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### 1. Introduction

EtOH is an interesting and versatile candidate for the synthesis of various important products such as polymers, synthetic fuel to be used in automobiles and other important chemicals.<sup>1</sup> Currently, EtOH is produced using mainly two approaches, the first is the fermentation process of sugars, while the second approach is through the catalytic conversion of syngas  $(CO + H_2)$ . However, several disadvantages such as poor selectivity, fast chain growth of C2 intermediates, low yield, and the high cost required for carrying out massive research and development effort have restricted their wide practical application.<sup>2,3</sup> Alternatively, the hydrogenation reaction of dimethyl oxalate (DMO) to produce the important platform chemicals methyl



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The environmentally benign hydrogenation reaction of dimethyl oxalate (DMO) to produce the important platform chemicals methyl glycolate (MG), ethylene glycol (EG) and ethanol (EtOH) has gained significant importance in recent years. In this work, novel and highly efficient catalysts composed of Zn-doped lamellar Cu nanocrystals supported on porous MgO nanoparticles were synthesized using an innovative and facile sonochemical approach, and applied in the DMO hydrogenation reaction. The obtained catalytic activity revealed that the addition of Zn was found to significantly enhance the catalytic performance. The product selectivity dramatically changed from MG selectivity (88%) for the un-doped catalyst to a high EtOH selectivity of 98% for the Zn-doped Cu/MgO catalyst. To understand the relationship between the catalyst structure and the catalytic performance, the prepared, reduced and spent Cu/MgO and Zn-doped Cu/MgO catalysts were thoroughly characterized using XRD, TEM, HR-TEM, EDS mapping analysis, N<sub>2</sub> physical adsorption, XPS, Cu-LMM, FTIR and H<sub>2</sub>-TPR techniques. The enhancement in the deep hydrogenation reaction for the Zn-doped catalyst to produce high EtOH selectivity is attributed to the improved dispersion, crystal defects, surface segregation and the synergistic ratio effect between  $Cu^{0}/(Cu^{0} + Cu^{+})$  in the catalyst. Moreover, the produced catalysts maintained high efficiency for DMO conversion and EtOH selectivity with long-term stability for at least 200 h. The developed sonochemical approach in this study seems to be promising for the green and surfactant-free aqueous synthesis of highly efficient heterogeneous catalysts.

glycolate (MG), ethylene glycol (EG), and ethanol (EtOH) has gained significant and great interest in recent few years as an environmentally benign and clean reaction for the utilization of biomass and coal.<sup>4</sup>

Numerous research groups have focused their effort towards the development of several approaches for the synthesis of highly efficient catalysts to be used in the DMO hydrogenation reaction and obtain high selectivity ratios for MG, EG and EtOH under mild reaction conditions. Particularly, Cu-based catalysts exhibited superb catalytic activity in the production of high EG and EtOH selectivity.<sup>5,6</sup> Nonetheless, the deactivation of the catalyst, which results from Cu sintering and leaching of silica, makes the longevity as well as stability unsatisfactory and consequently limits the catalyst application in the industrial scale.<sup>7</sup> Therefore, the development of approaches for enhancing the catalyst dispersion and making the sintering resistance highly efficient in the DMO hydrogenation reaction is of great interest. Incorporation of second metals as promoters to the catalysts or modification of the catalyst support via another oxide material could be an effective approach to modify the electronic characteristics and crystal structures of the active phase and thus



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control the selectivity to the target products. For instance, Kong *et al.* obtained high EG selectivity through the hydrogenation reaction of DMO using Mg<sup>2+</sup> doped nanoscale Cu–Mg/ZnO catalysts prepared by the co-precipitation method.<sup>8</sup> Jung Li *et al.* reported that doping of Ga<sup>3+</sup> promoted Cu catalysts with Zn can dramatically improve their stability against metal sintering and enable high EG selectivity.<sup>9</sup> Later, Qi *et al.* synthesized CuO–ZnO/SiO<sub>2</sub> catalysts with various Zn/Cu molar ratios using a precipitation method and observed high EG selectivity.<sup>7</sup>

