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Review

# Research progress on the copper-based catalyst design for dimethyl oxalate hydrogenation to ethylene glycol

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ABSTRACT

In this paper, the research progress of Cu-based catalyst and the activity enhancement strategies in the hydrogenation of dimethyl oxalate (DMO) to ethylene glycol (EG) was reviewed. As a green and economical ethylene glycol production path, the core of DMO hydrogenation of EG lies in the rational design and optimization of catalysts. This paper first introduces the background of the DMO hydrogenation system EG significance and the important effect of Cu-based catalyst in the reaction, particularly emphasizing the coordination with the $Cu^{+}$–$Cu^{0}$ species catalytic effect. Then, many factors affecting the activity of Cu-based catalysts were analyzed in detail, including the equilibrium effect between $Cu^{0}$ and $Cu^{+}$ species, the surface dispersion of Cu species, the interaction between metal and support, and the morphology effect of the catalyst. Regarding strategies for improving catalyst performance, this paper summarized effective measures such as optimizing support structure, adding promoters and optimizing preparation methods, and demonstrated the practical application effects of these strategies through representative catalyst examples. In addition, this paper also discusses the complex relationship between the influencing factors and catalyst performance. It points out the key directions for future research, with in-depth exploration of the correlation between catalyst structure and performance, the development of new catalysts, and the application of machine learning and big data technology in the catalyst research and development. In summary, this paper provides comprehensive theoretical guidance and practical reference for the performance optimization of Cu-based catalysts for DMO hydrogenation to EG.
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## 1. Introduction

Ethylene glycol (EG), as a key organic compound and chemical intermediate, is widely used in polyester, plastics, textiles, automotive antifreeze and industrial solvents [1–4], and its demand is increasing year by year with the growth of global economy and population. However, the traditional ethylene oxidation method to produce EG is limited by the scarcity of petroleum resources and environmental pressure. Thus, green and economic alternatives are urgently needed [5]. In this context, the dimethyl oxalate (DMO) hydrogenation to EG technology stands out [6], especially for the route of coal or syngas (derived from coal, natural gas, biomass, *etc.*) as feedstock [1], showing the potential to reduce dependence on oil, promote diversification of the energy mix, and meet the requirements of green chemistry and sustainable development.

DMO hydrogenation to EG is a complex chemical reaction process, the core of which is the design and optimization of catalyst. Cu-based catalysts exhibit excellent selectivity in DMO hydrogenation due to their selective activation of C=O/C—O bonds and low activity in C—C bond cleavage [7,8]. The synergistic effect of $Cu^{0}$ and $Cu^{+}$, especially the hydrogen activation ability of

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$Cu^0$ and the adsorption properties of $Cu^+$ on carbon-oxygen bonds [9], jointly promote the formation of an efficient reaction interface [10]. However, the activity of the mono-metallic copper catalyst is limited, the aggregation and sintering of nano-copper at high temperature, and the negative impact of Cu valence transition on catalytic performance need to be solved urgently.

To improve DMO conversion rate, EG selectivity and catalytic stability, researchers have focused on the innovation of catalyst preparation methods [11], the introduction of accelerators [12] and the exploration of their mechanism of action [8]. The main purpose is to significantly improve the catalytic performance by improving the dispersion of copper, adjusting the ratio of $Cu^+/Cu^0$, and enhancing the interaction between metal and support or promoter. At the same time, improving the activation ability of C═O/C—O and hydrogen is regarded as the key to improve catalytic efficiency [13].

Among many catalysts, Cu-based catalysts are favored in DMO hydrogenation EG technology because of their low cost and environmental friendliness. However, there is still room for improvement in its activity and stability. Existing studies have shown that the activity of Cu-based catalysts is significantly affected by factors such as Cu loading, dual active site $Cu^0/Cu^+$ ratio, promoters type and amount, Cu dispersion, metal-support interaction, acid-base of the support surface, morphology and structure, porosity and pore size distribution, and activation conditions.

