Insights into a New Formation Mechanism of Robust Cu/SiO₂ Catalysts for Low-Temperature Dimethyl Oxalate Hydrogenation Induced by a Chelating Ligand of EDTA

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Abstract: The Cu/SiO₂ catalyst has been widely used in dimethyl oxalate (DMO) hydrogenation due to its low cost and high efficiency. However, the reaction temperature of DMO hydrogenation is higher than the Hütting temperature of Cu, and the smaller Cu particles are easier to agglomerate. Therefore, there is much interest in constructing a catalyst with a small particle size and strong stability. In the present work, the effect of introducing EDTA on Cu/SiO₂ catalysts is systematically investigated. It not only was beneficial to form smaller copper nanoparticles (CuNPs) but also to enhance the stability of Cu species by introducing a suitable amount of EDTA. Furthermore, the surface Cu species were more evenly dispersed, and the number of active sites was increased with the introduction of EDTA; subsequently, the synergistic effect between Cu⁺ and Cu⁰ was enhanced. The best performance of 0.08E-Cu/SiO₂ had been achieved in the DMO hydrogenation to ethylene glycol (EG), and the DMO conversion and EG selectivity reached 99.9% and 97.7%, respectively. Above all, the 0.08E-Cu/SiO₂ catalyst exhibited a high level of stability during the 1200 h life test at 180 °C.

Keywords: ethylenediaminetetraacetic acid; Cu/SiO₂; dimethyl oxalate; ethylene glycol

1. Introduction

Ethylene glycol (EG) is an important organic chemical raw material, which is widely used in the production of antifreeze, polyester fiber, explosives, lubricants, plasticizers, surfactants and so on [1]. The majority of its consumption is in the field of polyester fiber [2–4]. The traditional route of ethylene glycol production is the petroleum route, which is subject to large fluctuations in oil prices and high energy consumption, so other emerging routes have appeared [5]. The technology of coal to ethylene glycol with coal (or natural gas) as the raw material has attracted great attention because of its advantages including short process, low cost and abundant raw material sources. Generally speaking, the technology of coal to ethylene glycol is to convert coal to syngas; then the oxalic ester obtained through carbonylation of CO is used to synthesize ethylene glycol by catalytic hydrogenation of the oxalic ester [4]. The hydrogenation of dimethyl oxalate (DMO) to ethylene glycol is a key step in this technology.

The Cu/SiO₂ catalyst has been widely studied for the hydrogenation of ester due to its low cost and high activity [6–10]. It is also a common catalyst for hydrogenation
of DMO to EG [11,12]. The Cu/SiO₂ catalyst shows high activity in the DMO catalytic hydrogenation. Unfortunately, it has the disadvantages of poor stability and a short lifetime, which severely limits its practical application. Hence, more recent research mainly focuses on further improving catalytic hydrogenation performance, enhancing stability and prolonging service life. It should be mentioned that for the Cu/SiO₂ catalyst the size and dispersion of copper particles as well as the synergistic mechanism of Cu⁺ and Cu⁰ determine the performance of the Cu/SiO₂ catalyst. Yin et al. [13] reported that the introduction of nickel was in favor of increasing copper dispersion. Zhu et al. [14] studied the influence of copper particle size and distribution on catalyst performance by means of different preparation methods. Toupance et al. [15] revealed in detail the influence of different preparation conditions and thermal pretreatment on the copper particle size of the Cu/SiO₂ catalyst. Chen et al. [16] explored the effect of different ammonia vaporization temperatures on the Cu/SiO₂ catalyst and proposed that the best catalytic activity of the catalyst was owing to the synergy between Cu⁰ and Cu⁺. It was generally believed that the copper particles with a smaller size and higher dispersion are more conducive to improving the activity of catalysts. However, the smaller Cu particles are easier to agglomerate in the reaction process on account of the Hüttig temperature of Cu, which is lower than the reaction temperature of DMO hydrogenation, leading to poor stability and short life of the catalyst. [17] How to improve the stability of the surface Cu⁰ species is the key to building a long-lived, copper-based catalyst. In our previous work [12,18,19], the dextrin, β-cyclodextrin and mannitol were introduced into the Cu/SiO₂ catalyst successfully by the ammonia evaporation (AE) method to improve the performance of the Cu/SiO₂ catalyst, but the optimal DMO hydrogenation temperature was still higher than 190 °C. If the optimum hydrogenation temperature could be further reduced, it would be more beneficial to improve the surface Cu⁰ species stability and prolong the catalyst life.