Herein, unlike the previously employed conventional synthesis approaches (the hydrolysis precipitation, urea-assisted gelation, hydrothermal and ammonia evaporation methods) for the synthesis of Cu-based catalysts<sup>10-12</sup> with a long synthesis reaction time and additional rigorous protection conditions, we have successfully developed a novel, convenient and eco-friendly sonochemical approach for the synthesis of Zn-doped lamellar Cu nanocrystals supported on MgO NPs and then both un-doped and Zn-doped Cu/MgO catalysts were employed in the DMO hydrogenation reaction. Porous MgO NPs are used as the catalyst support due to the irreducible and relatively inactive oxide, and they are also widely used as a catalyst support in several catalysis reactions such as CO<sub>2</sub> reforming of methane, reduction of *p*-nitrophenol and oxidative dehydrogenation of propane.<sup>13</sup> Unlike the most inorganic materials such as SiO<sub>2</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and active carbon, which have been extensively reported in the last few years as supports to Cu NPs in the DMO hydrogenation reaction, in this study, MgO NPs were employed as robust support materials. The synthesized Zn-doped Cu/MgO catalysts were subjected to comprehensive TEM, HR-TEM, EDS mapping, XRD, N<sub>2</sub> physical adsorption, XPS, FTIR, H<sub>2</sub>-TPR, and Cu-LMM analyses to well understand the relationships between the crystal structure and the catalytic activity.

### 2. Experimental section

#### 2.1. Chemicals and materials

Magnesium nitrate (Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), cupric nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>· 3H<sub>2</sub>O), zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), sodium hydroxide (NaOH), and ammonium hydroxide (NH<sub>4</sub>OH), were purchased from Sinopharm Chemical Reagent Co., Ltd, China.

#### 2.2. Synthesis of the Cu/MgO catalyst

Firstly, the synthesis of MgO NPs as a support material was carried out using a one-pot sonochemical method. Typically, 4 g of  $Mg(NO_3)_2 \cdot 6H_2O$  was dispersed in a suitable amount of di-H<sub>2</sub>O and the solution was transferred immediately to an ultrasonication vessel with a pulsed system of 3 s (ON):1 s (OFF). After that, NaOH was rapidly added into the reaction mixture within a few minutes of the ultrasonication. The reaction was continued for 60 min and the total reaction time is 20 min, and the ultrasonication was then turned off. The obtained MgO NPs were washed several times using water and ethanol. The precipitate was collected by means of centrifugation and then dried in a vacuum evaporator. Crystallization of the as-synthesized porous MgO NPs was carried out by

heating the sample in a boat crucible at a temperature of 400  $^\circ \rm C$  in open air.

50 wt% Cu with a lamellar structure wrapped on the MgO NPs was synthesized using a one-pot *in situ* sonochemical method. Typically, the above prepared MgO NPs and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O were dispersed in a suitable amount of di-H<sub>2</sub>O using a magnetic stirrer. The mixture was transferred to an ultrasonication reactor chamber for 30 min. Within a few minutes of initiating the ultrasonication, a solution of NaOH was injected rapidly. The reaction was continued, and after that, the ultrasonication was turned off. The resultant Cu/MgO catalyst was washed several times using water and ethanol and the precipitate was collected by means of centrifugation, and then dried at 80 °C. The prepared Cu/MgO catalyst was calcined at 400 °C in an oven.

#### 2.3. Synthesis of the Zn-doped Cu/MgO catalyst

A one-pot sonochemical route was designed to synthesize the Zn doped-Cu/MgO NP catalyst. Typically, 1 mol of  $Zn(NO_3)_2 \cdot 6H_2O$ , 3 mol of  $Cu(NO_3)_2 \cdot 6H_2O$  and the above prepared MgO NPs were dispersed in an aqueous solution. After that, the mixture was transferred to an ultrasonication vessel. 3 M NaOH was injected rapidly within 7 min of starting the ultrasonication process and the reaction was continued for 30 min and then turned off. The produced Zn-doped Cu/MgO NPs were washed several times using mixture of water and ethanol and the precipitated was collected through the centrifugation, and then dried at 80 °C for 6 h. The precipitate was collected using centrifugation, and then dried at 80 °C for 6 h. Finally, the catalyst was calcined at 400 °C for 3 h.

#### 2.4. Characterization methods

Powder X-ray diffraction (XRD) patterns were used to monitor the crystal structure and were collected on a Shimadzu XRD-6000 diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) at 40 kV and 150 mA and in the  $2\theta$  scanning range between 5° and 85°. A Hitachi H-7650 instrument, operated at an acceleration voltage of 100 kV and (HRTEM, JEM 2100F) was employed to investigate the shape and size of the catalysts, meanwhile, the chemical compositions of the catalysts were determined through EDS point and mapping analysis coupled with TEM. The pore size distribution and specific surface area were characterized using a N<sub>2</sub> adsorption analyzer. The BET surface area and the pore size distribution curves were estimated based on the Brunauer-Emmett-Teller model and the Barrett-Joyner-Halenda method. An inductively coupled plasma optical emission spectrometer (ICP-OES, Optima2100DV, PerkinElmer) was used to determine the actual Cu loading in the prepared catalysts. X-ray photoelectron spectroscopy was utilized to identify the elemental valence of the catalysts. H2-TPR experiments were carried out to measure the reducibility of the catalysis in the temperature range of 0 to 800  $^{\circ}$ C. In the range of 4000–500 cm<sup>-1</sup>, Fourier transform infrared spectroscopy (FTIR) was performed to analyse the functional groups on the catalyst surfaces.

