Enhanced Ethylene Glycol Selectivity of CuO–La2O3/ZrO2 Catalyst: The Role of Calcination Temperatures

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ABSTRACT: The CuO–La2O3/ZrO2 catalysts calcined at different temperatures from 500 to 800 °C were studied for the hydrogenation of oxalates to ethylene glycol (EG). Along with the increase of calcination temperatures, the BET surface area, pore volume, and Cu dispersion decreased, whereas the crystallite sizes of Cu species increased. Interestingly, the superior performance such as a 98% selectivity of EG in dimethyl oxalate hydrogenation or a 96.5% selectivity of EG in diethyl oxalate hydrogenation was obtained over the catalyst calcined at 700 °C. Essentially, the surface synergism between Cu species and monoclinic ZrO2 was enhanced by the higher calcination temperature, resulting in the remarkable surface adsorption and activation of H2. Besides, the increase of calcination temperature significantly reduced the surface acidity and basicity, which could effectively suppress the byproduct formation.

INTRODUCTION

Reasonable and effective utilization of coal or biomass is an important goal of coal/biomass chemical engineering at present and in the future. Among the possible technical routes, ethylene glycol (EG), which is widely used as an important chemical in polyester manufactures or as antifreeze and so forth, can be synthesized from syngas derived from coal and biomass gasification instead of the traditional manufacture from petroleum.

As is well known to all, supported metal catalysts with multicomponents are among the most commonly used catalysts because of their obvious advantages such as the enhanced activity and stability. Compared to the traditional support (silica, alumina, or titania), zirconia is frequently employed as a preferable support for Cu-based catalysts in hydrogenation reactions due to its ability to easily form strong metal–support interaction, which can produce distinctive active phases especially the Cu–ZrO2 interface. As a consequence, CuO–ZrO2 catalysts are considered to exhibit excellent catalytic performance in EG synthesis. Unfortunately, many drawbacks such as low selectivity and poor thermal stability in hydrogenation reactions are brought by the intrinsic disadvantages of traditional Cu-based catalysts. The deficiency in CuO–ZrO2 catalysts calls for a better solution to meet the tough challenges, which is also at the very heart of fabricating high-performance catalysts for EG synthesis. Regarding the extensively studied CuO–ZrO2 catalysts, the interaction between Cu species and support is generally believed to be pivotal in enhancing selectivity and stability. Research is therefore focused on the development of advanced synthetic methods with high uniformity in multicomponent distribution or focused on the addition of promoters. For the former, the simple one-pot complexation route offers flexibility in design to fabricate multicomponent catalysts. As a result, the obtained catalysts have higher uniformity and tightness in combination of various components, resulting in the enhanced synergistic effects in catalysis reaction. With regard to the latter strategy, various promoters are added to obtain the functional CuO–ZrO2 catalysts with desired physical and chemical properties. The introduction of La into Cu-based catalyst frequently changes the electron density of metal active sites, which thus enhances their catalytic activity and stability in hydrogenation reactions. To be honest, there is still some controversy about the influence of preparation conditions such as the calcination temperature on the complexation route. Hence, to find the appropriate calcination temperature is a precondition for catalyst preparation, which can modify the structural properties, avoid heterogeneous distribution of metal species, and strengthen their interaction with each other.

In this paper, the La-doping CuO–ZrO2 catalysts prepared by a simple one-pot salicylic complex process have been applied to selectively synthesize EG by hydrogenation of diethyl oxalate (DEO) or dimethyl oxalate (DMO). Effects of
calcination temperatures on the structure and activity of CuO–La2O3/ZrO2 catalyst were investigated, and the optimal temperature was found out. All the catalysts were characterized by N2-physisorption, chemisorption, and other techniques to study their structural features and catalytic properties. Combined with the activity evaluation results in hydrogenation study their structural features and catalytic properties.

**RESULTS**

**Physicochemical Characterization. N2-Adsorption and N2O Titration Analysis.** Nitrogen adsorption–desorption isotherms and the BJH pore size distribution of 32CLZT are shown in Figure S2. Clearly, all of them were intermediate between Langmuir type II and type III with the H3-type hysteresis loop, while the location of the hysteresis loop shifted to higher pressures and became smaller with the increase of calcination temperatures. These results indicated that there were a large amount of slit-slapped channels or ink bottle shape holes formed. The closure points of hysteresis loops occurred at a relative pressure of ca. 0.4 for 32CLZS00 and increased to more than 0.5 for 32CLZ700 and 32CLZ800, indicating the increase of pore diameter. The physicochemical properties of 32CLZT are summarized in Table 1. It can be seen that the calculated SA and \( V_p \) of 32CLZT decreased significantly with increasing calcination temperatures as well as the Cu dispersion and exposed Cu surface area, whereas \( d_p \) increased slightly. This could be contributed to the increase of pores collapsing and metal sintering.

**XRD Analysis.** Figure 1a shows the X-ray diffraction (XRD) patterns of as-prepared CuO–La2O3/ZrO2 catalysts. Clearly, the catalysts all exhibited main sharp peaks as an indication of the crystalline CuO phase with a tenorite structure (PDF#48-1548). Interestingly, the intensity of characteristic CuO peaks gradually increased with the increase of calcination temperatures and finally achieved maximum for 32CLZ800 catalyst. Correspondingly, the CuO crystallite sizes gradually increased from 9.1 nm (32CLZS00) to 20.3 nm (32CLZ800) (Table 1). As is well known to all, the thermal treatment of metal-supported catalysts usually leads to the change in the particle morphology and size. Especially, the sintering of metal particles is particularly remarkable on CuO–ZrO2 catalysts. XRD results implied that the highly dispersed copper species transformed into bigger even bulky CuO particles owing to the increase of calcination temperatures. Strangely, there was no indication for the crystalline lanthanum oxides phase. This meant that the La species was amorphous or the grain size was small (<3 nm) due to the lower La content. The strong diffraction peaks of ZrO2 dominated over all the 32CLZT. However, the crystalline phases differed obviously owing to the different calcination temperatures since ZrO2 existed as amorphous (am-), tetragonal (t-), or monoclinic (m-) phases. For example, the 32CLZS00 and 32CLZ600 presented a sharp peak at 30.3° corresponding to a crystalline t-ZrO2 phase (PDF#80-1089). Interestingly, the peaks at 28.0 and 31.4° corresponded to m-ZrO2 for 32CLZ700 (PDF#37-1484), which further intensified for 32CLZ800. In this case, both t-ZrO2 and m-ZrO2 existed in these two catalysts. As a comparison, 32CLZm showed weak diffraction peaks of t-ZrO2, but strong peaks of CuO (Figure 1a), which may be due to the smaller ZrO2 particles existing as amorphous/tetragonal phases and the bulky CuO particles forming.