Dimethyl oxalate hydrogenation to ethylene glycol is not only of great significance in environmental protection, industrial application and energy security, but also shows a broad space for technological innovation. In the future, through in-depth exploration of the relationship between catalyst structure and performance, the development of efficient, stable and low-cost Cu-based catalysts will further promote the industrialization process of the technology and achieve green transformation and sustainable development of EG production. This paper reviews the research progress on the factors affecting the activity of Cu-based catalysts in DMO hydrogenation of EG, discusses the strategies to improve the performance of catalysts, and forecasts the future development direction.

## 2. Reaction Mechanism of Catalytic Hydrogenation of DMO on Cu-Based Catalysts for Ethylene Glycol Production

The catalytic hydrogenation of DMO on Cu-based catalysts to produce EG is a complex process involving multi-step hydrogenation, activation of C═O bonds, and cleavage of C—O bonds. The reaction typically proceeds under conditions of 180–220 °C and 2–5 MPa $H_2$ pressure, with $Cu/SiO_2$ being the most widely used catalyst system. The reaction mechanism primarily follows the Langmuir-Hinshelwood model, wherein reactants (DMO and $H_2$) first adsorb onto the catalyst surface, followed by hydrogenation and dissociation steps.

The two carbonyl groups (C═O) in DMO serve as the active sites for hydrogenation. During the initial reaction stage, DMO adsorbs onto Cu active sites ($Cu^0$ or $Cu^+$) *via* the oxygen atom of its C═O bond, forming a surface-adsorbed species. $Cu^0$ sites primarily facilitate the dissociative adsorption of $H_2$ to generate active hydrogen species, while $Cu^+$ sites stabilize the C═O bond through Lewis acidity, enhancing its activation. After $H_2$ dissociation on the Cu surface, sequential attacks on the DMO C═O bonds occur. This first produces hydroxymethoxymethanoic acid methyl ester ($HOCH_2OCOOCH_3$), a key intermediate, *via* hydrogenation of the first C═O bond—a rate-limiting step with high activation energy [14]. Subsequent hydrogenation of the second C═O bond generates methylene glycolate ($HOCH_2COOCH_3$) or methyl glycolate ($HOCH_2OCH_2OH$). Further hydrogenation of these intermediates involves hydrogenolysis of C—$OCH_3$ bonds, ultimately yielding the target product ethylene glycol ($HOCH_2CH_2OH$) and byproduct methanol ($CH_3OH$) [15].

The reaction network faces challenges from side reactions that compromise EG selectivity. Over-hydrogenation may lead to ethanol ($CH_3CH_2OH$) formation, while C—C bond cleavage could produce methyl formate ($HCOOCH_3$) or CO. These byproducts reduce EG purity and increase separation complexity.

## 3. The Factors Affecting Catalyst Activity

### 3.1. Equilibrium effects in the synergistic catalysis of $Cu^0$ and $Cu^+$ species

The catalytic performance of Cu-based catalysts in DMO hydrogenation to ethylene glycol not only depends on the valence state of copper species (such as $Cu^0$, $Cu^+$) but also is greatly affected by the synergistic catalysis between $Cu^0$ and $Cu^+$ species [16]. Synergistic catalysis manifests as the collaborative interaction of copper species in different oxidation states or forms during the reaction, which enhances overall catalytic efficiency through mechanisms such as electron transfer, intermediate adsorption, or complementary active site interactions [17]. Balancing effects refer to the regulatory role of the $Cu^0/Cu^+$ ratio and its dynamic variations on catalytic activity. These effects not only correlate with the quantity of active sites but also directly influence reactant adsorption, intermediate stabilization, and product selectivity [18]. Recent studies demonstrate that the synergistic interplay between $Cu^0$ and $Cu^+$ plays a crucial role in DMO hydrogenation [19].