#### 2.5. DMO hydrogenation reaction test

The catalytic performance experiment was performed using 0.3 g of the calcined catalysts and using a stainless steel fixed-bed

reactor at different reaction temperatures (200–240 °C). However, before starting the reaction, the catalyst was reduced in a stream of mixed 10% H<sub>2</sub> in N<sub>2</sub> at 280 °C for a period of 4 h. For the reaction, 12.5 wt% DMO (purity > 99.5%) in methanol and pure H<sub>2</sub> were fed into the reactor at a molar ratio of 200 for H<sub>2</sub>/DMO, meanwhile, the pressure system is set at 2.5 MPa. A gas chromatograph (Shimadzu Trace GC ultra) fitted with a 30 m HP-5 capillary column and a flame ionization detector (FID) was used to analyze the catalyst performance.

### 3. Results and discussion

The morphology and size of the synthesized un-doped and Zn-doped Cu/MgO catalysts were analyzed using transmission electron microscopy. Fig. 1a and b show the TEM images of the porous MgO NPs synthesized using a sonochemical method. Fig. 1c and d show the TEM images for the Cu/MgO NPs, and from the figures, it can be seen that the lamellar Cu nanocrystals were impregnated into the MgO NPs with a homogenous and uniform narrow particle size distribution. Fig. 1e and f show the HRTEM images of the Cu/MgO NP catalyst, and from the figures, the lattice fringes of the lamellar CuO nanocrystal could be

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Fig. 1 (a and b) TEM images of the MgO NPs, (c and d) TEM images of the Cu/MgO NPs and (e and f) HRTEM images for the Cu/MgO NP catalyst.

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Fig. 2 EDS mapping analysis of the Cu/MgO catalyst.

observed clearly, which confirms the highly crystalline structure of the CuO nanocrystals. The interplanar distance value was calculated from the adjacent lattice fringes to be 0.247 nm for the (002) plane of the CuO phase.<sup>13</sup> Fig. 2 shows the EDS mapping analysis images of the MgO NPs impregnated with the lamellar Cu NP catalyst. From the figure, a spatial distribution of the elements Mg, O, and Cu is observed. Fig. 2a shows the TEM image of the Cu/MgO NP catalyst, which is to be characterized by EDS mapping analysis. Fig. 2b displays the EDS mapping analysis of the three elements Mg, O and Cu together in the Cu/MgO catalyst and the images in Fig. 2c–e reveal the elemental maps of the three elements separately.

Fig. 3 shows the TEM and HRTEM images for the Zn-doped Cu/MgO catalyst. From Fig. 3a and b, it can be observed that rod-like shapes are obtained within particle grain growth and are highly crystalline after doping with Zn metal. Besides, the calculated interplanar distance values from the HRTEM images in Fig. 3c and d were found to be 0.241 and 0.5 nm for the (002) and (001) planes of the CuO and ZnO phases, respectively, in the Zn-doped Cu/MgO catalyst, confirming the co-existence of both Cu and Zn NPs in the catalyst. It is noteworthy that the addition of Zn metal as a dopant has created the so-called crystal defects in the Zn-doped Cu/MgO catalyst, as shown in the HRTEM images in Fig. 3e and f. The presence of Zn, Cu, Mg and O elements together in the Zn-doped Cu/MgO catalyst is confirmed through EDS elemental analysis as shown in Fig. 4b, and the elemental composition is 56, 21, 16 and 7 wt% for Cu, O, Mg and Zn, respectively. Also the good homogenous distribution of the elements in the Zn-doped Cu/MgO catalyst is confirmed through EDS mapping analysis, as shown in Fig. 4. In addition, the obtained results from ICP-OES analysis demonstrated that the real Cu loading values in the un-doped and Zn-doped catalysts are 48.1 and 48.5, respectively, which are close to each other and a pre-set value of 50 wt%.