Ethylenediaminetetraacetic acid (EDTA) is a strong chelating agent, which can form stable, water-soluble complexes with alkali metals, rare earth metals and transition metals [20]. According to [16–19], EDTA as a promoter has been introduced into catalysts for the hydrodesulfurization reaction and has produced an outstanding promotion effect. Based on the formation mechanism of copper phyllosilicate [21], the absence of bridging ligand in EDTA is not conducive to the formation of copper phyllosilicate. Surprisingly, our research found that the Cu⁰ species were distributed more evenly and became more stable with the moderate introduction of EDTA during the catalyst preparation. The catalytic performance of the Cu/SiO₂ catalyst with EDTA was significantly improved and could promote long-term stability in lower DMO hydrogenation temperature.

2. Results

2.1. Structure and Physicochemical Properties of Catalysts

The results of N₂ adsorption–desorption and N₂O for all catalyst samples are summarized in Table 1 and Figure 1. The N₂ isotherms of all samples exhibited Langmuir type IV isotherms. It was observed that the introduction of EDTA affected the specific surface area of the catalysts. Briefly, the BET surface area increased gradually firstly with the increase of the amount of EDTA, whereas further increasing the introduction of EDTA resulted in a gradual decline in BET surface area. This trend brought about a maximal BET surface area of 429 m² g⁻¹ as the ratio of EDTA/Cu was 0.08. On the other hand, the pore volume was influenced slightly with the introduction of EDTA. The pore size distribution curves showed that the pore size of the pure Cu/SiO₂ samples was ca. 3–5 nm and that of xE-Cu/SiO₂ samples was basically 3–5.3 nm. As a whole, the pore size distributions of samples were not affected by the introduction of EDTA. The results of N₂O titration indicated that the surface area of active copper (SₐCu) increased firstly and then decreased with the increase of EDTA dosage and reached the maximum (12.8 m² g⁻¹) as EDTA/Cu = 0.08, which indicated that the appropriate amount of EDTA was beneficial to improve the surface area of active copper.
Table 1. Physical and chemical properties of xE-Cu/SiO$_2$ catalysts.

| Sample          | Cu Loading (wt%) $^a$ | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) $^b$ | $V_p$ (cm$^3$ g$^{-1}$) $^c$ | $d_p$ (nm) $^d$ | $S_{\text{Cu}}$ (m$^2$ g$^{-1}$) $^e$ | Cu Dispersion (%) $^e$ | C Loading (wt%) $^f$ | $d_{\text{Cu}}$ (nm) $^g$ | $d_{\text{CuO}}$ (nm) $^g$ |
|-----------------|-----------------------|----------------------------------------|-----------------------------|-----------------|--------------------------------------|------------------------|----------------------|------------------------|------------------------|
| Cu/SiO$_2$      | 21.6                  | 394                                    | 0.46                        | 3.8             | 11.2                                 | 8.0                    | <0.3                 | 4.9                    | 4.1                    |
| 0.04E-Cu/SiO$_2$| 22.2                  | 411                                    | 0.50                        | 4.0             | 12.4                                 | 8.6                    | <0.3                 | 4.5                    | 3.5                    |
| 0.08E-Cu/SiO$_2$| 22.2                  | 429                                    | 0.52                        | 4.2             | 12.8                                 | 9.3                    | <0.3                 | -                      | 2.9                    |
| 0.12E-Cu/SiO$_2$| 18.5                  | 400                                    | 0.46                        | 4.0             | 11.1                                 | 9.3                    | <0.3                 | -                      | 3.5                    |
| 0.3E-Cu/SiO$_2$ | 14.8                  | 354                                    | 0.47                        | 4.6             | 8.2                                  | 8.5                    | <0.3                 | -                      | 3.1                    |

$^a$ Determined by ICP-OES. $^b$ $S_{\text{BET}}$: specific surface area. $^c$ $V_p$: total pore volume. $^d$ $d_p$: average pore diameter. $^e$ Cu metal surface area and dispersion determined by N$_2$O titration. $^f$ Determined by EA for the dried catalyst precursors. $^g$ Calculated from the XRD data based on the Scherrer equation.

