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## Cu active sites confined in MgAl layered double hydroxide for hydrogenation of dimethyl oxalate to ethanol

Jianzhe Shi<sup>a</sup>, Yan He<sup>a</sup>, Kui Ma<sup>a,\*</sup>, Siyang Tang<sup>a</sup>, Changjun Liu<sup>a,b</sup>, Hairong Yue<sup>a,b,\*</sup>, Bin Liang<sup>a,b</sup>

<sup>a</sup> Low-Carbon Technology and Chemical Reaction Engineering Laboratory, School of Chemical Engineering, Sichuan University, Chengdu 610065, China <sup>b</sup> Institute of New Energy and Low-Carbon Technology, Sichuan University, Chengdu 610207, China

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### ABSTRACT

The dimethyl oxalate (DMO) hydrogenation reaction is the key step of indirect synthesis of  $C_2-C_4$  oxygenates (e.g., ethanol) from syngas. Copper-based catalysts have been extensively explored for DMO hydrogenation. However, the unstable copper active sites induced by metal-particle growth at high rection temperatures (e.g., > 553 K) is an impediment to the stable performance. Herein, we report a facile co-precipitation method to confine Cu active sites in the layered double hydroxide for the hydrogenation of DMO to ethanol. The effects of Mg/Al molar ratio on the catalytic performance were systematically investigated to get insights into the structure-activity relationship. The results indicate that the CuMgAl-LDH-1.25 catalyst possesses regular lamellar structures, highly dispersed Cu active sites, and moderate acidic sites, which synergistically achieves a stable performance with a DMO conversion of ca. 100 % and ethanol selectivity exceeding 83 % at 553 K, 3 MPa.

### 1. Introduction

Syngas is an important feedstock to produce various oxygenates chemicals such as ethanol, ethylene glycol and methyl glycolate [1]. However, the direct catalytic conversion of syngas to the  $C_2$ - $C_4$  intermediates suffers from low yield and poor selectivity due to slow kinetics of the initial CC- bond formation and fast chain growth of the  $C_2$  intermediates [2,3]. Alternatively, the indirect technology via carbonylation of CO to form dimethyl oxalate (DMO) and subsequent hydrogenation of DMO to corresponding diols presents reasonable advantages of high efficiency and accessibility in industry [4,5].

The DMO hydrogenation reaction is the key step of this indirect technology. Currently, the reported work for this reaction primarily focused on the development of homogeneous or heterogeneous catalytic systems. The copper-based heterogeneous catalysts are extensively investigated in selective hydrogenation of DMO due to their highly selective hydrogenation of carbon-oxygen bonds and relatively inactive for the hydrogenolysis of carbon-carbon bonds [6–8]. Our previous work on Cu catalysts indicated that the high dispersion of copper species and strong metal-support interactions are vital for the high activity and stability in hydrogenation to produce ethanol are usually operated under a high reaction temperature (e.g., > 553 K), which is higher than the Hütting temperature (407 K) of Cu metal. Thus, the metallic Cu

nanoparticles tend to migrate and coalesce into large crystallites [3], leading to an impediment to the stable performance. Furthermore, the hydrogenation of DMO is highly exothermic, and the calculated corresponding adiabatic temperature at 553 K is about 50-80 K (dependent on liquid hourly space velocity). Thus, it is particularly important to design catalysts with excellent catalytic activity and thermal stability.

Anchoring or partially embedding the metal nanoparticles in thermally stable mesoporous materials is an efficient strategy to prevent particle aggregation for various catalytic hydrogenation reactions [9]. For instance, Li et al. fabricated the Cu nanoparticles inlaved in ordered mesoporous alumina (OM-Al<sub>2</sub>O<sub>3</sub>) for the synthesis of ethanol with the remarkable stability (> 200 h at 543 K) [10]. Our previous work also reported the Cu avtive sites embedded in copper-phyllosilicate nanotube (CuPSNT) sheath [9], and mesoporous MCM-41 in DMO hydrogenation reaction with excellent catalytic performance [11,12]. Layered double hydroxide (LDH) is a lamellar material with unique structure for anchoring interlayer components and exchanging anions between layers, which has been widely used for catalysis and adsorption [13,14]. The layered structure of the hydrotalcite can trigger a strong anchoring effect for the active metallic nanoparticles during the reduction and reaction process to prevent them from agglomerating and sintering, and thereby prolong the catalyst life [12]. In addition, the surface acidity and alkalinity of the LDH materials can also be tuned by

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<sup>\*</sup> Corresponding authors at: Low-Carbon Technology and Chemical Reaction Engineering Laboratory, School of Chemical Engineering, Sichuan University, Chengdu 610065, China.