To study the crystal structure and Cu dispersion of the two prepared catalysts, XRD patterns for the calcined and reduced Cu/MgO and Zn doped Cu/MgO catalysts are recorded and shown in Fig. 5. From the XRD pattern of the calcined Cu/MgO catalyst, both un-doped and Zn-doped catalysts are found to show characteristic peaks for the crystalline phase of MgO (PDF no.: 45-0946),



Fig. 3 (a-d) TEM and HRTEM images of the Zn-doped Cu/MgO catalyst and (e and f) TEM images showing the crystal defects in the Zn-doped Cu/MgO catalyst.

and the CuO phase (PDF no.: 45-0937), while additional peaks for ZnO are only detected for the Zn-doped catalyst (PDF no.: 001-1136). It is noteworthy that significantly high intensities of the CuO peaks are observed for the Zn-doped catalyst, reflecting the role of Zn doping on the dramatically improved crystalline structure of the catalyst. Fig. 5b shows the XRD patterns for the reduced catalysts. From the figure, for both catalysts, characteristic peaks for the reduced Cu metal are detected at  $2\theta = 43.3^{\circ}$ ,  $50.5^{\circ}$  and  $74.1^{\circ}$  (card no.: 04-0836), meanwhile, a similar behaviour with large differences in the peak intensities is observed again for the reduced catalysts, which confirms the importance of Zn in enhancing the reduced catalyst crystallinity. Besides, an additional small peak at 37° corresponding to  $Cu_2O$  (JCPDS 05-0667) is observed, which confirms that  $Cu^+$ existed in both catalysts along with Cu<sup>0</sup> after reduction.<sup>3</sup> It is noteworthy that the observed shift to a higher  $2\theta$  value for the reduced Zn-doped Cu/MgO catalysts in the high magnification image in the inset of Fig. 5b is mostly attributed to the crystal disorders and defects,<sup>14,15</sup> which supports the obtained above TEM result. On the other hand, as can be seen from the XRD pattern, the Scherrer formula  $(D = K\lambda/\beta\cos\theta)$  was employed to measure the crystallite sizes of the reduced un-doped and



Fig. 4 EDS mapping and elemental analysis of the Zn-doped Cu/MgO NP catalyst.

Zn-doped Cu/MgO catalysts and the calculated sizes are 31.4 and 38 nm, respectively.

The BET N<sub>2</sub> adsorption/desorption and BJH methods were employed to measure the specific surface area  $(S_{\text{BET}})$  and pore size distribution of the prepared catalysts. Fig. 6a shows the N<sub>2</sub> adsorption/desorption isotherms for the Cu/MgO NP catalysts, and from the figure, the un-doped and Zn doped Cu/MgO catalysts were found to exhibit Langmuir type IV isotherms. The obtained IV isotherm for the prepared catalysts is reflecting the typical shape of a mesoporous material based on the IUPAC classification.<sup>16</sup> Besides, a H2 hysteresis loop type is observed for the Zn-doped catalyst, which mostly comes from the presence of uniform channel-like pores and pores within narrow mouths (ink-bottle pores).<sup>17</sup> The estimated specific surface area values through the BET method are 32  $m^2 g^{-1}$  for the Cu/MgO catalyst and 39 m<sup>2</sup> g<sup>-1</sup> for the Zn doped Cu/MgO catalyst. Fig. 6b shows the pore diameter curves for the prepared materials, and the estimated average pore diameters based on the BJH methods are 50 nm for the Cu/MgO NPs and 48 nm for the Zn doped catalyst. In addition, the estimated copper surface areas for the un-doped and Zn-doped Cu/MgO catalysts are 18 and 26 m<sup>2</sup>  $g_{cat}^{-1}$ , respectively, according to the calculation from the dissociative N<sub>2</sub>O chemisorption method.

The surface properties of the prepared catalysts were investigated through FTIR absorption analysis, which was performed in the spectral range of 4000 to 400 cm<sup>-1</sup>. Fig. 7 shows the FTIR



Fig. 5 XRD pattern of the (a) calcined and (b) reduced Cu/MgO and ZnCu/MgO catalysts synthesized by a sonochemical method.

spectra for the un-doped Cu/MgO and Zn doped catalysts synthesized by a sonochemical method. In the spectra of both catalysts, the peak at 400 cm<sup>-1</sup> is assigned to the stretching vibration of Cu–O, while the peak at 490 cm<sup>-1</sup> for the Zn-doped catalyst corresponds to the stretching vibration of Zn–O. In addition, a broad absorption band at around 3500 cm<sup>-1</sup> is observed, which corresponds to the OH-stretching vibrations of the hydroxyl group in the MgO NPs. Besides, the peak at around 400 cm<sup>-1</sup> is attributed to the Mg–O stretching vibration, while the bands in the range of 1500 cm<sup>-1</sup> are assigned to the –OH asymmetric stretching mode of water molecules.<sup>18</sup>