Figure 1. N$_2$ adsorption–desorption isotherms (A) and pore size distribution curves calculated by BJH equation in desorption branch (B) of the calcined xE-Cu/SiO$_2$ samples. (a) Cu/SiO$_2$, (b) 0.04E-Cu/SiO$_2$, (c) 0.08E-Cu/SiO$_2$, (d) 0.12E-Cu/SiO$_2$, (e) 0.3E-Cu/SiO$_2$.

The results of ICP (Table 1) showed that the Cu loading in catalysts decreased significantly once the ratio of EDTA/Cu was above 0.08 because the excessive EDTA took away a large amount of copper through chelation. It should be pointed out that the C loading (Table 1) for all the dried samples was below the minimum detection line according to the elemental analysis results, that is, there was little EDTA in the dried samples, indicating that EDTA had been eliminated from the samples by means of filtration and washing.

2.2. Evolution of Crystalline Phase and Morphology

It could be observed by the TEM images (Figure 2) of the reduced samples that the size of copper crystallites on the surface of the samples with EDTA was between 3.5 and 4.3 nm, which was smaller than that on the surface of the Cu/SiO$_2$ sample without EDTA (4.7 nm). The characterization results showed that the introduction of EDTA inhibited the agglomeration of copper species.
2.2. Evolution of Crystalline Phase and Morphology

It could be observed by the TEM images (Figure 2) of the reduced samples that the peak shape was more symmetrical with the increase of EDTA introduction, which suggested that the dispersion of copper species had been improved [27]. As shown in the TPR profiles (Figure 4), only one strong reduction peak appeared around 205 °C for all catalyst samples, which should be attributed to the collective contribution of the reduction of copper phyllosilicate, highly dispersed CuO and Cu-O-Si species. It is worth noting that the shoulder peak at ca. 195 °C became weak gradually and that the peak shape was more symmetrical with the increase of EDTA introduction, which suggested that the dispersion of copper species had been improved [27].

Figure 5 shows the Fourier transform infrared spectra (FT-IR) of calcined samples. The δ_{OH} deformation vibration peak at 673 cm^{-1} and the ν_{SiO} asymmetric stretching vibration peak at 1035 cm^{-1} indicate the presence of copper phyllosilicate [15], coinciding with the results obtained by XRD. The relative content of copper phyllosilicate could be qualitatively evaluated using the ratio I_{673}/I_{800}, in which I_{673} represents the intensity of the δ_{OH} band of copper phyllosilicate at 673 cm^{-1}, and I_{800} represents the intensity of the symmetric ν_{SiO} band of amorphous silica at 800 cm^{-1} [16,21]. Figure 5 shows that the decline of I_{673}/I_{800} ratio for the calcined samples was not obvious until EDTA/Cu > 0.08. This suggests that the formation of copper phyllosilicate would be inhibited with the introduction of EDTA, but this inhibition could be limited to a small magnitude by controlling the amount of EDTA.

![Figure 2. TEM images of reduced samples: (A) Cu/SiO_2, (B) 0.04E-Cu/SiO_2, (C) 0.08E-Cu/SiO_2, (D) 0.12E-Cu/SiO_2, (E) 0.3E-Cu/SiO_2.](image-url)
Figure 3. XRD patterns of (A) the calcined catalysts and (B) the reduced catalysts xE-Cu/SiO₂. (a) Cu/SiO₂, (b) 0.04E-Cu/SiO₂, (c) 0.08E-Cu/SiO₂, (d) 0.12E-Cu/SiO₂, (e) 0.3E-Cu/SiO₂.

Figure 4. H₂ TPR profiles of the calcined xE-Cu–SiO₂ catalysts. (a) Cu/SiO₂, (b) 0.04E-Cu/SiO₂, (c) 0.08E-Cu/SiO₂, (d) 0.12E-Cu/SiO₂, (e) 0.3E-Cu/SiO₂.