A strong diffraction peak at 43.3° along with two weak peaks at 50.4 and 74.1° in the XRD pattern of reduced catalysts were the characteristic of fcc Cu (JCPDS#04-0836). Besides, no characteristic diffraction peaks of CuO (2θ = 36.4°) or CuO phases were observed in the XRD patterns (Figure 1b). Results showed that the Cu species transformed into Cu0 after reduction which was in agreement with ref 22. On the one hand, the change of Cu0 crystallite size followed the same trend as CuO crystallite size in calcined catalysts (Table 1). On the other hand, the crystallite size of metallic Cu obviously increased comparing to CuO because the chemical structural

### Table 1. Physicochemical Properties of the As-Preared CuO–La2O3/ZrO2 Catalysts

| catalyst   | SA (m² g⁻¹) | \( V_p \) (m³ g⁻¹) | \( d_p \) (nm) | \( d_{CuO} \) (nm) | \( d_{Cu} \) (nm) | D (%) | SACu (m² g⁻¹) |
|------------|-------------|-------------------|---------------|------------------|------------------|------|---------------|
| 32CLZS00   | 69.1        | 0.142             | 8.7           | 9.1              | 12.4             | 22.7 | 49.2          |
| 32CLZ600   | 27.5        | 0.094             | 13.9          | 14.5             | 15.7             | 18.7 | 40.4          |
| 32CLZ700   | 9.3         | 0.061             | 26.4          | 16.8             | 19.1             | 12.6 | 27.4          |
| 32CLZ800   | 8.1         | 0.054             | 26.7          | 20.3             | 24.6             | 8.2  | 17.8          |
| 32CLZm     | 26.7        | 0.078             | 21.3          | 19.8             | 25.3             | 4.7  | 10.1          |

"SA and \( V_p \) was calculated from the volume of nitrogen adsorbed at \( P/P_0 > 0.95 \); \( d_p \) was calculated by \( 4 \times V_p / SA \); \( d_{CuO} \) and \( d_{Cu} \) was calculated by the Scherrer equation based on the XRD data of calcined and reduced CuO–La2O3/ZrO2 catalysts. \( D \) and SACu were determined by N₂O titration.

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c03982)
Scanning Electron Microscopy and Energy-Dispersive X-ray Analysis. To capture the surface morphology, all CuO–La2O3/ZrO2 catalysts calcined at different temperatures were visualized by SEM and are shown in Figure S3. Fluffy bulk materials consisted of small spherical particles with sizes ranging from 100 to 200 nm were found for 32CLZ500 (Figure S3a), while the structure became more compact and particles aggregated in 32CLZ600 catalyst as confirmed by XRD patterns. After further increasing the temperature, the fluffy body cracked and the particle sizes continually increased in 32CLZ700, which was in good agreement with the N2-physisorption and N2O titration results (Table 1). Moreover, the sintering of disordered particles became serious and bulk sintered materials began to emerge when calcination temperature was 800 °C, as indicated by Figure 1.

The EDX mapping of randomly selected area in SEM images demonstrated different distributions of Cu, La, and Zr species over the surface of 32CLZT and 32CLZm. Table 2 summarizes the surface component content based on EDX mapping images from several areas to acquire the average distribution of elements. It can be confirmed that the measured values of 32CLZ700 were close to the bulk phase composition for 32CLZ500, 32CLZ600, and 32CLZ800. Unfortunately, the Cu, La, and Zr components in 32CLZm individual accumulated, and especially no La Kα was detected out over the catalyst surface. The different elements distributions of 32CLZT meant that the obvious changes in 32CLZT about the surface-bulk phase composition were resulted by the different calcination temperatures. Most importantly, the uneven distribution of Cu and La species on support would be harmful to the formation of La doping CuO–ZrO2 interfaces and consequently deteriorate the catalytic activity.15 Owing to the complexation process which promoted the efficient mixing of metal species and the uniform contacting of Cu, La, and Zr species, Cu–La–Zr–O interactions were established smoothly. As a result, the formation of the La doping CuO–ZrO2 interface could be realized and enhanced by calcining at 700 °C.

Raman Analysis. Figure 2 shows the visible Raman spectra of 32CLZT and 32CLZm which is an effective technique to study the surface properties. Several distinct Raman bands for 32CLZT broadened and shifted to lower wave numbers. For instance, the band at 297 cm−1 for 32CLZm shifted to ca. 281 cm−1 with the band width significantly extending for 32CLZT. Thus, the red shift with bandwidth broadening could be ascribed to the change of the vibrations of Cu–O bonds. To some extent, the results indicated the existence of a strong interaction in a CuO–La2O3–ZrO2 multicomponent system, which was in good accordance with actual surface element distribution (Table 2).5,7,22 In addition, the 32CLZ600 exhibited essentially the same Raman features that can be assigned to t-ZrO2, while the bands shifted to lower wave numbers and became stronger. The red shifts and broadening of peaks showed the strong interactions among metal species, that is, the incorporation of Cu2+ and La3+ with ZrO2. With the increase of calcination temperature to 700 °C, new bands at 344, 465, 548, and 630 cm−1 appeared which can be identified as m-ZrO2. Combined with the XRD patterns, the transformation of tetragonal zirconia to monoclinic zirconia occurred on the surface of 32CLZ700. Further calcination at 800 °C resulted in an appreciable enhancement of these bands, suggesting the m-ZrO2 was well crystallized. It should be noted that the band at 281 cm−1 inferred to CuO became sharper, indicating the remarkable increase of the CuO particle size in 32CLZ700 and 32CLZ800 as can be seen in the XRD patterns (Figure 1a).