Reducibility measurement is an important tool to measure the reduction behaviour of a catalyst and consequently the active phase in the catalysis reaction. Therefore, H<sub>2</sub>-TPR analysis was utilized to study the degree of reduction as well as the metal–support interaction for the prepared catalysts. Fig. 8 shows the H<sub>2</sub>-TPR profile for the un-doped and Zn-doped Cu/MgO catalysts. From the H<sub>2</sub>-TPR profile, only a single distinguished peak is observed for both catalysts, meanwhile, the Zn-doped Cu/MgO catalyst displayed a reduction peak at a lower temperature of 287 °C compared with a reduction temperature of 296 °C for the un-doped Cu/MgO catalyst, which reflected the easy reduction of the Zn-doped catalyst. Moreover,



Fig. 6  $N_2$  physisorption results. (a)  $N_2$  adsorption–desorption isotherms and (b) BJH pore size distribution curves for the Cu/MgO and Zn-doped Cu/MgO catalysts.

the observed high intensity and widening in the reduction peak for the Zn-doped Cu/MgO catalyst reflected the strong interaction between the Zn and CuO NPs, which reduced the strong interaction between the catalyst support MgO and Cu species, and thereby improved the catalyst dispersion, which leads to the consumption of more hydrogen, and consequently many more CuO NPs were reduced into the active metallic Cu species. Therefore, Zn incorporation into the catalyst increased the dispersion and the reducibility. Similar results were reported previously by Qi *et al.*<sup>7</sup>

XPS analysis was carried out to determine the surface composition and valence state of the calcined Cu/MgO catalysts. Fig. 9a shows peaks corresponding to Mg, Cu and O in the XPS survey spectra for the un-doped Cu/MgO catalyst and Mg, Cu, Zn and O in the XPS survey spectra for the Zn-doped catalyst. Fig. 9b shows high resolution spectra of Cu, and from the figure, two major peaks positioned at 933 eV and 953 eV for Cu( $2p_{3/2}$ ) and Cu( $2p_{1/2}$ ) with a splitting of 20 eV corresponding to Cu<sup>2+</sup> of Cu<sup>0</sup> on the surface of both catalysts were observed, while two other



Fig. 7 FTIR spectra for the Cu/MgO and Zn-doped Cu/MgO catalysts.



Fig. 8 H<sub>2</sub>-TPR profile for the Cu/MgO and Zn-doped Cu/MgO catalysts.

shake-up peaks at 942 eV and 962 eV further confirmed the existence of the  ${\rm Cu}^{2+}$  chemical state.<sup>19</sup>

Fig. 9c shows Mg high resolution spectra, and the spectra show a single peak at 1303.2 for Cu/MgO and 1304 eV for the Zn doped-Cu/MgO catalysts, which are typically due to the Mg<sup>2+</sup> species in the two catalysts. High resolution O spectra are shown in Fig. 9d, and from the figure, two similar peaks were found for the two catalysts at 529.4 and 531.4 eV. The first peak corresponds to the lattice oxygen in MgO and Cu, while the second peak at 531.4 eV may have originated from the adsorbed oxygen and water molecules on the surface of the catalyst.<sup>20,21</sup> It is worth mentioning that the shift in the binding energy peak for the Zn-doped catalyst (Fig. 9) is mostly attributed to the resulting crystal defects of the catalyst after doping with Zn NPs, which is in good agreement with the obtained above TEM and XRD results.<sup>22</sup>

Fig. 10 shows Cu-LMM Auger electron spectra for the reduced un-doped and Zn-doped Cu/MgO catalysts to distinguish the concentration of the active sites  $Cu^0$  and  $Cu^+$  in the catalysts. From the figure, two peaks at 911.3 eV and 916.2 eV for the sonochemically synthesized catalysts are found to be overlapping and they correspond to the kinetic energy of  $Cu^+$  and  $Cu^0$ , respectively. The calculated deconvolution results revealed that the intensity of  $Cu^0/(Cu^0 + Cu^+)$  is 59% and 68.5% for the un-doped and Zn-doped Cu/MgO catalysts, respectively.