Figure 5. FT-IR spectra of the calcined catalysts. (a) Cu/SiO₂, (b) 0.04E-Cu/SiO₂, (c) 0.08E-Cu/SiO₂, (d) 0.12E-Cu/SiO₂, (e) 0.3E-Cu/SiO₂.
2.3. Chemical States of Surface Species

The chemical environment of Cu species on the surface of catalyst samples could be elucidated by XPS analysis. As shown in Figure 6, the Cu 2p3/2 XPS spectra of the calcined samples showed a characteristic satellite peak at ca. 945.0 eV, while the reduced samples basically did not appear the satellite peak. Thus, it is believed that the oxidation state of copper was +2 in all the calcined samples [19]. Typically, the photoelectron peaks at ca. 936.0 eV and 933.5 eV have been attributed to copper phyllosilicate and CuO or well-dispersed Cu2+ species, respectively [16,28].

Figure 6. XPS spectra of (A) the calcined catalysts and (B) the reduced catalysts of xE-Cu/SiO2. (a) Cu/SiO2, (b) 0.04E-Cu/SiO2, (c) 0.08E-Cu/SiO2, (d) 0.12E-Cu/SiO2, (e) 0.3E-Cu/SiO2.

After reduction, the Cu2p3/2 XPS spectra of the samples only showed a photoelectron peak at ca. 932.9 eV without the corresponding satellite peak, which indicated that the Cu2+ was reduced to Cu+ and (or) Cu0 [29,30]. In order to identify further Cu+ and Cu0, the XAES analysis was carried out, and the results are illustrated in Figure 7. After deconvolution, the relevant data are listed in Table 2. In general, the peaks at ca. 913.0 eV and 916.0 eV are attributed to Cu+ and Cu0, respectively [16]. Moreover, the Auger parameter of Cu+ was ca. 1845.8 eV, and that of Cu0 was ca. 1844.1 eV, but the Auger parameter of Cu+ should be ca. 1849.0 eV. The smaller Cu+ Auger parameter was the result of the strong interaction between Cu+ and SiO2 [16,19]. Another interesting finding was that the Cu+/Cu0 ratio had little change with the increase of EDTA introduction.

Table 2. Surface Cu species of the reduced xE-Cu/SiO2 catalysts derived from Cu LMM XAES spectra.

| Catalysts     | KE (eV) a | AP (eV) b | BE of Cu2p3/2 (eV) | X Cu+ (% c) |
|---------------|-----------|-----------|-------------------|-------------|
| Cu/SiO2       | Cu+ 913.1 | Cu0 916.1 | Cu+ 1846.1        | Cu0 1849.1  |
|               |           |           |                   | 933.0       | 61.3        |
| 0.04E-Cu/SiO2 | Cu+ 913.2 | Cu0 916.2 | Cu+ 1846.0        | Cu0 1849.0  |
|               |           |           |                   | 932.8       | 60.5        |
| 0.08E-Cu/SiO2 | Cu+ 912.7 | Cu0 916.0 | Cu+ 1845.8        | Cu0 1849.1  |
|               |           |           |                   | 933.1       | 63.0        |
| 0.12E-Cu/SiO2 | Cu+ 913.0 | Cu0 916.0 | Cu+ 1846.1        | Cu0 1849.0  |
|               |           |           |                   | 933.0       | 61.6        |
| 0.3E-Cu/SiO2  | Cu+ 912.5 | Cu0 915.8 | Cu+ 1845.6        | Cu0 1849.9  |
|               |           |           |                   | 933.1       | 55.8        |