Zhao *et al.* [20] investigated the $Cu^+$ surface area in $Cu/SiO_2$ catalysts *via* hydrolysis-precipitation method (HP) and found that the 30Cu-TEOS catalyst exhibited the optimal space-time yield ($1.74\ g \cdot g^{-1} \cdot h^{-1}$, g EG/g cat. per hour)) due to its highest $Cu^+$ specific surface area ($31.4\ m^2 \cdot g^{-1}$), confirming $Cu^+$ as the key active site for EG generation. XPS and $N_2O$ titration results revealed that the synergistic interaction between $Cu^+$ and $Cu^0$ optimized the activation of DMO's C═O bond and intermediate hydrogenation. Similarly, Chen *et al.* [21] synthesized a series of $Cu/SiO_2$ catalysts, observing a volcano-type curve for EG selectivity as the $Cu^0/Cu^+$ ratio increased from 0.16 to 1.22. Maximum EG yield (98%) was achieved when $Cu^+$ accounted for approximately 50% ($Cu^+/(Cu^+ + Cu^0) = 0.52$), indicating that imbalance in their ratio reduces catalytic efficiency. Theoretical calculations further elucidated the synergistic mechanism. An *et al.* [14] employed density functional theory (DFT) to demonstrate functional division between $Cu^0$ and $Cu^+$ during DMO hydrogenation: $Cu^0$ dissociates $H_2$ to provide active hydrogen, while $Cu^+$ polarizes the C═O bond to activate DMO and stabilize intermediates. Yan *et al.* [15] integrated microkinetic modeling with DFT calculations (Fig. 1), showing that $Cu^+$ enhances reactant adsorption and intermediate desorption, reducing the activation energy of DMO dissociation from 299 to 168.6 $kJ \cdot mol^{-1}$ (Fig. 2), thereby significantly accelerating the reaction. Furthermore, kinetic simulations of $Cu/SiO_2$ catalysts prepared *via* precipitation-decomposition revealed that DMO hydrogenation follows a bidirectional Hougen-Watson mechanism, with DMO dissociative adsorption as the rate-determining step. $Cu^+$ optimizes the reaction pathway by modulating surface hydrogen coverage [22].

Notably, the optimal $Cu^0/Cu^+$ ratio is influenced by multiple factors. Chen *et al.* [21] observed that $Cu/SiO_2$ prepared by ammonia evaporation achieved 54.9% $Cu^+$ at 363 K, yielding 98% EG selectivity, whereas Zheng *et al.* [23] reported peak performance for ion-exchange-prepared catalysts at ~40% $Cu^+$. These differences arise from method-dependent control over copper dispersion and