H2-TPR Analysis. Figure 3 compares the H2 temperature-programmed reduction (H2-TPR) profiles of as-prepared CuO–La2O3/ZrO2 catalysts. At first, H2-TPR experiments of La2O3 and ZrO2 prepared by the salicylic complex process had been separately carried out. It should be noted that few reduction peaks can be observed in the curve of ZrO2, while a weak peak appeared for the partially reduction of La2O3. Hence, the slight reduction of these species did not impact the H2-TPR results of CuO–La2O3/ZrO2 catalysts because of the low La2O3 concentration and the irreducibility of ZrO2. For 32CLZm, a broad reduction peak spanned from 265 to 495 °C appeared. It can be attributed to the reduction of bulk CuO. In general, all of the 32CLZT displayed reduction profiles containing a slight peak (α) and a sharper peak (β) with a maximum between 132 and 276 °C, which were well below that of the 32CLZm (ca. 395 °C) and the standard bulk CuO (ca. 285 °C).26 In fact, the interaction among the multi-components facilitated the reduction of CuO.15 Specifically, the profile of 32CLZ500 displayed the α peak centered at 152

| catalyst    | Cu  | La  | Zr  | O  |
|-------------|-----|-----|-----|----|
| 32CLZ500    | 27.4| 1.4 | 4.9 | 90.2|
| 32CLZ800    | 32.7| 2.1 | 4.3 | 31.9|
| 32CLZ700    | 30.1| 2.0 | 4.5 | 24.4|
| 32CLZ800    | 18.2| 3.0 | 4.9 | 29.7|
| 32CLZm      | 7.1 | 0.0 | 2.0 | 70.9|

Figure 2. Raman spectra of the calcined CuO–La2O3/ZrO2 catalysts.
Cu in 32CLZm. This further indicated that the interaction between Cu, La, and contrast, the reduction degree of 32CLZm was only 79.1%. However, three obvious H2 desorption peaks named well activated to participate in the hydrogenation reaction. propane γ were observed in the temperature span, while di and the β peak reached highest (232 °C) for 32CLZ800 with a slight α peak. Besides, the deconvolution of overlapped peaks as can be seen in Table S3 (columns 2 and 3) showed that the area of α peak decreased sharply, while the area of β peak gradually increased with the calcination temperatures increased from 500 to 800 °C.

In general, the reduction peak gradually shifting to higher temperatures for 32CLZ600, 32CLZ700, and 32CLZ800 may be partially ascribed to increased copper particle sizes due to the increase of calcination temperatures. However, Cu species strongly interacting with the support also caused the increase of reduction temperature, which can be covered up by the reduction of large CuO particles. Thus, the β peak in H2-TPR profiles of 32CLZT would be a diagnosis of the formation of La doping Cu−ZrO2 interface. Moreover, the reduction degrees of 32CLZ500, 32CLZ600, 32CLZ700, and 32CLZ800 calculated based on the peak area in H2-TPR experiments (Table S3) were 90.0, 92.0, 89.1, and 88.7%, respectively. In contrast, the reduction degree of 32CLZm was only 79.1%. This further indicated that the interaction between Cu, La, and Zr species facilitated the reduction of CuO, which was absent in 32CLZm.

H2-TPD Analysis. With the help of the H2 temperature-programmed desorption (H2-TPD) technique, the affinity of surface active sites to H species over CuO−La2O3/ZrO2 catalysts can be identified effectively. As shown in Figure 4, the physically adsorbed H2 that remain over the catalyst resulted the obvious curve fluctuation in the form of desorption peaks or sharp decline of baseline located at the temperature lower than 100 °C. The chemical inert H2 is not well activated to participate in the hydrogenation reaction. However, three obvious H2 desorption peaks named α, β, and γ were observed in the temperature range of 100−560 °C. All of them were similar at temperature span, while differed greatly in the peak area (Table S3, columns 4−6). Based on previous articles, the resolved peak at low temperature (ca. 125 °C) could be ascribed to the desorption of associative adsorbed H2 on highly dispersed metallic Cu. However, the smaller α peak was observed in the low temperature range for 32CLZ700 and 32CLZ800 because of the loss of highly dispersed copper species as certified by H2−TPR profiles (Figure 3). The much broader β peak centered at ca. 305 °C monitored the desorption of moderately adsorbed hydrogen from surface active sites, and the shoulder peak (γ) in the range of 360−560 °C was caused by the split H−H over the surface active sites. Most importantly, the β and γ peaks were both helpful to form CuHx species. As is well known to all, the surface CuHx species play a key role in hydrogenation of oxalates. Apparently, the β and γ peaks enhanced in the profiles of 32CLZ700 and 32CLZ800 while lowered in the profiles of 32CLZ500 and 32CLZ600 because of the higher calcination temperatures. Deconvolution of the overlapped peaks in the H2-TPD profiles of CuO−La2O3/ZrO2 catalysts showed that the sum of β and γ peaks area achieved maximum for 32CLZ700 catalyst which were 2.7, 1.9, 1.4, and 1.2 times than 32CLZm, 32CLZ500, 32CLZ600, and 32CLZ800, respectively. Thus, 32CLZ700 was supposed to possess superior surface adsorption and activation properties of H2. In this case, a high surface concentration of atomic hydrogen would endow 32CLZ700 with excellent catalytic activity for EG synthesis.

NH3-TPD Analysis. As is well known, zirconia possesses acidic property since both Brønsted-acidic hydroxyl groups and coordinatively unsaturated Lewis-acidic Zr4+−O2− pairs exist on the zirconia surface. Moreover, the combination of La oxides with Cu and Zr oxides probably a strong acidic site centered at 205 °C (α), the medium acidic site centered at 358 °C (β), and the strong acidic site centered at 468 °C (γ). Regarding the location of peaks in H2-TPD profiles, each peak was similar at temperature span but differed greatly in intensity for reduced 32CLZT and 32CLZm. With the aid of quantitative analysis, all the peaks were discerned by computer software and were integrated to evaluate their individual amounts (Table S3, columns 7−9). As a standard for comparison, it should be noted that 32CLZm afforded substantial surface acidic sites. Similarly, the 32CLZ500 exhibited the highest total peak areas (4.85) as equal to a surface acid concentration of 4.20 × 10−4 mmol gcat−1 among 32CLZT. However, the overall amounts of surface acidic sites decreased seriously to 1.60 × 10−4 mmol gcat−1 for 32CLZ600 due to the increase of calcination temperature. Moreover, the total peaks area further decreased.
Figure 5. NH$_3$ temperature-programmed desorption (NH$_3$-TPD) profiles of the reduced 32CLZT and 32CLZm.

to 0.35 and 0.30 since the 32CLZ700 and 32CLZ800 only possessed slight surface acidity (0.30 × 10$^{-4}$ and 0.26 × 10$^{-4}$ mmol g$_{\text{cat}}^{-1}$). Obviously, the amounts of surface acidic sites in reduced 32CLZT gradually decreased when the calcination temperatures were increased from 500 to 800 °C.