a Kinetic energy. b Auger parameter. c Intensity ratio between Cu+ and (Cu+ + Cu0) by deconvolution of Cu LMM XAES.
The DMO hydrogenation reaction was used to test the performance of a series of samples, and Table 3 shows the results of xE-Cu/SiO$_2$ samples. It was observed that the DMO conversion and EG selectivity first increased with the increase of EDTA introduction, then decreased when the ratio of EDTA/Cu was higher than 0.08 under 2 MPa at 160 °C; at last, the DMO conversion of 60.9% could be obtained over the 0.08E-Cu/SiO$_2$ sample. In addition, the TOF of the 0.08E-Cu/SiO$_2$ sample was 15.95 h$^{-1}$, which was much higher than that of the pure Cu/SiO$_2$ sample (8.62 h$^{-1}$). The evaluation results of the 0.08E-Cu/SiO$_2$ sample at different reaction temperatures show that the optimum reaction temperature was 180 °C, in which the DMO conversion was 99.99% and the EG selectivity was 97.70%. Of note, the conversion of the 0.3E-Cu/SiO$_2$ sample was lower than that of the pure Cu/SiO$_2$ sample, while the TOF value was higher than that of the pure Cu/SiO$_2$ sample, at 160°C. The conversion of the 0.3E-Cu/SiO$_2$ sample was higher than that of the pure Cu/SiO$_2$ sample at 180 °C. In general, the activity of the 0.3E-Cu/SiO$_2$ sample was higher than that of the pure Cu/SiO$_2$ sample.

2.4. Catalytic Activity and Stability

It is also worth noting that, as shown in Figure 8, the performance of the 0.08E-Cu/SiO$_2$ sample was stable during the 1200 h of time on stream. Neither DMO conversion nor EG selectivity decreased significantly; namely, their average values kept constant at 99.9% and 98.3%, respectively. It was evident that the lifetime of 0.08E-Cu/SiO$_2$ catalyst...
was much longer than the lifetime of the pure Cu/SiO₂ catalyst prepared by the same method [12,31,32].

![Graph](image-url)

**Figure 8.** DMO hydrogenation over 0.08E-Cu/SiO₂ catalyst as a function of time on stream. Reaction conditions: T = 180 °C, P(H₂) = 2.0 MPa, H₂ /DMO = 100 (mol mol⁻¹).

### 3. Discussion

#### 3.1. Interaction between EDTA and Silica Sol

EDTA (H₄Y) is not only a strong chelating agent but also a hexabasic weak acid [33], and only the Y⁴⁻ ions produced by hydrolysis are an effective form of chelation, so it could chelate with Cu²⁺ ions to form CuY²⁻ ions. Moreover, the chelate ability of Cu²⁺ ions with EDTA is stronger than that with NH₃ under the same conditions [21,34]. Thus, the concentration of Cu(NH₃)₄²⁺ ions decreased with the introduction of EDTA, while the concentration of CuY²⁻ ions increased in the precursor solution.

The elemental analysis results of the dried xE-Cu/SiO₂ samples showed that the content of C in all samples was below the minimum detection limit (C ≤ 0.3%), which could be considered that there was no EDTA in the dried samples. In this work, it was also found that the filtrate of the sample without EDTA was colorless, while the filtrates of samples with EDTA were blue, and the color changed from blue to dark blue with the increase of the amount of EDTA. Dark blue was identified as the color of CuY²⁻ ions. Moreover, on the basis of the ICP results, it could be confirmed that EDTA was able to reduce the Cu loading of the xE-Cu/SiO₂ catalysts. It could be speculated that the CuY²⁻ ions were hard to adsorb by the SiO⁻ groups on the surface of silica sol, because the SiO⁻ groups and CuY²⁻ ions in the solution had the same charge under alkaline conditions. Therefore, the CuY²⁻ ions would be removed from the surface of the catalyst via filtration and washing, resulting in the reduction of catalysts’ actual Cu loading when the theoretical Cu loading was the same during preparation.

In brief, EDTA could not interact directly with the silica sol but coordinated with Cu²⁺ ions to form CuY²⁻ ions; certainly, CuY²⁻ ions were incapable of grafting to the surface of the silica sol owning to the same charge. Consequently, most CuY²⁻ ions were eliminated from the catalyst precursors during washing and filtration, leading to the decrease of the actual Cu loading of the samples.
3.2. Effect of EDTA on Surface Copper Species of the Catalysts

In the calcined samples, the presence of copper phyllosilicate was detected by XRD, and confirmed by the results of the FT-IR and the Cu2p3/2 XPS. In addition, the presence of CuO was also confirmed by the Cu2p3/2 XPS spectra of calcined samples. A characteristic satellite peak at ca. 945.0 eV also showed that the oxidation state of copper was +2 in all the calcined samples. For the reduced samples, it could be known that there were Cu+ -O-Si, Cu2O and Cu0 on the surface, according to the results of XRD, Cu2p3/2 XPS and XAES.

