mg/ZnO catalysts.



Fig. 7 Cu2p (A), Zn2p (B) XPS spectra of the activated catalysts, Cu LMM spectra of the activated xCu-Mg/ZnO catalysts (C): (a) 40Cu-Mg/ZnO, (b) 30Cu-Mg/ZnO, (c) 20Cu-Mg/ZnO, (d) 10Cu-Mg/ZnO.

Table 2 Surface	Cu component of	the reduced	catalysts based	on Cu LMM XAE	S spectra.
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Cotaluata	KE (eV)	X Cu ^{+ a}	S _{Cu} ^{0 b}	$S_{Cu}{}^{+c}$
Catalysis	Cu^+	Cu ⁰	(%)	$(m^2 \cdot g^{-1})$	$(m^2 \cdot g^{-1})$
10Cu-Mg/ZnO	909.1	914.0	72.7	0.73	1.95
20Cu-Mg/ZnO	911.8	917.4	47.8	1.84	1.73
30Cu-Mg/ZnO	911.8	917.4	37.8	2.16	3.50
40Cu-Mg/ZnO	911.8	917.4	44.8	2.42	1.92

a Intensity ratio between Cu^+ and $(Cu^+ + Cu^0)$ by deconvolution of Cu LMM spectra. b Metallic Cu surface area determined by N₂O titration. c Calculated based on X_{Cu^+} and S_{Cu^0} assuming that Cu^+ ion occupies the same area as that of the Cu^0 atom, and has the same atomic sensitivity factor as that of Cu^0 .

XPS was conducted to explore the surface chemical states of the Cu and Zn species

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in the activated catalysts, and the results were depicted in the Fig. 7. The $C\Phi^{1/2}p3^{1/2}/CNJJGG085E$ spectra [Fig. 7(A)] of the catalysts suggest that all the Cu species are in the reduced state with the binding energy only at 933.5 and 952.0 eV, also, the disappearance of the satellite peaks at 940.5 eV implies that surface Cu²⁺ species were completely reduced [42]. The Zn2p spectra [Fig. 7(B)] suggest that that Zn²⁺ species were not reducible [43]. Additionally, the binding energy of Zn2p shifted to larger binding energy with reduced Cu loading, confirming that the gradually strengthened electronic interaction. It is well accordance with the experiment result of the results of the H₂-TPR results (Fig. 5), depicting that the IMS are closely related to the Cu and ZnO NPs distribution.

The binding energy distinction is very minimal between Cu⁰ and Cu⁺ species. Thus, the kinetic energy of the Cu LMM and the binding energy of the Cu2p3/2 together make up an Auger parameter, which is used to distinguish Cu⁺ and Cu⁰ species. As shown in Fig. 7(C), the presence of Auger kinetic energy peaks ranging from 905 to 925 eV suggests of the co-existence of the Cu⁺ and Cu⁰ sites on the reduced catalysts surface [44]. The deconvolution of Cu LMM (Table 2) shows that the amount of surface Cu⁺ species increases with the Cu loading increasing from 10 wt.% to 30 wt.%, but decreased with excess 40.0 wt.% Cu loading. Most of all, the 30Cu-Mg/ZnO possesses the highest S_{Cu}^+ of 3.50 m² • g⁻¹. Except for the surface Cu⁰ concentrations, the proportions of surface Cu⁺ sites of the reduced catalysts can be modulated. The surface Cu⁺ sites should be created by the Cu-O-Zn species existing in the Cu-ZnO interface [19][45]. Moreover, the highest surface Cu⁺ sites concentration should originate from the maximum Cu-ZnO interface area. Thus, it is induced that the Cu loading in the Cu-Mg/ZnO system shows great influence on the Cu and ZnO interaction, further determining the surface chemical properties of catalysts. New Journal of Chemistry Accepted Manuscript

3.5. Catalytic performance

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Fig.8 The catalytic performance of the Cu-Mg/ZnO catalysts [(A) and (B)]. Reaction conditions: 2.5 MPa H₂, 220 °C, LHSV=2 h⁻¹, and H₂/DMO ratio 100: 1 (mol/mol).