**CO$_2$-TPD Analysis.** Generally, zirconia possesses surface low-coordination O$_2$− ions, Zr$^{4+}$−O$_2$− pairs, and surface OH groups corresponding to strong, medium-strength, and low-strength basic sites, which are able to adsorb CO$_2$ and show various desorption peaks under the condition of gradually increasing temperatures. CO$_2$ temperature-programmed desorption (CO$_2$-TPD) profiles of reduced 32CLZT and 32CLZm are shown in Figure 6. As can be verified, the catalysts showed different profiles regarding their interaction with CO$_2$. In simple words, two obvious CO$_2$ desorption peaks (α and β) could be distinguished on the CO$_2$-TPD curves. The weak basic sites were related to the α peak which centered at a temperature of ca. 95 °C, while the β peak between 270 and 585 °C was an indication of the surface strong basic sites. Thus, the CO$_2$-TPD profiles disclosed a clear concentration of varied basic sites on surface. As can be seen in Table S3 (columns 10 and 11), 32CLZ500 showed the largest peak areas denoting the existence of both abundant weak and strong basic sites as well as 32CLZm. When the calcination temperature was increased to 600 °C, both α and β peaks decreased clearly and the sum of peak areas fell to one-third of that of the 32CLZ500. Similarly, the quantity and intensity of surface basic sites decreased significantly as the calcination temperature further increased to 700 °C. 32CLZ800 exhibited no distinct desorption peaks of CO$_2$ instead of a broad peak spanning from 340 to 550 °C, indicating only a small amount of strong acidic sites on the surface without weak basic sites. Therefore, the CO$_2$-TPD profiles implied an increasing contribution on reduction of surface basicity associated with the calcination temperatures.

**Catalytic Performance of CuO−La$_2$O$_3$/ZrO$_2$ Catalysts for EG Synthesis.** DEO Hydrogenation to EG. As summarized in Table 3, the main products of hydrogenation of DEO over the CuO−La$_2$O$_3$/ZrO$_2$ catalysts were ethyl glycolate (EGT), EG, and ethanol, while the selectivity to other byproducts was extremely low. In fact, these catalysts showed different catalytic activities in DEO conversion and EG selectivity. Specifically, 32CLZ500 displayed the highest DEO conversion (98.5%). The conversion over 32CLZ600 and 32CLZ700 remained at high levels (98.2 and 97.7%). Then, the conversion gradually dropped to 93.9% over 32CLZ800 even to 26.9% over 32CLZm. The turnover frequency (TOF) values were investigated to compare the intrinsic catalytic activities of the CuO−La$_2$O$_3$/ZrO$_2$ catalysts. Interestingly, the TOF values increased with the increase of calcination temperatures except of 32CLZ800. As indicated by Table 3, the 32CLZ700 exhibited the highest TOF value (66.9 h$^{-1}$), which was about 4, 1.7, 1.5, and 1.2 times higher than those of 32CLZm, 32CLZ500, 32CLZ600, and 32CLZ800. It was worth noting that the 32CLZ700 realized superior selectivity to EG (96.5%), followed by the 32CLZ800 which also showed a higher EG selectivity of 87.3%. Unfortunately, it dropped sharply over 32CLZm, 32CLZ500, and 32CLZ600. The STY to EG over as-prepared catalysts followed the sequence of 32CLZ700 (0.58 h$^{-1}$), 32CLZ800 (0.53 h$^{-1}$), 32CLZ600 (0.44 h$^{-1}$), 32CLZ500 (0.22 h$^{-1}$), and 32CLZm (0.05 h$^{-1}$). It can be concluded that the catalytic activities especially selectivity of EG exhibited a strong dependence on calcination conditions.

Figure 6. CO$_2$-TPD profiles of the reduced 32CLZm and 32CLZT.

| catalyst    | conversion$^a$ of DEO/% | selectivity$^a$/% | STY/(h$^{-1}$) | TOF/(h$^{-1}$) |
|-------------|-------------------------|------------------|----------------|---------------|
| 32CLZ500    | 98.5                    | 55.9             | 3.7            | 34.1          | 6.3           | 0.22           | 40.3           |
| 32CLZ600    | 98.2                    | 25.4             | 2.3            | 69.6          | 2.7           | 0.44           | 43.5           |
| 32CLZ700    | 97.7                    | 2.6              | 0.7            | 96.5          | 0.2           | 0.58           | 66.9           |
| 32CLZ800    | 93.9                    | 6.5              | 4.5            | 87.3          | 1.7           | 0.53           | 54.2           |
| 32CLZm      | 26.9                    | 45.1             | 12.8           | 33.7          | 8.4           | 0.05           | 16.2           |

$^a$Reaction conditions: P = 2.4 MPa, T = 220 °C, H$_2$/DEO = 80, WLHSV = 1.4 h$^{-1}$. $^b$Other byproducts included 1,2-butanediol, 1,4-dioxane, and so forth.
DMO Hydrogenation to EG. Figure 7 displays the catalytic performance of as-prepared catalysts in gas-phase hydrogenation of DMO. The DMO conversion and EG selectivity over 32CLZT showed a dramatic improvement compared with 32CLZm. Furthermore, the selectivity of EG significantly increased with increase of calcination temperatures. For example, the 32CLZ700 showed the highest selectivity of EG (ca. 98%) based on a high DMO conversion (ca. 97%) and was stable for no less than 100 h. Besides, the STY of EG reached a maximum value (0.59 h⁻¹). Unfortunately, attributed to the serious sintering of Cu species after calcined at 800 °C as confirmed by XRD and N₂O oxidation (Figure 1 and Table 1), 32CLZ800 displayed poorer performance than 32CLZ700 in conversion of DMO (ca. 92%), selectivity of EG (ca. 94%), and STY of EG (0.55 h⁻¹). In addition, the selectivity of EG was no more than 70% for the 32CLZ500 and 32CLZ600 regardless of a higher conversion of DMO. In this case, the appearance of ethanol and other byproducts cannot be ignored.