Wang et al. [35] pointed out that the evaporation of ammonia pushed the balance of reaction (1) moving rightward, thus promoting the formation of copper phyllosilicate. Cu(OH)2(H2O)4 was an important intermediate during the formation of copper phyllosilicate [21]. The chelation between Cu2+ ions and EDTA would decrease the concentration of Cu(NH3)42+ ions in the solution, which went against the rightward progress of reaction (1). In this way, the amount of copper phyllosilicate would be decreased.

\[
\text{Cu(NH}_3\text{)}_4^{2+} + 6\text{H}_2\text{O} \rightarrow \text{Cu(OH)}_2(\text{H}_2\text{O})_4 + 2\text{NH}_4^+ + 2\text{NH}_3
\]  

However, not all the Cu(NH3)42+ could be formed into Cu(OH)2(H2O)4, so the concentration of Cu(NH3)42+ ions decreased slightly when EDTA was introduced in small amounts, which had little effect on the formation of Cu(OH)2(H2O)4. Namely, there were only a handful of Cu2+ ions that were chelated by EDTA, as the EDTA/Cu was lower than 0.08; thus, the downward trend of the copper phyllosilicate formation amount was barely obvious for the calcinated samples. Furthermore, for the calcinated samples, there was a serious decline trend of copper phyllosilicate with the ratio of EDTA/Cu above 0.08; that was because the amount of Cu(NH3)42+ ions in the solution was greatly reduced as the introduction amount of EDTA continuously increased. Thus, the effect on the formation of copper phyllosilicate became more and more serious.

In addition, Wang et al. [35] also proposed that the slow dissolution rate of silica was conducive to polymerization of Cu(OH)2(H2O)4 to form copper hydroxide. Moreover, the low pH value went against the dissolution of silica [21]. A pH meter was used to measure the pH value of copper ammonia solutions. The results (Table S1) showed the introduction of EDTA reduced the pH of the copper ammonia solutions. Thus, the slow dissolution rate of silica promoted the formation of more copper hydroxide. Then the copper hydroxide would be translated into well-dispersed CuO particles after calcination. In contrast, it was prone to good dispersion of the Cu(NH3)42+ ions that were absorbed in the accumulation channels with the Cu(NH3)42+ ions concentration decreasing; then it would also form well-dispersed CuO particles after calcination. The BET surface of the samples with suitable EDTA were higher, which was favorable to form well-dispersed CuO particles with a smaller size. According to literature [12,16,36], the well-dispersed CuO particles would be reduced to Cu0 species. The XRD results showed that Cu0 nanoparticles on the surface of the reduced catalysts still maintained good dispersion, which indicated that the uniform dispersion of surface Cu0 species was conducive to inhibition of Oswald Ripening and the stability of Cu0 species on the surface of the catalysts could be enhanced with the introduction of EDTA.

In brief, the strong chelation between EDTA and Cu2+ reduced the concentration of Cu(NH3)42+ ions in the solution, which was responsible for affecting the formation of the surface Cu species. Fortunately, the appropriate introduction amount of EDTA had little effect on the formation of copper phyllosilicate, and it was beneficial to form more well-dispersed CuO particles.

3.3. Structure–Performance Relationship

The main factors affecting the activity of Cu/SiO2 catalysts include the number of active sites, the synergy between Cu+ and Cu0 and the size and dispersion of active species. Gong et al. [37] believed that the Cu0 was the main active site in the hydrogenation reaction, while the Cu+ mainly promoted the further transformation of methyl glycolate and ethylene
glycol. When Cu⁰/(Cu⁺ + Cu⁰) was 0.33, the highest hydrogenation activity was obtained. Ma et al. [38] found that esters (methyl acetate, ethyl acetate, dimethyl oxalate) could oxidize Cu⁰ of the reduced Cu/SiO₂ catalyst to Cu⁺, and the obtained Cu⁺ could be reduced back to Cu⁰ by H₂ under reaction conditions. Cu⁰ and Cu⁺ were in a dynamic cycle during ester hydrogenation. When the Cu⁺/Cu⁰ ratio reaches equilibrium in the dynamic redox cycle, the Cu⁺ active center would not affect the catalytic equilibrium. However, before the equilibrium of Cu⁺/Cu⁰ ratio, the change of the amount of Cu⁺ would affect the amount of C=O absorbed and the balance of the redox cycle, and the catalytic balance would be affected, ultimately. The synergistic effect of the two enabled the catalyst to have high catalytic performance under mild conditions. Wang et al. [39] synthesized a Cu@CeO₂ catalyst by the sol-gel method and suggested that the close relative position of Cu⁺ and Cu⁰ in the catalyst might be the main reason for the enhancement of synergistic effect.