The catalytic activity of the Cu-Mg/ZnO catalysts was assessed in vapourphase DMO hydrogenation. It is well established that DMO hydrogenation undergoes unsaturated hydrogenation to methyl glycolate (MG), then hydrogenation to EG, even exceedingly hydrogenation to ethanol. During the thermal hydrogenation, the intermolecular dehydration reaction occurred on the strong acid sites and Guerbet reaction catalysed by the strong basic sites can actually determine EG yield [10]. The catalytic activity and selectivity for DMO hydrogenation of Cu-Mg/ZnO catalysts via Cu loading was given in the Fig. 8. From the Fig. 8(A) and Fig. 8(B), it is found that the catalytic effectiveness of the Cu-Mg/ZnO catalysts shows an enhanced trend with the Cu loading increasing from 10.0 wt.% to 30.0 wt.%, but dropped with excessive 40.0 wt.%

Cu loading. Most of all, DMO was completely converted and the EG selectivity/C9NJ06085E can reach up to 98.0 % even at a LHSV of 3.5 h⁻¹ over the 30Cu-Mg/ZnO catalysts, superior to that of the other catalysts. Meanwhile, 0.5 % ethanol, 1.0 % 1, 2-BDO and 0.5 % other by-products were yielded. Particularly, the selectivity toward ethanol and 1, 2-BDO was found to be the least among the as-synthesized catalysts, suggesting that the 30Cu-Mg/ZnO catalyst possesses the optimistic surface properties.

Based on the above results, it is summarized that the physicochemical properties of the Cu-Mg/ZnO closely were closely related to the Cu and ZnO NPs size effect, which depends critically on the Cu loading in the system. It is well established that the surface Cu⁰ sites can dissociate H₂ affording H· atoms, while surface Cu⁺ sites can serve as active sites for acyl group dissociation [1]. And the synergetic effect between Cu⁺ and Cu^0 sites was proposed to be responsible for gas-phase ester hydrogenation [1]. Generally, high S_{Cu}⁰ in the Cu/ZnO based catalyst intends to improve the hydrogenation activity [46]. In this case, Zhang et al reported that the C=O bond hydrogenation activity can be effectively promoted by forming Cu⁰ZnO sites [47]. Herein, the distinct activity between the 20Cu-Mg/ZnO and 40Cu-Mg/ZnO catalysts confirmed that higher S_{Cu}^{0} is advantageous to the hydrogenation activity of Cu catalyst. This because that high copper surface area can supply more active sits for hydrogen dissociation, thus promoting the hydrogenation activity [46]. Whereas, the 20Cu-Mg/ZnO catalyst possessing higher S_{Cu}^{0} , but lower S $_{Cu}^{+}$ exhibits superior catalytic activity to that of the 10Cu-Mg/ZnO catalyst with less surface Cu⁺ sites. This fact that argues that the hydrogenation activity is not in line with the S_{Cu}^{0} , and the cascade reaction of DMOto-EG over the Cu-Mg/ZnO catalysts is not governed by the single S_{Cu}⁺. Thus the synergistic effect between the active Cu⁰ and Cu⁺ sites should be responsible for the catalytic DMO hydrogenation activity, which can be modulated by the Cu loading. Particularly, it has been reported that the ZnOx species bond with Cu⁺ species can promote ester dissociating [48]. Yao et al [19] proposed that Cu sites generated on the Cu-ZnO interface have a high tendency to adsorb the ester in the form of a surface bound species, which is the rate controlling step in ester hydrogenolysis. It is concluded

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the DMO dissociating on the Cu⁺ sites should be the rate-determining step in presence/C9NJ06085E of enough exposed Cu⁰ sites over the Cu-Mg/ZnO catalyst. Moreover, the EG yield and stability can be guaranteed by the interfacial between Cu and ZnO, due to the optical surface chemical properties and strengthened IMS.

4. Conclusions

In summary, a series of nano-scaled Cu-Mg/ZnO catalysts with different Cu loading were synthesized via facile co-precipitation method exert excellent performance in DMO hydrogenation to EG. The Cu loading shows great effect on the resultant textural properties and catalytic activity of the catalysts. The catalytic activity increased with the Cu loading increasing from 10.0 wt.% to 30.0 wt.%, but excessive 40.0wt.% Cu loading cause severe copper amalgamation, and consequently reduce the catalytic activity. Among the as-synthesized samples, the 30Cu-Mg/ZnO catalyst presents outstanding hydrogenation activity. Appropriate Cu loading produces sufficient surface active Cu⁰ sites, which is essential for the synergistic effect between Cu⁰ and Cu⁺ZnO sites in DMO hydrogenation to EG. Furthermore, the maximal Cu-ZnO interface leads to a strengthened MSI, which can effectively restrain the sintering and growth of the active Cu NPs, contributing to the catalytic stability.

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Proper Cu loading introduced in the Cu-Mg/ZnO system facilitates strengthened/contine Cu-Zn synergistic effect and optical surface chemical properties.