DISCUSSION
Role of Multicomponent Interfaces on the Activity of CuO−La₂O₃/ZrO₂ Catalyst. As we know, metallic copper has great effects in the hydrogenation of oxalates to alcohols because the catalytic activities of Cu-based catalysts are frequently found to be proportional to Cu dispersion.35−38 Hence, the decrease in Cu⁰ surface area would impair the hydrogenation performance. However, many literature studies also show that both Cu²⁺ and Cu⁺ species are crucial because of the cooperative effect between Cu²⁺ and Cu⁺ species.39,40 Generally speaking, H₂ was dissociatively adsorbed over the surface Cu⁰, while the intermediates decomposed from oxalates such as alkoxy and acyl species were stabilized by surface Cu⁺. Most importantly, Cu⁺ will act as electrophilic groups or Lewis acidic sites which can polarize the carbon oxygen double bonds via the electron lone pair of oxygen. As an alternative form to the above descriptions, the multicomponent interface is believed to play a vital role in hydrogenation reactions owing to the distinguished atomic arrangement and charge state of multicomponent heterostructures.3 For example, not only the highly dispersed Cu nanoparticles but also Cu−SiO₂, Cu−La₂O₃−SiO₂, or CuO−Al₂O₃−ZrO₂ interfaces provide the surface sites with high catalytic activity for EG production from DMO hydrogenation as evidenced in many reports.41,42 Similarly, it suggests the diversity of active sites besides Cu species in CuO−La₂O₃/ZrO₂ catalyst.43 As kindly mentioned by many research studies, the interface formed by multicomponent species are the most common explanations for the Cu-based catalyst with a lower Cu dispersion while showing preferable catalytic performance.43−45 Thus, a large number of La doping Cu−ZrO₂ interface formed as a result of Cu and ZrO₂ closely interacting with each other and the derived synergistic effect could open a new way to get better performances in dialkyl oxalates hydrogenation.46

As confirmed, high copper dispersion could be obtained only if the particle size of CuO is smaller.46 It was true that the catalyst calcined at 500 °C (32CLZ500) with smaller CuO particles possessed a higher copper dispersion and was more favorable for hydrogenation of DMO or DEO. When the calcination temperatures increased, the surface area and pore volume decreased. The particle sizes and Cu dispersion also decreased seriously which are shown in Table 1. Naturally, a slight deterioration of oxalates conversion was observed on 32CLZ700 and 32CLZ800 because of the decreased Cu dispersion. In this case, the highly dispersed Cu nanoparticles seem to provide the main active sites for hydrogenation of dialkyl oxalates. However, the nonlinearity was frequently observed in correlations between Cu surface area (Table 1) and dialkyl oxalates conversion especially for the CuO−La₂O₃/ZrO₂ catalysts calcined at higher temperatures,44−46 implying some other complicated factors in the formation of active sites with high efficiency for the hydrogenation of oxalates to EG. The results from Raman spectra indicated the incorporation of Cu²⁺ and La³⁺ into ZrO₂ (Figure 2). Since the Cu, La, and Zr oxides were present in the form of uniform combination (Table 2), it was greatly helpful to the formation of the La

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Figure 7. Changes in conversion of DMO (a), selectivity of EG (b), and STY to EG (c) with time on stream over 32CLZT and 32CLZm. Reaction conditions: 2.4 MPa, 220 °C, H₂/DMO = 80, and WLHSV = 1.2 h⁻¹.
doping Cu–ZrO2 interface. As shown in Figure 3, H2-TPD profiles also suggested the interaction among the components of 32CLZT which facilitated the reduction of CuO comparing to 32CLZm. In fact, the distribution of Cu species in contact with the promoter or support was heterogeneous, which will lead to a broader peak even peak splitting corresponding to the reduction of heterogeneous Cu particles, while highly dispersed CuO often has a much narrower peak width as can be seen in Cu/SiO2 or Cu/mesoporous materials. The H2-TPR profiles of 32CLZT, the α peak denoting the reduction of highly dispersed Cu species decreased, while the β peak assigned to the reduction of Cu species interacting with support increased with the increase of calcination temperatures from 500 to 800 °C. In other words, the La doping CuO–ZrO2 interface obviously increased.

In general, H2-TPD profiles of as-prepared catalysts spanning a wide range of temperature are a diagnostic index of different H2 activation capacity of active sites over the catalyst surface. In other words, the enhanced H2 activation ability especially H2-dissociative adsorption over CuO–La2O3/ZrO2 catalysts could contribute markedly to the yield of EG thanks to the formation of La doping Cu–ZrO2 interface, which can act as a supplement for the loss of highly dispersed Cu sintered under high calcination temperature. Notably, the 32CLZ700 with a large amount of La doping CuO–ZrO2 interface showed the maximum amount of β and γ peak areas (Figure 4 and Table S3), which also performed best in the EG synthesis.

Effects of Calcination Temperatures on EG Selectivity. The results from XRD patterns and Raman spectra (Figures 1 and 2) indicated that the transformation of t-ZrO2 to m-ZrO2 occurred already on the surface of 32CLZ700 and 32CLZ800 due to the gradually increased calcination temperatures. Thus, the catalytic behavior affected by t-ZrO2 or m-ZrO2 needs to be considered. As is well known to all, t-ZrO2 and m-ZrO2 have different effects on the copper species or Cu–ZrO2 interaction since the different spacing and symmetry of the Zr–O bonds on the surface of t-ZrO2 or m-ZrO2 are considered to play key roles in the catalytic properties of Cu/ZrO2 catalyst. For example, the alteration of electron density for O species, that is, the oxygen vacancies derived from oxygen extraction would introduce Cu atoms into ZrO2 and result in some changes on synergetic effect, which possibly endows the composite catalysts with much improved catalytic properties. In other words, the high oxygen mobility of m-ZrO2 can generate the required lattice defects for trapping Cu which are the catalytically active sites. Thus, the formed synergism facilitates the reactions between the activated O-containing intermediates and nearby highly active H atoms dissociated by Cu sites. Indeed, when the m-ZrO2 is observed the selectivity towards EG increased both in hydrogenation of DEO and DMO. For example, the presence of m-ZrO2 in 32CLZ700 and 32CLZ800 greatly improved the catalytic behavior especially the selectivity of EG. To be honest, the different influence of monoclinic or tetragonal phase on the catalytic performance of ZrO2-supported Cu catalyst and how the acyl species of oxalates and H atoms react over Cu/t-ZrO2 or Cu/m-ZrO2 interface is complicated and remains a systematic study. The follow-up results will be addressed in our future work.