E-mail addresses: kuima@scu.edu.cn (K. Ma), hryue@scu.edu.cn (H. Yue).

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### J. Shi, et al.

changing their composition (e.g., MgO and ZrO). For DMO hydrogenation, it has been reported that the strong acidic sites can induce the intermolecular dehydration of methanol, ethanol and diols to ether products, whereas the strong basic sites catalyze the Guerbet reaction to form 1,2-butanediol (1,2-BDO), which will definitely diminish the selectivity to ethanol [3,6]. Therefore, choosing the interlayer components of LDH and modulating their composition to optimize the surface acidity and alkalinity are effective to improve the selectivity of ethanol in DMO hydrogenation.

Herein, we use a facile co-precipitation strategy to prepare CuMgAl-LDH catalysts confining Cu nanoparticles by using alkaline MgO and acidic  $Al_2O_3$  as the layer components. The Mg/Al molar ratios in CuMgAl-LDH have been tuned to investigate their influence on the morphology and texture properties, acidity and alkalinity of the laminate, as well as the Cu nanoparticles dispersion. The obtained catalysts were systematically characterized and tested for understanding the effect of the structures and surface chemical properties on the catalytic performance of DMO hydrogenation.

#### 2. Experimental

#### 2.1. Materials

Dimethyl oxalate was purchased from Aladdin (Shanghai) Biochemical Technology Co., Ltd. Methanol, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Mg (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, anhydrous sodium carbonate, sodium hydroxide, and ethanol (all analytical grade) were bought from Kelong Chemical Co., Ltd. Hydrogen gas (99.99 %), H<sub>2</sub>-Ar (10 %), pure N<sub>2</sub> (99.999 %) and pure He (99.999 %) were from Tianyi Gas Co., Ltd. All the chemicals above were used as received and without any purification.

### 2.2. Catalysts preparation

CuMgAl-LDH hydrotalcite catalysts were prepared by a classic coprecipitation method. The specific preparation process is as follows: Cu (NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O with Cu content of ca. 17 % were firstly dissolved in 100 mL of deionized water to obtain a mixed solution.  $Na_2CO_3$  (providing  $CO_3^{2-}$  as the interlayer anions) and NaOH were added in 300 mL of deionized water to obtain an alkali solution as a precipitant, ensuring  $n(CO_3^{2-})/n(M^{n+}) > 0.667$  and n  $(OH^{-})/n(M^{n+})$  of 2.2. The precipitation process was performed under an oil bath at 343 K with stirring (1000 r min<sup>-1</sup>). The two mixed solution were added dropwise into a three-necked flask to control the pH value of the co-precipitation solution between 9.0 and 10.0. After continuously stirred at 343 K for 24 h, the suspension was separated by vacuum filtration and washed for several times until the pH value of the solution decreased to  $\sim$ 7. The filter cake was dried under vacuum at 353 K for 10 h and then calcined at 773 K for 4 h (heating rate: 5 K min<sup>-1</sup>). The final obtained catalysts were denoted as CuMgAl-LDH-x, where x represents the Mg/Al molar ratios of 1.0, 1.25, 1.5, 2.5, 3.0 and 3.5, respectively.

### 2.3. Catalytic characterization

Textural properties were measured at 77 K by N<sub>2</sub> adsorption-desorption using a Micromeritics ASAP 2460 instrument. The specific surface areas were calculated from the isotherms using Brunauer-Emmett-Teller (BET) method, and the pore size distributions were calculated by the Barrett-Joyner-Halenda (BJH) method. The actual Cu, Mg and Al contents were determined by the inductively coupling plasma optical emission spectrometry (ICP-OES). X-ray diffraction (XRD) spectra were implemented on the Empyrean diffraction meter using Cu k $\alpha$  radiation ( $\lambda = 1.5406$  Å) at 40 kV and 35 mA, and the particle sizes of copper species were calculated by the Scherrer equation. Transmission electron microscopy (TEM) images were taken using a Tecnai-G20 electron

micro-scope at 200 kV. The catalyst powders were well dispersed in ethanol solution and then dropped and dried on a copper grid supported transparent carbon foil. The morphology of the prepared catalysts was analyzed using a JEOLJSM-6360LV scanning electron microscope (SEM) (voltage: 5.0 kV). Fourier transform infrared spectroscopy (FT-IR) experiments were carried out on a Nicolet iS-50 spectrometer. The samples were finely ground and dispersed in KBr. The spectra were collected from 4000 to 500 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

The H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR) of the catalysts was performed on a ChemStar TPx chemisorption analyzer. About 50 mg of catalysts were pretreated in argon atmosphere at 393 K for 1 h. Next, the reduction step was carried out under 10 vol % H<sub>2</sub>-Ar (30 mL min<sup>-1</sup>) atmosphere with the temperature increased from 323 K to 1000 K (heating rate: 5 K min<sup>-1</sup>). TCD detector was employed to determine the amount of hydrogen consumption during this process.