The catalytic activities of the calcined catalysts were investigated for the hydrogenation reaction of DMO at different temperatures (200–240 °C). Fig. 11 shows the effect of the reaction temperature on the DMO conversion ratio. From the figure, it can be seen that the DMO conversion rate increased progressively and reached the maximum of 100% at 230 °C and then remained stable for the un-doped Cu/MgO catalyst, while the DMO conversion ratio is much improved for the Zn-doped Cu/MgO catalyst and reached 100% at 220 °C and then remained stable at 100% ratio with a further increase in the reaction temperature up to 240 °C.

Fig. 12 shows the EtOH and MG selectivity at different reaction temperatures for the un-doped and Zn-doped Cu/MgO catalysts. As can be seen from Fig. 12a, the Cu/MgO catalyst shows a relatively low EtOH selectivity at all reaction temperatures. However, a remarkable enhancement in the EtOH selectivity is observed for the Zn-doped Cu/MgO catalyst and the selectivity increased dramatically with reaction temperature to reach the maximum value of 98% at 240 °C. Fig. 12b shows the MG selectivity of the two catalysts, and from the figure, it can be observed that the MG selectivity of the un-doped Cu/MgO catalyst reached the maximum value of 88% at 210 °C and then decreased along with the increase in the reaction temperatures.

Generally, the DMO hydrogenation reaction involves the following successive reactions: MG formation, followed by EG formation and finally the deep hydrogenation reaction leading to the EtOH product. It is worth mentioning that, in most of the reported studies on the DMO hydrogenation reaction, it has been confirmed that Cu<sup>0</sup> is the main active site and primarily responsible for the activity of the catalyst, and also a proper amount of Cu<sup>+</sup>/Cu<sup>0</sup> plays a crucial role in controlling both DMO conversion and product selectivity ratios in the DMO hydrogenation reaction.<sup>1</sup> Thus, in this study, the obtained high DMO conversion ratio for the Zn-doped Cu/MgO catalyst at all reaction temperatures below 230 °C is mostly attributed to the high Cu<sup>0</sup> ratio in the catalyst. A similar result is also recently reported by our group for the obtained high DMO conversion ratio at a high concentration of Cu<sup>0</sup> in the Cu/SiO<sub>2</sub> catalytic system.<sup>23</sup>

According to the series of characterization experiments performed for our Zn-doped Cu/MgO catalyst, the obtained remarkable high EtOH selectivity will be explained in the following points. Incorporation of Zn into the Cu/MgO catalyst resulted in an improvement in the copper dispersion, and subsequently increased the active sites *i.e.*, Cu species and the catalytic activity. Furthermore, the generated crystal defects in the Zn-doped catalyst, as confirmed by the obtained above TEM images, also contributed to promote the dispersion of the Cu species, and consequently provided more active sites and then boosted the deep hydrogenation reaction to produce EtOH.



Fig. 9 (a) XPS survey spectra of the Cu/MgO and Zn-doped Cu/MgO catalysts and (b-d) are high resolution Cu, Mg and O spectra, respectively.

Moreover, the ratio of  $Cu^0/(Cu^0 + Cu^+)$  increased from 59% to be 68.5% for the Zn-doped Cu/MgO catalyst, and based on the work reported by Gong *et al.*,  $Cu^0$  is the sole active site for the chemoselective synthesis of ethanol and is responsible for the activity of the catalyst, therefore, the obtained high EtOH selectivity in the Zn-doped catalyst compared with the un-doped one is mostly ascribed to the pivotal role of the  $Cu^0$  species. In addition, from the obtained  $H_2$ -TPR results, incorporation of Zn into the Cu/MgO catalysts caused a reduction in the strong interaction between the catalyst supports MgO and Cu species, and thereby improved the Cu dispersion as well as reducibility, and thus the catalytic activity.