As we know, the reduction of alkyl oxalates is determined by the hydrogenation of surface acyl species to alcohols. Thus, it is important to explore the H2 activation over the surface of CuO–La2O3/ZrO2 catalysts. In fact, a strong dependence on EG selectivity with adsorption and activation of H2 emerged when we correlated the data from deconvolution of H2-TPD profiles and EG selectivity (Figure 8). This clearly indicated the great contribution of the increased calcination temperatures in the synthesis of EG because of the enhanced surface adsorption and activation of H2.

Based on the results from NH3-TPD and CO2-TPD profiles, the reduced 32CLZT and 32CLZm showed significant differences in surface acidic and basic properties which also played key roles in oxalates hydrogenation. As reported, the hydrogenation of dialkyl oxalates proceeds via alkyl glycolate to EG, while EG can dehydrate further to ethanol. Under the reaction conditions specified in Table 3, most of the converted DEO had been turned into EG, EG, and ethanol. However, the product distributions in DEO/DMO hydrogenation over 32CLZT were largely altered according to the calcination temperature. For example, although a slight decrease of oxalates conversion was observed due to the decrease of Cu dispersion, the highest selectivity to EG more than 96.5% was obtained over 32CLZ700 both in hydrogenation of DEO and DMO with lower selectivity to other byproducts. It was partially attributable to the less acidic and basic sites on catalyst surface due to the higher calcination temperature (Figures 5 and 6). On the contrary, the inferior selectivity to EG around 70% was observed on 32CLZ600, which further decreased to below 40% on 32CLZ500. In this case, the presence of EG was giving way to the formation of ethanol because of the higher surface acid and base concentration, as can be seen in Table 3 and Figure 7.

In summary, the increase of calcination temperatures brought about a decline of the Cu dispersion but significantly reduced the number of surface acidic/basic sites, which in principle inhibit the further hydrogenation of EG to ethanol or suppress other byproducts formation. Furthermore, the surface activation of H2 was enhanced as a result of the higher calcination temperatures. Thus, the synergism between Cu

Figure 8. Correlation of EG selectivity with the total area of the β and γ peaks in H2-TPD profiles over CuO–La2O3/ZrO2 catalysts.
species and m-ZrO₂ in 32CLZ700 and 32CLZ800 affords a higher selectivity to EG and enhances the stability in oxalates hydrogenation.

**Role of La Addition on the Structure and Activity of CuO–La₃O₆/ZrO₂ Catalyst.** As confirmed by Zhao et al., the addition of La₂O₃, assisted activation of C=O and C−O groups over La₃O₆−PdAu−Cu nanocomposite catalyst for oxalates hydrogenation. Besides, the formation of Cu−O−La bonds between La₃O₆ and Cu species was responsible for the improved catalytic performance of La−Cu/SiO₂ catalyst. Thus, the addition of proper La to Cu-based catalyst is beneficial to enhance the catalytic activities. Thanks to the salicylic complex process and the high calcination temperature (especially 700 °C), the efficient mixing of metal species and the uniform distribution of La species could be realized, and the Cu−La−Zr−O interactions were established smoothly. As a result, the formation of La doping Cu−ZrO₂ interface was enhanced especially over the 32CLZ700. However, the different La content could have a greater influence on the catalytic properties. In Table S2, the activity of CuO−La₃O₆/ZrO₂ catalysts increased when the addition of lanthanum oxide increased, but further increase in La content will lead to an obvious decrease of EG yield. Hence, the desirable La doped amount was 2 wt %. In the meantime, the amorphous La species were uniformly dispersed over the surface especially 32CLZ700 from the XRD patterns (Figure 1) due to the lower La content as well as having been disclosed by EDX mapping of randomly selected area in SEM images (Table 2). H₂-TPR tests demonstrated that the addition of La did not impact the H₂−TPR results of CuO−La₃O₆/ZrO₂ catalysts because of the lower La₃O₆ concentration (Figure 3). These results represent a point of reference and provide the preliminary data necessary for further research about the reaction mechanism of La involved.

**CONCLUSIONS**

In conclusion, kinds of CuO−La₃O₆/ZrO₂ catalysts with 32.0 wt % Cu content and 2.0 wt % La content were calcined at different temperatures and were applied in hydrogenation of oxalates to EG. As characterized by N₂ adsorption, XRD, Raman, SEM, and N₂O oxidation, the decreased Cu dispersion with increased crystallite sizes of 32CLZT was due to the increase of calcination temperatures. However, the catalytic performances showed a volcano-shaped trend with respect to calcination temperatures. Among these catalysts, the remarkable hydrogenation performance such as 98 or 96.5% EG selectivity in hydrogenation of DMO or DEO could be obtained over the one calcined at 700 °C, which was attributed to the remarkable surface adsorption and activation behaviors of H₂ as shown by H₂-TPD profiles. Furthermore, as characterized by NH₃-TPD and CO₂-TPD, the byproduct formation was greatly suppressed since the number of surface acidic and basic sites over 32CLZ700 was significantly reduced by increasing calcination temperature. Results showed the diversity of active sites on CuO−La₃O₆/ZrO₂ catalysts since the La doping Cu−ZrO₂ interface could effectively provide the active sites for EG synthesis besides Cu sites. It may be related to changes in the surface structure and which depend on the calcination temperatures definitely.