The CO<sub>2</sub> and NH<sub>3</sub> temperature-programmed desorption (TPD) was also carried out on ChemStar TPx chemisorption analyzer to quantify the surface basic sites or acid sites over the catalysts. 100 mg of catalysts were placed in a quartz U tube and reduced in 10 vol% H<sub>2</sub>-Ar (30 mL min<sup>-1</sup>) at 623 K for 4 h before the gas switched to CO<sub>2</sub> or NH<sub>3</sub>, which passed through the U tube for 1 h to reach adsorption saturation. After removeing the weak adsorption by argon sweeping, the temperature was increase from room temperature to 1073 K at a heating rate of 10 K min<sup>-1</sup> under pure helium atmosphere.

The specific surface area of the metallic copper species was quantified by N<sub>2</sub>O adsorption and H<sub>2</sub>-TPR reverse titration. Typically, after pretreated in Ar at 473 K for 2 h, 50 mg of catalysts were reduced with the temperature increased from 323 K to 973 K (this process was defined as total TPR). Then the samples were switched to 10 vol% N<sub>2</sub>O-Ar mixture under room temperature and pulse titrated for 2 h, oxidizing copper species to higher valence states. Finally, the reduction process was defined as surface TPR). The dispersion (D<sub>Cu</sub>), specific surface area (S<sub>Cu</sub>) and particle size of copper species (d<sub>Cu</sub>) were calculated by the following equations:

$$D_{Cu}(\%) = \frac{2 \times H_{2 \text{ consumption (Surface TPR)}}}{H_{2 \text{ consumption (Total TPR)}}} \times 100\%$$
(1)

$$S_{Cu^{0}}(m^{2}g^{-1}Cu) = \frac{D_{Cu} \times N_{av}}{M_{Cu} \times 1.46 \times c} \approx 649 \times D_{Cu}$$
(2)

$$d_{Cu}(nm) = \frac{6}{S_{Cu} \times \rho_{Cu}} \approx \frac{1.0}{D_{Cu}}$$
(3)

Where assuming the Cu species are sphere and contains  $1.46 \times 10^{19}$  copper atoms per square meter.

### 2.4. Catalytic performance

The vapor-phase hydrogenation of DMO was tested in a fixed-bed tubular reactor (length of 50 cm, inner diameter of 0.8 cm and external diameter of 1.6 cm). Typically, 0.4 g of catalyst (40–60 mesh) was placed in the middle section of the reactor. After the reduction in H<sub>2</sub> atmosphere at 623 K for 2 h, the temperature was cooled to the reaction temperature of 553 K and DMO (15 wt% dissolved in methanol) was injected into the reactor. The H<sub>2</sub>/DMO molar ratio, reaction pressure and weight hour space velocity (WHSV) were 200, 3.0 MPa and 0.5 h<sup>-1</sup>, respectively. The reaction products were analyzed by GC SP-2100A equipped with the flame ionization detector (FID) and a DB-WAX capillary column (Agilent Technologies Company, 30 m × 0.250 mm). All experimental data was averaged from three to six GC samples to ensure the repeatability.

Catalysis Today xxx (xxxx) xxx-xxx



Fig. 1. N2 adsorption-desorption isotherms and pore size distribution of the calcined CuMgAl-LDH-x catalysts.

#### 3. Results and discussion

### 3.1. Physico-chemical properties of the CuMgAl-LDH-x catalysts

### 3.1.1. Textural and morphology properties

The textural properties of the calcined CuMgAl-LDH-x catalysts were determined by the  $N_2$  adsorption-desorption (Fig. 1), and the data were listed in Table 1.

As shown in Fig. 1, all the calcined CuMgAl-LDH-x samples possess the highly similar isothermal curves with Langmuir type IV shape. According to the classification of IUPAC, this belongs to the type of mesoporous capillary condensation [15]. According to the pore size distribution curve, micropores and macropores were presented in the CuMgAl-LDH-x catalysts [16]. The hysteresis loop is generally caused by the non-overlapping of adsorption and desorption curves by capillary condensation, which belongs to H1 and H3 types [17]. With the decrease of Mg/Al ratio, the type H1 turns to type H3, suggesting that the CuMgAl-LDH samples with low molar ratio of Mg/Al contain cylindrical, V-shaped, as well as slit pores with high specific surface area. The formation of these pores is primarily due to the dehydration of the hydroxyl groups on the layer and thermal decomposition of the  $CO_3^{2-}$ 

Table 1 shows that the specific surface area of the catalysts firstly increases and then decrease with the elevated Mg/Al ratios. Notably, the CuMgAl-LDH-1.0 sample possesses the lowest surface area (92.68  $m^2/g$ ), which could be attributed to the hybridization of the crystal phase in the hydrotalcite precursor. Therefore, appropriate Mg/Al molar ratio could increase the specific surface area of the CuMgAl-LDH catalysts.