In this work, the evolution of the structure–performance relationship with the introduction of EDTA is shown in Figure 9. It was found that it could provide more Cu⁰ sites with the introduction of EDTA; meanwhile, the Cu⁰ nanoparticle accumulation layer number was reduced, and the size of Cu⁰ nanoparticle particles became smaller. Therefore, there were more Cu⁰ sites that were in a close relative position to Cu⁺ sites on the surface of catalysts, and it also could inhibit the aggregation of Cu⁰ nanoparticles. Ultimately, the stability of Cu⁰ active sites and the synergistic effect between Cu⁰ and Cu⁺ sites were enhanced, which improved the catalytic hydrogenation performance and stability of the catalysts. Compared with pure Cu/SiO₂ sample, the 0.3E-Cu/SiO₂ sample had lower DMO conversion and higher TOF value, which showed that the synergistic effect between Cu⁺ sites and Cu⁰ sites had a greater effect on the activity than the number of active sites, as the number of active sites decreased in a certain range.

**Figure 9.** The evolution of the structure–performance relationship caused by the introduction of EDTA.

4. Experimental
4.1. Catalyst Preparation

The catalysts with different EDTA contents employing the ammonia-evaporation method were prepared according to our previous work [12,19,40]. A certain amount of EDTA and 10.6 g of Cu(NO₃)₂·3H₂O as well as 6 g of urea were dissolved in deionized water under stirring until the EDTA was completely dissolved, then 24 mL of 25–28 wt% ammonia aqueous solution was added to the mixed solution. After 10 min, we added 21.0 g of 40 wt% silica sol under stirring at room temperature. The suspension was subsequently
heated to 80 °C and kept at this temperature for 1 h under sealed conditions. After that, the seals were removed for the evaporation of ammonia until pH 6–7. The filter cakes obtained by means of filtration and washing were dried at 120 °C for 24 h and calcined at 450 °C for 5 h in an air atmosphere. Hereinafter, the calcined catalysts were named as xE-Cu/SiO2, where x was the molar ratio of EDTA and Cu.

4.2. Catalyst Characterization

The N2 adsorption and desorption experiment (BET) was carried out at −196 °C by temperature-programmed physical adsorption apparatus Micromeritics ASAP 2020. The adsorption–desorption isotherms of samples were measured, and the specific surface area of samples was calculated by the BET equation. The mesopore volume (Vp), pore size (Dp) and pore size distribution of samples were obtained by the BJH method.

The actual copper loading of samples was measured by the inductively coupled plasma optical emission spectrometer (ICP-OES), and the instrument model was Jobin Yvon Ultima2. The contents of C, H and N elements in the samples were measured by the element analyzer (EA), whose model was Vario EL-Cube.

The N2O pulse titration was used to measure the surface area and dispersion of active copper in samples. Its principle was to reduce the samples with H2 first, then oxidize all Cu0 in samples to Cu+ with N2O, which subsequently reduced Cu+ with H2 pulse; finally, we calculated the amount of Cu by measuring the amount of hydrogen consumption. The N2O titration equation was 2Cu (s) + N2O → N2 + Cu2O (s), and the atomic density of copper was calculated as 1.46 × 1019 copper atoms per m2.

The H2-temperature-programmed reduction (H2-TPR) was performed on a Micrometrics Autochem II 2920 instrument. All samples taken were about 30 mg (20–40 mesh) and pretreated for 2 h at 120 °C in an argon flow atmosphere to remove moisture and impurities and then cooled to 50 °C. After that, the Ar flow was converted into 10% H2–90% Ar, and the temperature was raised to 800 °C at a rate of 10 °C min−1. The consumption of H2 was measured by the TCD detector and MS signal.