**MATERIAL AND METHODS**

**Materials.** All the reagent grade chemicals (Sinopharm Chemical Reagent Co. Ltd. China) were used as received. Additionally, the purity of gases used in experiments such as Ar, H₂, He, N₂O, NH₃, and CO₂ was greater than 99.99%. Prior to use, the pure gases were blended to obtain required mixing gas (e.g., 5% H₂/Ar) and pretreated to remove the possible impurities by silica gel desiccant, 5 Å molecular sieve, silver molecular sieve, and so forth. Especially, the silver molecular sieve was employed to eliminate the trace O₂ possibly included in H₂, Ar, or He gas by highly active Ag atoms.

**Catalyst Preparation.** The CuO−La₃O₆/ZrO₂ catalysts were prepared by a simple one-pot salicylic complex process as reported in our previous articles. Basically, the Cu or La weight content was expressed as the quality of Cu or La per gram of the calcined catalyst [eqs 1 and 2].

\[
\text{Cu wt }\% = \frac{m_{\text{Cu}}}{m_{\text{CuO}} + m_{\text{La}O_3} + m_{\text{ZrO}_2}} \times 100\% \\
\text{La wt }\% = \frac{m_{\text{La}}}{m_{\text{CuO}} + m_{\text{La}O_3} + m_{\text{ZrO}_2}} \times 100\%
\]

Prior to explore the effect of calcination temperatures on Cu-based catalysts, CuO−La₃O₆/ZrO₂ catalysts containing 2.0 wt % La with different Cu content (10.0, 28.0, 32.0, 39.0, and 58.0 wt %) were prepared in order to search the optimal Cu content. The obtained catalysts were referred to as wCLZT700, where w is the actually Cu wt % and 700 °C is the final calcination temperature. For the purpose of investigating the optimal La addition of CuO−La₃O₆/ZrO₂ catalysts, four samples named 32CLZ700 containing 32.0 wt % Cu with different La content (w = 0.5, 1.5, 2.0, and 3.0) were prepared by the same method. As can be identified by the evaluation results of catalytic activities (Tables S1 and S2), the one with 32.0 wt % copper and 2.0 wt % lanthanum was the best choice and had been chosen as the precursor to suffer from different calcination temperatures. In a typical synthesis, Cu(NO₃)₂·3H₂O (12.08 g), La(NO₃)₃·6H₂O (0.62 g), and Zr(NO₃)₄·2H₂O (20.09 g) were dissolved in 20.0 mL of ethanol. An alcoholic solution (30.0 mL) of salicylic acid (42.28 g) was added into a flat-bottomed glass beaker drop by drop and mixed with above solution at 70 °C under magnetic stirring. The mixture within pH range of 1–2 was subsequently dried in a vacuum oven at 70 °C for a night. The obtained precursors were grinded into powders and referred to as 32CLZ. Finally, the resulting powders were calcined in air at different temperatures (500, 600, 700, and 800 °C) for 3 h with a heating rate of 1 °C min⁻¹ to give 32CLZT, where T denotes the calcination temperature. Note that the physical mixing 32CLZm which was used as a standard for comparison was also prepared by drying an alcoholic solution of Cu(NO₃)₂·3H₂O, La(NO₃)₃·6H₂O, and Zr(NO₃)₄·2H₂O without the salicylic complex process and subsequently calcining at 500 °C.

**Catalyst Characterization.** The amounts of Cu and La species in the calcined catalysts were approximately same with the theoretical metal content (32.0 and 2.0 wt %). In principle, there was no need to further quantitative analysis of constituents and contents. However, EDX mapping was carried out to analyze the surface chemical composition and elemental distribution.
The texture properties of obtained catalysts were determined by the nitrogen sorption technique. The sample was outgassed first in an oven at 200 °C for 12 h. Subsequently, the nitrogen physisorption isotherms were recorded at −196 °C with the relative pressure (P/P₀) from 0.005 to 0.995 on a Micromeritics ASAP 2460 instrument. Based on the adsorption isotherm, specific surface area (SA) was calculated according to Brunauer—Emmett—Teller method. Besides, pore volume (Vₚ) and average pore diameter (dₚ) were deduced by using Barrett—Joyner—Halenda pore analysis.

The powder XRD patterns of as-prepared CuO−La₂O₃/ZrO₂ catalysts had been recorded on the DX-2700 instrument. The measurements were operated at 40 kV and 30 mA with the monochromatic Cu Kα (λ = 0.15405 nm) radiation source. Diffraction peaks were collected over the 2θ range of 5−85° with a scanning speed of 2° min⁻¹. The average crystallite size of CuO and Cu (dCuO and dCu) was calculated by the Scherrer equation from the line-broadening of XRD peaks [eq 3]

\[
d = \frac{K\lambda}{FW \cos \theta}
\]

Here, K is the constant unity (0.89). FW is the full width at half-maximum of the CuO (1 1 1) or Cu (1 1 1) peak, and θ is the peak position.

Raman spectra were collected on a HORIBA LabRaman HR800 spectrometer equipped with an Ar⁺ laser, and the excitation wavelength was 514 nm. Microscopic images were obtained using a focused ion beam/hot field emission scanning electron microscope (FIB/FE-SEM, GAIA3 TESCAN) accompanied by EDX equipment. The operating voltage for SEM was 15 kV.

The Cu dispersion (D) and exposed Cu surface area (SAcu) of as-prepared CuO−La₂O₃/ZrO₂ catalysts were measured by N₂O oxidation using the VDSorb-91i apparatus and subsequently calculated as described in our previous articles. The reducibility of CuO−La₂O₃/ZrO₂ catalysts and the potential interactions between Cu species and support were studied by H₂-TPR. In simple terms, 15 mg of the calcined catalyst was placed in a U-shaped quartz tube under a flow of 5% H₂/Ar with a constant flow rate (30 mL min⁻¹) and was heated from 50 to 600 °C by 10 °C min⁻¹. During the process, the formed water vapor was removed using a molecular sieve trap before detection and the hydrogen consumed was monitored continuously.