SEM and TEM imagesare shown in Fig. 2 to illustrate the morphologies of the fresh and reduced CuMgAl-LDH-x samples. Clear flaky crystal structures are observed in the SEM images of the CuMgAl-LDH-1.0, CuMgAl-LDH-1.25 and CuMgAl-LDH-1.5 catalysts. These flaky laminates are staggered to form a "sand rose" flower-like morphology with slit pores [20,21], which is consistent with the N<sub>2</sub>-physisorption results. It is also noted that the flower-like structure of the CuMgAl-LDH-1.25 catalyst is more regular than that of the others. But for the reduced CuMgAl-LDH-x samples, only the CuMgAl-LDH-1.25

Table 1	
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Physical	properties	of the	calcined	and reduced	CuMgAl-LDH-x cata	lvst

Catalyst	M <sub>Cu</sub> <sup>a</sup> (%)	M <sub>Mg</sub> <sup>a</sup> (%)	M <sub>Al</sub> <sup>a</sup> (%)	S <sub>BET</sub> <sup>b</sup> (m <sup>2</sup> /g)	V <sub>pore</sub> <sup>c</sup> (cm <sup>3</sup> /g)	D <sub>pore</sub> <sup>c</sup> (nm)	$S_{Cu}^{0d} (m^2/g)$	D <sub>Cu</sub> <sup>d</sup> (%)	d <sub>Cu</sub> <sup>e</sup> (nm)	d <sub>Cu</sub> <sup>f</sup> (nm)
CuMgAl-LDH-3.5	17.38	25.71	8.22	110.63	0.75	24.18	30.37	4.68	11.27	18.32
CuMgAl-LDH -3.0	17.21	24.41	9.34.	114.29	0.72	22.27	33.81	5.21	9.88	15.47
CuMgAl-LDH-2.5	16.98	23.12	10.61	153.32	1.22	27.98	43.94	6.77	6.92	12.14
CuMgAl-LDH-1.5	17.42	19.22	13.72	174.02	1.25	28.48	42.37	6.53	6.36	12.05
CuMgAl-LDH -1.25	17.02	17.04	15.13	116.49	0.84	33.30	57.89	8.92	5.64	8.13
CuMgAl-LDH -1.0	17.24	14.21	15.98	92.68	0.68	35.02	66.45	10.24	8.89	7.21

<sup>a</sup> Cu, Mg, and Al contents determined by ICP-OES analysis.

 $^{\rm b}~S_{\rm BET}$  determined by the BET equation.

 $^{\rm c}\,$  Pore volume and pore diameter determined by the BJH method from  $N_2$  desorption branch.

 $^{d}$  Surface area of Cu<sup>0</sup> (S<sub>Cu0</sub>) and Cu dispersion (D<sub>Cu</sub>) determined by the N<sub>2</sub>O titration.

<sup>e</sup> Metallic Cu size of the reduced catalysts calculated from the TEM images based on statistical analysis.

 $^{\rm f}\,$  Mean Cu particle size calculated from the XRD data by Scherrer equation.



Fig. 2. SEM and TEM images of the as-prepared and reduced CuMgAl-LDH-x catalysts.

and CuMgAl-LDH-1.5 samples maintain the flaky structures of LDH, and the average size of copper particles on the surface is about 5.5–6.5 nm according to the statistical analysis. On the contrary, the other samples all show destroyed flaky structures and serious agglomeration behavior of the Cu nanoparticles (average particle sizes of 7-10 nm). The difference is probably attributed to the crystal stability of the laminates influenced by the Mg/Al ratio and the dispersion of the Cu species.

### 3.1.2. Crystal structures and surface functional groups

The ICP-OES results summarized in Table 1 show that the copper contents of all catalysts were consistent, and Mg and Al contents of all samples were similar to the target value of Mg/Al ratio.