On the other hand, to understand the obtained relatively high MG selectivity of 88% for the un-doped Cu/MgO catalyst, and based on the recent research on the DMO hydrogenation reaction,  $Cu^+$  is more disposed to stabilize the intermediate product of DMO hydrogenation such as MG compared with  $Cu^{0.24}$  Therefore, MG is formed when the concentration of  $Cu^+$ is more or in a proper amount. Chen *et al.* employed Ag NPs to stabilize the Cu<sup>+</sup> concentration in the Ag-CuO<sub>r</sub> catalyst to obtain high MG selectivity since the high concentration of Cu<sup>+</sup> on the catalyst surface would enhance the activation of the acyl and methoxy groups of MG to compensate for the weakening of H<sub>2</sub> activation because of the fewer Cu<sup>0</sup> species in the catalyst surface.<sup>25</sup> Thus, this agrees well with the obtained results in our study and the obtained relatively high MG selectivity of the un-doped Cu/MgO catalyst is ascribed to a high Cu<sup>+</sup>/(Cu<sup>+</sup> + Cu<sup>0</sup>) ratio of 41%. Moreover, based on the above obtained FTIR result, the un-doped catalyst possesses a large amount of OH groups on the surface and it is worth noting that Wen et al. and Yin et al. have found that the presence of hydroxyl groups on the surface of the catalysts profoundly promotes the hydrogenation process of DMO to MG,<sup>24,26</sup> because the increase in the OH amount leads to an increase in the amount of weak acids for the catalysts and consequently makes the desorption process of MG over EG and EtOH easier.27,28

The long term stability of catalysts is an important indicator of the potential of their catalytic industrial application. Thus,



Fig. 10 Cu-LMM Auger spectra for the (a) Cu/MgO and (b) Zn-doped Cu/MgO catalysts.



Fig. 11 DMO conversion ratios for the un-doped and Zn-doped Cu/MgO catalysts at different reaction temperatures.

the Zn-doped Cu/MgO catalyst was subjected to the DMO hydrogenation reaction for a period of 200 h and the catalyst performance *versus* time on stream is shown in Fig. 13. As shown in the figure, the catalyst maintained high ratios of both



Fig. 12 EtOH and MG selectivity for the un-doped and Zn-doped Cu/MgO catalysts at different reaction temperatures.



Fig. 13 Catalytic performance of the Zn-doped Cu/MgO catalyst for 200 h of time on stream.



Fig. 14 TEM and HR-TEM images of the spent catalyst (a and b) Cu/MgO and (c–e) Zn-doped Cu/MgO catalysts and (f) HR-TEM of Zn-doped Cu/MgO catalysts.

DMO conversion as well as EtOH selectivity under reaction conditions of  $H_2/DMO$  of 200 mol mol<sup>-1</sup>, 2.5 MPa, and WLHSVDMO of 0.257 g g<sub>catal</sub><sup>-1</sup> h<sup>-1</sup>, which confirms its high stability. The morphology of the spent Cu/MgO catalysts in the DMO hydrogenation reaction was analyzed by TEM as shown in Fig. 14. From the figures, it can be seen that the shape of the un-doped Cu/MgO catalyst changed to a core/shell like-shape, while the shape of the Zn-doped Cu/MgO catalyst was stable and without any dramatic evolution, which reflected the high stability and this agrees well with the obtained long-term stability test for 200 h. Notably, as can be obviously seen from the HRTEM images in Fig. 14, the lattice fringes of the Cu NPs reflect the highly crystalline structure of the Cu NPs in the spent catalysts.

### 4. Conclusions

In summary, a highly efficient and surfactant-less sonochemical approach was demonstrated for the facile synthesis of Cu/MgO and Zn-doped Cu/MgO catalysts. Both catalysts were applied in the DMO hydrogenation reaction and the un-doped Cu/MgO catalyst exhibited a relatively high MG selectivity at 210  $^\circ$ C,

while the Zn-doped Cu/MgO catalyst displayed a high EtOH selectivity of 98% at 240 °C. Moreover, the synthesized Zn-doped Cu/MgO catalyst maintained high efficiency for DMO conversion and EtOH selectivity with long-term stability for at least 200 h. In light of the full characterization of the catalyst, the obtained high EtOH selectivity for the Zn-doped Cu/MgO catalyst is attributed to the improved dispersion, crystal defects, surface segregation with Zn doping and also a high ratio of 68.5 of  $Cu^0/(Cu^0 + Cu^+)$  in the catalyst. However, the relatively high MG selectivity of the un-doped Cu/MgO catalyst is mainly due to the high ratio of  $Cu^+/(Cu^+ + Cu^0)$  in the catalyst. The developed facile sonochemical route in this study is expected to extend to the synthesis of several highly efficient heterogeneous catalysts.

# Conflicts of interest

There are no conflicts to declare.