The different H₂ activation properties over the surface of reduced catalysts were identified by H₂-TPD. Initially, the catalyst (120 mg) was reduced in situ by the H₂/Ar gas flow (30 mL min⁻¹) at 220 °C for 2 h. Then, the reduced sample was swept at 220 °C for 1 h and was subsequently cooled to room temperature in an Ar gas flow (30 mL min⁻¹). After exposure to H₂ (30 mL min⁻¹) for 20 min, the sample was heated to 750 °C with a heating rate of 15 °C min⁻¹ and the desorbed H₂ was closely monitored. The overall surface acidity and surface basicity of the reduced samples were determined by NH₃−TPD and CO₂−TPD. Typically, the catalyst (150 mg) was pretreated by the 5% H₂/He gas flow (30 mL min⁻¹) at 220 °C for 2 h. Prior to NH₃ or CO₂ adsorption, the reduced catalyst was swept at 220 °C for 1 h and subsequently cooled to 50 °C by a He gas flow (30 mL min⁻¹) for cleaning the catalyst surface. Then, NH₃ or CO₂ was introduced to the tube to obtain a saturated adsorption. After swept by He to eliminate the physically adsorbed NH₃/CO₂, the sample was finally heated to 750 °C by steps of 15 °C min⁻¹ with He as carrier gas (30 mL min⁻¹), and the effluent was online monitored to discern the desorbed NH₃ or CO₂.

The TPR and TPD experiments described above were carried out using the same apparatus employed by N₂O oxidation experiment. Moreover, the particle sizes used for chemisorption experiments were the same as that in hydrogenation of oxalates to EG.

**Catalytic Activity Tests.** Evaluations were conducted within an electrically heated stainless steel fixed-bed reactor equipped with online gas chromatography (GC). The tubular reactor was an isothermal fixed-bed with 290 mm length and 10.0 mm internal diameter. For the purpose of maintaining a uniform temperature distribution throughout the catalyst bed, CuO−La₂O₃/ZrO₂ catalysts were first mixed with inert quartz sand to avoid the formation of local hot spots. The mixture was loaded between two layers of quartz sands and then was reduced in situ at 220 °C for 6 h by H₂ flow (30 mL min⁻¹) under atmospheric pressure. After cooled to room temperature, the reactor was electrically heated to 220 °C by a step of 2 °C min⁻¹ with the pressure being raised to 2.2 MPa. Subsequently, the 15.0 wt % DMO in methanol or pure DEO was fed by a double-plunger pump and was vaporized under 190 °C. The produced vapor was thoroughly mixed with H₂ and then passed through the catalyst bed with a controlled weight liquid hourly space velocity (WLHSV). The easily condensed products were collected in a trap with glycol as refrigerant. Subsequently, the organic content was analyzed off-line by a Shimadzu GC-14C with a capillary column (19091N-213, HP-INNOWax) using a flame ionization detector, while the water content was determined by the same GC equipped with a packed column (TDX-101) and thermal conductivity detector. The noncondensable tail gas was periodically analyzed on-line by GC (Shanghai Haixin GC-950). Note that the catalyst was pelleted and sieved to get particles with a grain size of 60–80 meshes, and the loading amount was 0.5 g, which could eliminate the impacts of mass transfer limitation according to Madon–Boudart test (Figure S1). Significantly, no conversion of DMO/DEO was observed in the blank experiment when only quartz sands were loaded in the reactor.

For DMO hydrogenation, the conversion and selectivity were determined as follows [eqs 4 and 5]

\[
\text{conversion} = \left(1 - \frac{\text{mol of DMO after reaction}}{\text{total mol of DMO in feed}}\right) \times 100\% \tag{4}
\]

\[
\text{selectivity} = \frac{\text{mol of a product}}{\text{total mol of DMO converted}} \times 100\% \tag{5}
\]

where the space time yield of EG (STY, h⁻¹) was calculated as eq 6

\[
\text{STY}_{\text{EG}} = \frac{\text{conv. of DMO} \times \text{WLHSV} \times \text{sel. of EG} \times M_{\text{EG}}}{M_{\text{DMO}}} \tag{6}
\]

For DEO hydrogenation, the conversion, selectivity, and STY were calculated by the following equations [eqs 7–9]

\[
\text{conversion} = \left(1 - \frac{\text{mol of DEO after reaction}}{\text{total mol of DEO in feed}}\right) \times 100\% \tag{7}
\]
yield was less than 20%.

calculated when DEO conversion was less than 30% and EG
1 h. In order to obtain the intrinsic activity, the TOF was
the number of converted molecules to EG per active Cu site in

where the products in eq 8 stemmed from the conversion of
oxalates; thus, the hydrogenation of ethyl groups to ethanol
can be excluded in the calculation of ethanol selectivity.\(^3,4\)

The TOF value in the hydrogenation of DEO was de
ned as the number of converted molecules to EG per active Cu site in
1 h. In order to obtain the intrinsic activity, the TOF was
calculated when DEO conversion was less than 30% and EG
yield was less than 20%.

■ ASSOCIATED CONTENT

The Supporting Information is available free of charge at
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Madon–Boudart test; \(\text{N}_2\) adsorption–desorption isotherms and the BJH pore size distribution; SEM photograph; peak fitting of \(\text{H}_2\)-TPR, \(\text{H}_2\)-TPD, \(\text{NH}_3\)-TPD, and \(\text{CO}_2\)-TPD profiles; catalytic performance of the CuO–\(\text{La}_2\text{O}_3/\text{ZrO}_2\) catalysts with different Cu content in DMO hydrogenation; catalytic performance of the CuO–\(\text{La}_2\text{O}_3/\text{ZrO}_2\) catalysts with different La content in DMO hydrogenation; and deconvolution of the overlapped peaks in the \(\text{H}_2\)-TPR, \(\text{H}_2\)-TPD, \(\text{NH}_3\)-TPD, and \(\text{CO}_2\)-TPD profiles (PDF)

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Notes

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■ ADDITIONAL NOTE

“Conv.—conversion; sel.—selectivity; \(M_{\text{EG}}\)—molecular weight of EG; \(M_{\text{DMO}}\)—molecular weight of DMO; and \(M_{\text{DEO}}\)—molecular weight of DEO.

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selectivity = \(\frac{\text{mol of a product}}{\text{total mol of DEO converted}} \times 100\%\) (8)

\(\text{STY}_{\text{EG}}\) = \(\frac{\text{conv. of DEO} \times \text{LHSV} \times \rho_{\text{DEO}} \times \text{sel. of EG} \times M_{\text{EG}}}{M_{\text{DEO}}}\) (9)
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