The X-ray powder diffraction (XRD) was carried out on the Rigaku Miniflex 600 bench powder X-ray diffractometer with Cu target. The scanning range was 2θ = 10°–80°, and the scanning speed was 2.7° min−1. The Fourier transform infrared (FT-IR) measurements were performed using a Bruker Vertex 70 FT-IR. The measurement wavenumber range was from 4000 cm−1 to 400 cm−1 with a spectral resolution of 4 cm−1. The transmission electron microscopy (TEM) images were obtained on a Tecnai F20 instrument at an acceleration voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) and the Auger electron spectroscopy (XAES) were obtained on the ESCALAB 250Xi with Al Kα X-ray radiation (Hv = 1486.6 eV). The binding energy (BE) values were corrected using 103.7 eV as a reference for Si2p binding energy (BE).

4.3. Catalytic Reaction

The catalytic hydrogenation of DMO was carried out in a stainless steel continuous-flow fixed-bed reactor. The bottom of the reaction tube was filled with high-temperature resistant quartz cotton, and then 1 g of the calcined catalyst (20–40 mesh) was loaded. The remaining space of the reaction tube was filled with quartz sand, and the quartz cotton was used to separate the catalysts from the quartz sand. Before the reaction, the catalysts were prereduced for 5 h at 300 °C under 2 MPa by H2 atmosphere with the flow of 100 mL min−1. The temperature of the catalyst bed was monitored by a thermocouple inserted into the reaction tube. DMO (99%) was dissolved in methanol to prepare a feedstock solution with a mass concentration of 0.1 g mL−1. The weight liquid hour space velocity of DMO (WLHSVDMO) was 1.0 h−1, and the ratio of H2/DMO was 100 (mol/mol). The products were condensed by the condenser and stored in the product tank. The products were taken every 1 h and analyzed by gas chromatography (GC-7820A) with a flame ionization detector.
5. Conclusions

Based on the above findings, the following conclusions could be summarized: (1) The chelation of EDTA and Cu$$^{2+}$$ ions affected the formation of Cu species by changing the concentration of Cu(NH$_3$)$_4$$^{2+}$ ions. (2) The Cu surface area and dispersion were improved with the introduction of suitable EDTA in the preparation process. (3) There were more Cu$^0$ sites that were in a close relative position to Cu$^+$ sites on the surface of catalysts; thereby, the stability of Cu$^0$ active sites and the synergistic effect between Cu$^0$ and Cu$^+$ would be enhanced. (4) In the end, the catalytic hydrogenation performance and stability were improved greatly with the introduction of EDTA, and the optimum reaction temperature of DMO hydrogenation was further reduced.

For 0.08E-Cu/SiO$_2$ sample, more Cu$^0$ active sites were highly dispersed on the sample surface with a larger specific surface area, and the proportion of Cu$^+$ was appropriate. These factors together enhanced the synergistic effect between Cu$^+$ sites and Cu$^0$ sites, and finally made the 0.08E-Cu/SiO$_2$ sample have the optimal catalytic performance. The DMO conversion and EG selectivity were 99.9% and 97.7% at 180 $^\circ$C, respectively. Its catalytic performance also showed high stability without obvious decline or deactivation during the 1200 h life test at 180 $^\circ$C.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12030320/s1, Table S1: The pH value of copper ammonia solutions with different introduction amount of EDTA.

Author Contributions: Investigation, T.L.; Writing—Original Draft, T.L.; Visualization, T.L., C.C., L.H., J.Y. and P.Z.; Validation, T.L.; Formal analysis, T.L.; Writing—Reviewing and Editing, L.L. and R.Y.; Supervision, L.L.; Conceptualization, L.L.; Project administration, Y.Q.; Resources, Y.Q., J.C. and Y.Y.; Funding acquisition, Y.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by National Key R&D Program of China (2018YFA0704500); the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA21020800); the National Natural Science Foundation of China (22102186) and the Science Foundation of Fujian Province (2019J05156, 2019H0053).

Data Availability Statement: Data sharing is not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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