In order to explore the changes of crystal structure and the evolution of activity sites over the catalysts by varying the Mg/Al molar ratios, the wide-angle XRD patterns of the as-prepared, calcined, reduced and spent CuMgAl-LDH-x samples are depicted in Fig. 3. All the as-prepared CuMgAl-LDH-x samples possess the peaks at 12.5°, 22.4°, and 34.7° in Fig. 3(a), which belong to the (003), (006), (009) crystal planes, respectively [22]. Additionally, the two diffraction peaks at 58°–61° are attributed to the (110) and (113) crystal planes, respectively. The results indicate that ordered hydrotalcite phase with high crystallinity appeared in the CuMgAl-LDH precursors [23]. With the decrease of molar ratio of Mg/Al, the peak intensity of the (003) crystal plane gradually increases and reaches the maximum at Mg/Al = 1.25, implying a better crystallinity of CuMgAl-LDH-1.25. Since the charge density of Al<sup>3+</sup> is greater than that of Mg<sup>2+</sup>, the elevated content of Al<sup>3+</sup> enhances the charge density on the layer, leading to an regular layered structure and strong lamellar interaction of CuMgAl-LDH-1.25 [22]. The interplanar spacing values of the CuMgAl-LDH samples was calculated by the Bragg formula (2dsin $\theta = n\lambda$ ) and listed in Table 2, further illustrating the structures and crystallinity of the laminates. With the decrease of Mg/Al molar ratio, the values of interplanar spacing (d<sub>003</sub>, d<sub>006</sub>, d<sub>009</sub>, and d<sub>110</sub>) and the layer spacing (d<sub>LDH</sub>, a, and c) of the samples both decline, which is consistent with the results in Fig. 3.

XRD patterns of the calcined CuMgAl-LDH catalysts in Fig. 3(b) show no obvious diffraction peaks of CuO and  $Al_2O_3$  phases, indicating a high dispersion of CuO and  $Al_2O_3$  in the catalysts [24]. However, the MgO diffraction peaks are obviously observed at 20 of 37.0°, 43.0°, and 62.4° on all the CuMgAl-LDH catalysts, and the intensity of these peaks are slightly strengthened with the increase of Mg/Al molar ratio. It is worth mentioning that the diffraction peaks of the CuMgAl-LDH samples at 20 of 43.0° and 62.4° are much weaker than that of the MgAl-LDH-1.25 sample without Cu loading. The reason is that partial of the metal oxides (MgO, CuO and  $Al_2O_3$ ) in the CuMgAl-LDH catalysts tends to formsolid solutions during the calcination process, which could weaken and shift the MgO diffraction peaks [25]. These results also indicate that the Cu species are highly dispersed on the layered hydrotalcite structures [26].

Upon reduction in Fig. 3(c), no characteristic peak of CuO in the spectra indicates that all the CuO species were reduced to metallic Cu or Cu<sub>2</sub>O. The characteristic diffraction peaks of Cu<sub>2</sub>O (JCPDS 05-0667) are observed at 36.5° and 61.8°, which were attributed to the (111) and (220) crystal planes of Cu<sub>2</sub>O, respectively [20]. Meanwhile, the characteristic diffraction peaks of metallic Cu were observed at 43.5°,



Fig. 3. XRD patterns of the (a) as-prepared, (b) calcined, (c) reduced and (d) spent CuMgAl-LDH samples.

 Table 2

 Structure parameters of CuMgAl-LDH-x catalysts derived from XRD patterns.

Samples	d <sub>003</sub> (nm)	d <sub>006</sub> (nm)	d <sub>009</sub> (nm)	d <sub>110</sub> (nm)	d <sub>LDH</sub> (nm) <sup>a</sup>	a(nm) <sup>b</sup>	c(nm) <sup>c</sup>
CuMgAl-LDH-3.5	0.7838	0.3891	0.2603	0.1583	0.2938	0.3166	2.3513
CuMgAl-LDH-3.0	0.7823	0.3890	0.2594	0.1540	0.2923	0.3079	2.3470
CuMgAl-LDH-2.5	0.7792	0.3872	0.2594	0.1535	0.2892	0.3070	2.3375
CuMgAl-LDH-1.5	0.7689	0.3816	0.2581	0.1530	0.2789	0.3059	2.3068
CuMgAl-LDH-1.25	0.7687	0.3801	0.2580	0.1526	0.2787	0.3052	2.3061
CuMgAl-LDH-1.0	0.7593	0.3783	0.2579	0.1523	0.2693	0.3047	2.2778

<sup>a</sup>  $d_{LDH}$  representing the layer spacing of the CuMgAl-LDH-x catalysts calculated by the subtraction between the  $d_{(003)}$  crystal plane spacing and the layer structure thickness of the typical MgAl-LDH hydrotalcite of ~0.39 nm.