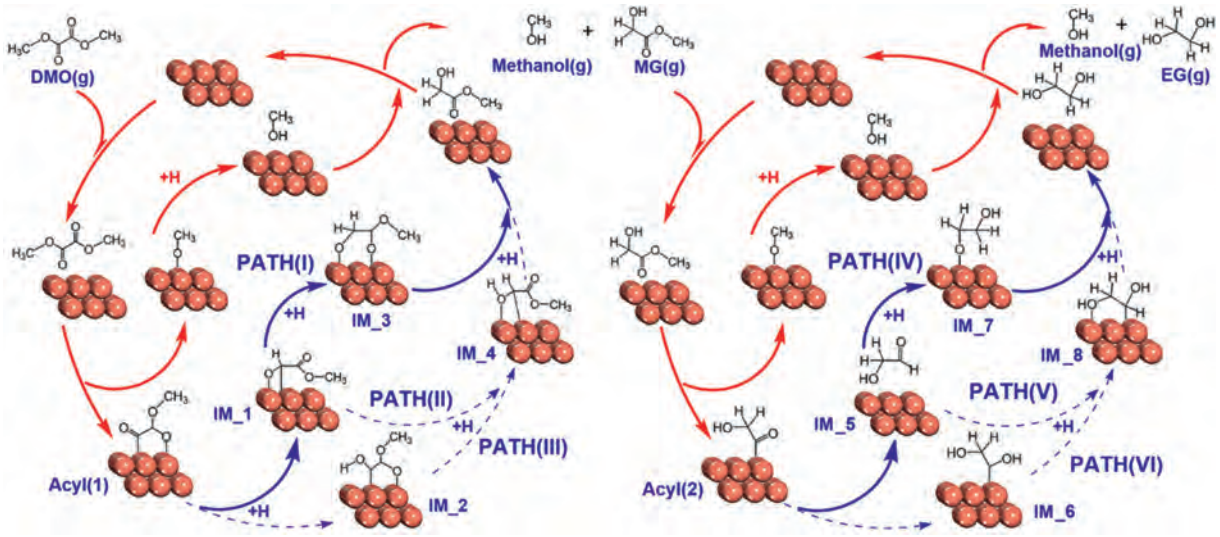



**Fig. 1.** Reaction mechanism for DMO hydrogenation to EG. The possible pathways of the successive hydrogenation of Acyl(1) and Acyl(2) are colored blue, and the dominant reaction pathway is highlighted by a solid line. Reprinted with permission from Ref. [15]. Copyright 2020 American Chemical Society.

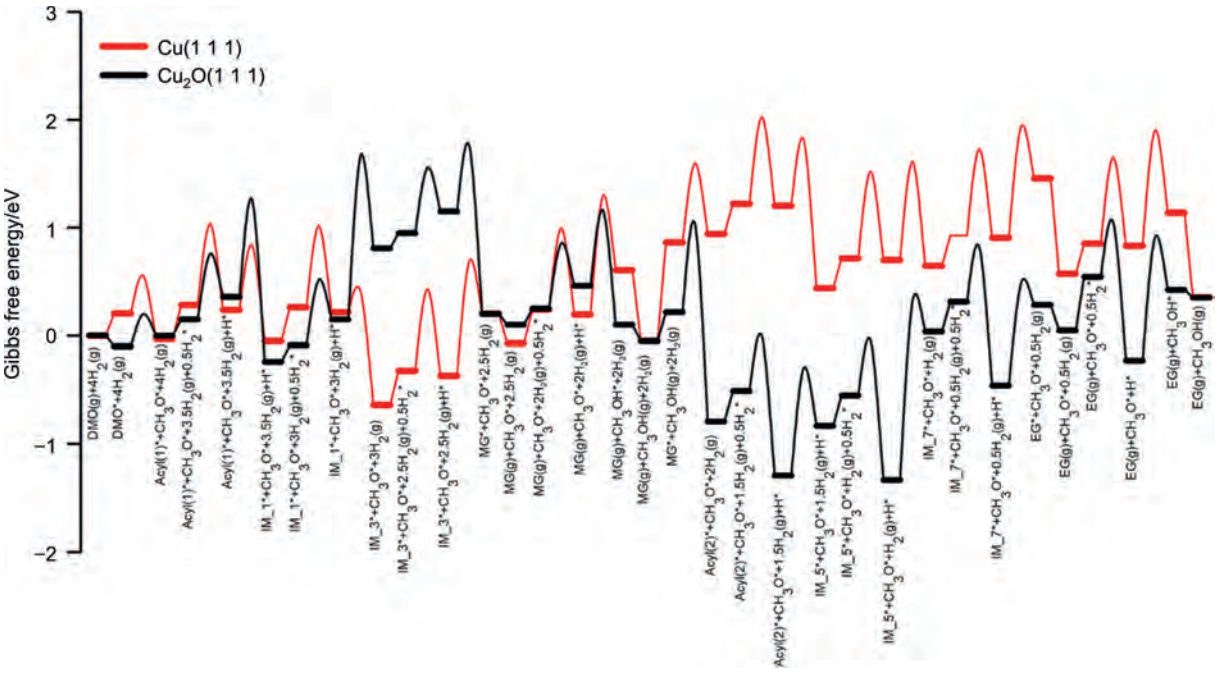



**Fig. 2.** Gibbs free-energy diagrams for DMO hydrogenation on Cu(1 1 1) and $Cu_2O$(1 1 1) at 473 K. Reprinted with permission from Ref. [15]. Copyright 2020 American Chemical Society.