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### References

- 1 J. Gong, H. Yue, Y. Zhao, S. Zhao, L. Zhao, J. Lv, S. Wang and X. Ma, *J. Am. Chem. Soc.*, 2012, **134**, 13922–13925.
- 2 W. Di, J. H. Cheng, S. X. Tian, J. Li, J. Y. Chen and Q. Sun, *Appl. Catal.*, *A*, 2016, **510**, 244.
- 3 Z. Chen, J. Zhang, M. Abbas, Y. Xue, J. Sun, K. Liu and J. Chen, *Ind. Eng. Chem. Res.*, 2017, **56**, 9285–9292.
- 4 M. M. Li, L. Ye, J. Zheng, H. Fang, A. Kroner, Y. Yuan and S. E. Tsang, *Chem. Commun.*, 2016, **52**, 2569.
- 5 C. Wen, Y. Cui, W. Dai, S. Xie and K. Fan, *Chem. Commun.*, 2013, **49**, 5195.
- 6 J. Gong, H. Yue, Y. Zhao, S. Zhao, Li. Zhao, J. Lv, S. Wang and X. Ma, *J. Am. Chem. Soc.*, 2012, **134**, 13922–13925.
- 7 W. Qi, Q. Ling, D. Ding, C. Yazhong, S. Chengwu, C. Peng,
  W. Ye, Z. Qinghong, L. Rong and S. Hao, *Catal. Commun.*, 2018, 108, 68–72.
- 8 X. Kong, Z. Chen, Y. Wu, R. Wang, J. Chen and L. Ding, *RSC Adv.*, 2017, 7, 49548.
- 9 M. M. Jung, Li, J. Zheng, J. Qu, F. Liao, E. Raine1, W. C. H. Kuo, S. S. Su, P. Po, Y. Yuan and S. C. E. Tsang, *Sci. Rep.*, 2016, 6, 20527.
- 10 Y. Zhao, S. Li, Y. Wang, B. Shan, J. Zhang, S. Wang and X. Ma, *Chem. Eng. J.*, 2017, 313, 759–768.
- Y. Huang, H. Ariga, X. Zheng, X. Duan, S. Takakusagi, K. Asakura and Y. Yuan, *J. Catal.*, 2013, 307, 74–83.
- 12 S. Zhu, X. Gao, Y. Zhu, W. Fan, J. Wang and Y. Li, *Catal. Sci. Technol.*, 2015, 5, 1169–1180.
- 13 S. K. Alla, A. D. Verma, V. Kumar, R. K. Mandal, I. Sinha and N. K. Prasad, *RSC Adv.*, 2016, 6, 61927.

- 14 A. Sahai, Y. Kumar, V. Agarwal, S. F. Olive-M\_endez and N. Goswami, *J. Appl. Phys.*, 2014, **116**, 164315.
- 15 R. Kumaria, A. Sahaib and N. Goswami, *Prog. Nat. Sci.: Mater. Int.*, 2015, **25**, 300–309.
- 16 A. Parma, I. Freris, P. Riello, D. Cristofori, C. Fernandez, V. Amendol, M. Meneghettid and A. Benedetti, *J. Mater. Chem.*, 2012, 22, 19276.
- 17 M. Kruk and M. Jaroniec, *Chem. Mater.*, 2001, **13**, 3169–3183.
- 18 M. Rezaei, M. Khajenoori and B. Nematollahi, Powder Technol., 2011, 205, 112–116.
- 19 O. Akhavan and E. Ghaderia, J. Mater. Chem., 2011, 21, 12935.
- 20 H. Liu, Q. Hu, G. Fan, L. Yang and F. Li, *Catal. Sci. Technol.*, 2015, 5, 3960–3969.

- 21 D. P. Dubal, G. S. Gund, R. Holze, H. S. Jadhav, C. D. Lokhande and C. Park, *Dalton Trans.*, 2013, 42, 6459–6467.
- 22 X. Yang, X. Yu, M. Lin, M. Ge, Y. Zhaod and F. Wang, J. Mater. Chem. A, 2017, 5, 13799.
- 23 M. Abbas, Z. Chen, J. Zhang and J. Chen, *New J. Chem.*, 2018, 42, 10290.
- 24 C. Wen, Y. Cuia, X. Chen, B. Zong and W. L. Dai, Appl. Catal., B, 2015, 162, 483–493.
- 25 Y. Chen, L. Han, J. Zhu, P. Chen, S. Fan, G. Zhao, Y. Liu and Y. Lu, *Catal. Commun.*, 2017, 96, 58–62.
- 26 A. Yin, X. Guo, W. Dai and K. Fan, *Chem. Commun.*, 2010, 46, 4348.
- 27 A. Jentys, K. Kleestorfer and H. Vinek, *Microporous Mesoporous Mater.*, 1999, 27, 231.
- 28 S. Kwon, R. Vidic and E. Borguet, Surf. Sci., 2003, 522, 17.