<sup>b</sup> Parameter a representing the distance between metal ions in two adjacent hexagonal system, calculated from the XRD patterns refinement.

<sup>c</sup> Parameter c representing the thickness of crystal cell calculated from the XRD patterns refinement.

belonging to Cu(111) crystal planes. In addition, the CuMgAl-LDH catalysts with low Mg/Al ratio (1.0 and 1.25) show a stronger intensity of Cu<sub>2</sub>O peaks, suggesting a poor reducibility over the CuMgAl-LDH-1.0 and CuMgAl-LDH1.25 catalysts. But for the spent catalysts in Fig. 3(d), the intensity of peaks attributed to Cu<sub>2</sub>O over all the samples are weakened, while that of Cu becomes stronger. This further demonstrates that Cu<sub>2</sub>O species are dispersed or partial reduced during the reaction. We also conclude that the CuMgAl-LDH catalysts with low Mg/Al ratio could maintain the valence states of the Cu species, providing stable Cu species during the reaction [12].

structures and understand the evolution of the active sites over the CuMgAl-LDH-x samples. As shown in Fig. 4(a), a broad and strong absorption band is observed at 3540 cm<sup>-1</sup>, which can be attributed to the overlap of the  $\nu_{O-H}$  and the  $\nu_{O-H...O}$  of the interlayer water molecules. This peak shows a red shift compared with the  $\nu_{O-H}$  absorption band of free water at 3600 cm<sup>-1</sup> due to the hydrogen bond (O–H...O) between interlayer H<sub>2</sub>O and interlayer –OH on the layers [27]. With the decrease of Mg/Al ratio, the peak gradually shifts to a low frequency to 3482 cm<sup>-1</sup> at the Mg/Al ratio of 1.50. The reason is that the high content of Al<sup>3+</sup> could gradually strengthen the layer structures of the hydrotalcite, leading to a reduced layer spacing, and thus results in

FTIR spectra was used to discriminate the layered double hydroxide

Catalysis Today xxx (xxxx) xxx-xxx



Fig. 4. FT-IR spectra of the (a) as-prepared and (b) calcined CuMgAl-LDH-x samples.

a gradually enhanced hydrogen bonding force.

The FT-IR spectra of the calcined catalyst in Fig. 4(b) show that the interlayer water and hydroxyl groups on the hydrotalcite layers were removed after calcination. The hydrogen bond stretching vibrations of the composite oxides appears at 3482 cm<sup>-1</sup>, 2970 cm<sup>-1</sup>, and 1643 cm<sup>-1</sup>, while the bending vibration absorption bands of the water molecules are significantly weakened. Although the calcined samples have lost their layered structures and interlayer anion  $CO_3^{2-}$ , but an asymmetric stretching vibration of the C–O bond in  $CO_3^{2-}$  still exists at 1397 cm<sup>-1</sup>. It could be attributed to the hydrotalcite-derived metal oxides with strong alkalinity, which are readily to adsorb H<sub>2</sub>O and CO<sub>2</sub> in the air. Generally, the infrared absorption bands below 1000 cm<sup>-1</sup> are indexed to the skeleton vibration of the metal–oxygen bond (M–O). Obviously, the peak intensity of Mg–O at 839 cm<sup>-1</sup> is gradually enhanced, while the peak intensity of Al-O at 647 cm<sup>-1</sup> is weakened with the increase of Mg/Al ratios.

### 3.1.3. The reducibility and surface density of Cu species

The H<sub>2</sub>-TPR profiles were collected to clarify the reducibility of the CuMgAl-LDH-x catalysts. As shown in Fig. 5, all the samples exhibit an obvious peak at 554-570 K, ascribing to the reduction of CuO. These single and sharp reduction peaks indicate that the copper species in the catalysts are highly dispersed with uniform particle size distribution. The CuMgAl-LDH-1.25 catalyst possesses a much intense reduction peak at low temperature, indicating a better Cu dispersion than the other samples. As the Cu component exists in the laminates of the catalysts as eutectic phases with MgO and Al<sub>2</sub>O<sub>3</sub>, the interaction between Cu-O-Mg structures is much stronger than that of the Cu-O-Al structures. Therefore, the high Mg/Al molar ratio facilitates the formation of more Cu-O-Mg structures in the CuMgAl-LDH catalysts, and thus elevates the reduction temperature. However, when the Mg/Al molar ratio lower than 1.25, the Cu species sligtly agglomerate during the reaction process due to the weak stabilization induced by the less Cu-O-Al structure, also leading to an increase of the reduction temperature [28,29]. Therefore, the moderate Mg/Al could not only improve the Cu species dispersion, but also boost the interaction between the Cu species and hydrotalcite layers to facilitate the reducibility.

The  $N_2O$  pulse titration results also illustrate that appropriate Mg/Al ratio could appreciably enhance the surface density of metallic Cu sites



Fig. 5. H<sub>2</sub>-TPR profiles of the CuMgAl-LDH-x catalysts.

over the CuMgAl-LDH-x catalysts. As presented in Table 1, CuMgAl-LDH-1.25 and CuMgAl-LDH-1.0 possess a much larger surface area of Cu<sup>0</sup> active sites and smaller Cu particle sizes, indicating a much higher Cu dispersion than the other samples, in consistent with the results of H<sub>2</sub>-TPR and XRD.

#### 3.1.4. Surface acidity and basicity

In order to evaluate the acidic and basic sites on the catalysts,  $NH_3$ -TPD and  $CO_2$ -TPD were employed and the results were depicted in Fig. 6. The  $CO_2$ -TPD profiles of the CuMgAl-LDH-x samples in Fig. 6(a) point out that the desorption peaks at 373 - 573 K are attributed to the weak basic sites, and the desorption peaks at 573 - 973 K are interpreted to medium-strong basic sites. The other peaks with desorption temperature higher than 973 K belong to the strong basic sites. Generally, the weak basic sites of the LDH are originated from the -OH on the metal oxides, and the medium and strong basic sites are derived from the M–O and lattice oxygen ( $O^{2-}$ ), respectively [30]. From Fig. 6(a), all the CuMgAl-LDH-x samples present weak and moderate strong basic sites, indicating that the oxygen on the oxides surface



Fig. 6. (a)  $CO_2$ -TPD and (b)  $NH_3$ -TPD profiles of the CuMgAl-LDH-x catalysts.

mainly exists in the form of -OH and M-O groups. The double-medium strong basic sites could be attributed to the Cu-O-Mg and Cu-O-Al structures after calcination, which is consistent with the XRD and FT-IR results. The Cu-O-Mg structures contain CuO and MgO components, which possess strong alkalinity with a high  $CO_2$  desorption temperature. With the decrease of Mg/Al ratio, the proportion of MgO decreased and the desorption peaks of Cu-O-Mg was decreased and shifted to lower temperatures [31,32]. In addition, the oxygen atoms in the M–O transferred to surface hydroxyl groups with the decrease of Mg/Al ratio, which could gradually increase the weak basic sites of the samples.

The NH<sub>3</sub>-TPD profiles in Fig. 6(b) display the desorption peaks in NH<sub>3</sub>-TPD of weakly acidic sites at 350-500 K, medium-strong acidic sites at 500-600 K, and strong acidic sites above 600 K [33]. It is noted that all the CuMgAl-LDH-x catalysts present weak and strong acidic sites. The low-temperature desorption peaks are corresponding to the physical adsorption of NH<sub>3</sub> on the catalyst surface, which is mainly determined by the specific surface area of the catalyst. Therefore, a larger specific surface area leads to a high density of the weak acidic sites. The high-temperature peaks are attributed to the desorption of NH<sub>3</sub> on the Lewis acidic site of metal oxides (Al<sub>2</sub>O<sub>3</sub>), which is consistent with the continuous introduction of the strong acidic sites of Al<sub>2</sub>O<sub>3</sub> via reducing the Mg/Al ratio [17,18].

# 3.2. Catalytic activity of DMO hydrogenation over the CuMgAl-LDH catalysts

The catalytic performance of the CuMgAl-LDH catalysts was investigated to understand their catalytic activity of DMO hydrogenation. As shown in Fig. 7, all of the catalysts exhibit DMO conversion of approximate 100 %. The selectivity of ethanol shows an opposite trend compared with the selectivity toward  $C_{3}$ - $C_{4}$  products (including n-propanol, ethylene glycol monomethyl ether, and diethyl ether) with the variation of Mg/Al molar ratio. And the highest ethanol yield of 83.75 % is achieved over the CuMgAl-LDH-1.25 catalyst at a WHSV of 0.5 h<sup>-1</sup>.

It has been reported that Cu is responsible for the  $H_2$  adsorption and dissociation, and Cu<sub>2</sub>O functions as electrophilic or Lewis acidic sites to polarize the C=O bond via the electron lone pair in oxygen, synergistically improving the hydrogenation activity [6,9]. Combined with the results of characterization, it could be proposed that both the surface density of the Cu active sites and the basic/acidic sites are contributed to the catalytic activity. The CuMgAl-LDH-x catalysts with low Mg/Al



Fig. 7. Catalytic activity of the CuMgAl-LDH catalyst for DMO hydrogenation. Reaction condition: WHSV =  $0.5 h^{-1}$ , H<sub>2</sub>/DMO = 200 (mol/mol), T = 553 K, P = 3.0 MPa.

ratio (e.g., 1.0 and 1.25), which possess higher surface area of Cu species (57.89 m<sup>2</sup>/g of CuMgAl-LDH-1.25 and 66.45 m<sup>2</sup>/g of CuMgAl-LDH-1.0), exhibit excellent catalytic activity. Previous work has reported that the DMO hydrogenation is a cascade reaction, involving the DMO hydrogenation to ethylene glycol, and then the further hydrogenation of ethylene glycol to ethanol. Therefore, the deep hydrogenation to ethanol can be promoted by the fast dissociation rate of H<sub>2</sub>induced by the Cu<sup>0</sup> sites. However, the yield of ethanol over the CuMgAl-LDH-1.25 catalyst is much higher than that of CuMgAl-LDH-1.0. On the other hand, appropriate Lewis acidic sites could polarize the C=O/C-O bond via the electron lone pair in oxygen to enhance the hydrogenation reaction, but strong acidic sites will lead to the formation of alkanes [34,35]. Moreover, the basic sites facilitate the Guerbet reaction to from C<sub>3</sub>-C<sub>4</sub> byproducts (n-propanol, 2-methyl-n-propanol, tbutanol, n-butanol). In our system, the moderate Mg/Al ratio of the LDH facilitated the formation of the regular laminate structures to highly disperse Cu nanoparticles and produce appropriate Lewis acidic sites, which leads to the highest yield ethanol in the DMO hydrogenation over CuMgAl-LDH-1.25. On the basis of the characterization and the catalytic performance results, we could summarize that the



Fig. 8. Stability test of the CuMgAl-LDH-1.25 catalyst. Condition: WHSV = 0.5  $h^{-1}$ , H<sub>2</sub>/DMO = 200 (mol/mol), T = 553 K, P = 3.0 MPa.

combined effect of the high surface density of Cu sites and acidic sites play a synergistic role in the catalytic activity of DMO hydrogenation.

### 3.3. The catalytic stability

The catalytic stability of catalysts is significant for the hydrogenation of DMO to ethanol from the viewpoint of further industrialization, because Cu active species are readily to agglomerate and sinter at high temperatures. The CuMgAI-LDH-1.25 catalyst was selected to perform a 100-h long-term stability test. As shown in Fig. 8, the catalyst exhibits steady conversion of DMO and yield of ethanol (80 %~84 %) during 100-h reaction. The morphology and FT-IR characterizations have confirmed the formation of LDH structures, which could confine the anchored Cu nanoparticles and thereby enhance the catalytic stability. In addition, the doping of acid oxides can also promoted the stability of catalysts due to its inhibition of agglomeration [18,23]. Therefore, we conclude that the moderate amount of Al in the CuMgAI-LDH-1.25 catalyst successfully decreased the degree of aggregation, which can maintain the excellent selectivity of ethanol and suppress by-reactions after a long-term reaction [36].

### 4. Conclusions

The CuMgAl-LDH catalysts were prepared by a facile co-precipitation method to confine Cu active sites in the layered double hydroxide for the hydrogenation of DMO to ethanol. The Mg/Al molar ratio was tuned to investigate their effects on the evolution of active sites and the catalytic performance was evaluated to get insight into structure-activity relationship for DMO hydrogenation. The results indicate that the Mg/Al ratio significantly affacts the microstructures of hydrotalcite and the surface acidic sites, as well as the Cu dispersion over the catalysts. The CuMgAl-LDH-1.25 catalyst achieves a remarkable catalytic performance with DMO conversion of ca. 100 % and ethanlol selectivity exceeding 83 %, ascribed to the regular layered structures, high surface Cu dispersion and proper acidic sites. Furthermore, the laminate structures of LDH can anchor Cu nanoparticles between the neighbour layers, leading to a steady performance during 100-h reaction. Our work provides a simple and accessible approach to anchor Cu nanoparticles into the layered double hydroxide, and paves a new way to the design of efficient and stable Cu-based catalysts for the related reactions.

### CRediT authorship contribution statement

Jianzhe Shi: Methodology, Validation, Formal analysis, Writing - original draft. Yan He: Validation, Formal analysis, Investigation. Kui

Ma: Conceptualization, Supervision, Writing - review & editing. Siyang Tang: Validation, Investigation. Changjun Liu: Validation, Investigation. Hairong Yue: Conceptualization, Supervision, Writing review & editing. Bin Liang: Conceptualization, Supervision.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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J. Shi, et al.

### Catalysis Today xxx (xxxx) xxx-xxx

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