support interactions. Additionally, reaction conditions (*e.g.*, $H_2$/DMO ratio, pressure, temperature) and catalyst deactivation (*e.g.*, excessive $Cu^+$ reduction to $Cu^0$) may cause fluctuations in the optimal ratio [24]. Nevertheless, maintaining moderate $Cu^+$ active site density (typically 10% to 50% of $Cu^0$) is critical for achieving high EG selectivity. These studies provide solid theoretical evidence that the synergistic interaction between $Cu^+$ and $Cu^0$ sites plays an important role in improving the catalytic performance of Cu-based catalysts in DMO hydrogenation of EG. Therefore, the $Cu^0/Cu^+$ ratio is an important factor affecting the conversion, selectivity and turnover of EG by DMO hydrogenation. However, no studies have shown that what the best $Cu^0/Cu^+$ ratio is for the DMO hydrogenation, which remains the focus of the future research.

### 3.2. Surface dispersity of Cu species

The dispersion degree of active components in heterogeneous catalysts plays a decisive role in their activity and stability [25–27]. Studies have demonstrated that highly dispersed Cu species significantly enhance catalytic performance. For instance, the 20Cu/OMS catalyst loaded on ordered mesoporous silica achieves uniform pre-distribution of $Cu^{2+}$ precursors in mesoporous channels through optimized ammonia evaporation conditions. After reduction, this forms dual active sites of $Cu^0$ and $Cu^+$ with an average size of 3.16 nm, achieving 100% DMO conversion at 453 K (20Cu/OMS) [28]. This dispersion optimization increases the total surface area of $Cu^0$ and $Cu^+$ per gram of catalyst to 78.5 $m^2 \cdot g^{-1}$,

nearly threefold higher than conventionally impregnated $Cu/SiO_2$ ($20Cu/SiO_2$, 27.3 $m^2 \cdot g^{-1}$) [28,29]. XPS and $N_2O$ titration results reveal a positive correlation between $Cu^+/(Cu^+ + Cu^0)$ ratio and dispersion degree (53% for 20Cu/OMS *vs.* 45.8% for 25Cu/OMS), confirming that high dispersion favors enrichment of oxidized $Cu^+$ species [28]. This electronic state regulation mechanism is also verified in B-doped Cu/HMS catalysts: when the Cu/B molar ratio is 2:1, the $Cu^+$ proportion reaches 74.8%, and DMO conversion increases to 100% (200 °C, 2 MPa), representing a 12% improvement over undoped samples [30]. TEM characterization shows that MOF-derived $Cu/SiO_2$ (MOF-CmS) catalysts exhibit uniform Cu nanoparticles with an average size of 4.2 nm anchored on $SiO_2$ surfaces, maintaining 98.1% EG selectivity after 100 h of continuous reaction, whereas conventional $Cu/SiO_2$ suffers from particle aggregation leading to a 46.6% selectivity drop [25]. The dispersion effect on reaction pathway regulation is particularly evident in the $Cu/ZnO/Al_2O_3$ system: at a Cu/Zn/Al molar ratio of 2:2:1, ZnO synergism facilitates isolated Cu dispersion on $Al_2O_3$ surfaces, enabling C═O selective activation with 95% EG selectivity. In contrast, Cu excess (Cu/Zn/Al = 3:1:1) causes particle aggregation and intensified C—C bond cleavage side reactions, increasing 1,2-butanediol selectivity to 15.9% [29]. Kinetic studies reveal that high-dispersion Cu catalysts ($d$~5 nm) exhibit significantly lower apparent activation energy (115 $kJ \cdot mol^{-1}$) compared to low-dispersion counterparts (132 $kJ \cdot mol^{-1}$), confirming the direct impact of active site accessibility on reaction kinetics [27–30]. Regarding stability, the MOF-CmS catalyst maintains 92% $Cu^0$ surface area after 100 h at 200 °C/2 MPa, while conventional $Cu/SiO_2$ loses 42% activity sites due to sintering [28]. HAADF-STEM observation of HKUST-1-derived $Cu/SiO_2$ shows strong metal-support interactions (Cu-O-Si bonds) firmly anchor Cu species, effectively suppressing $Cu^0$ migration/aggregation at high temperatures [28]. These findings collectively demonstrate that tuning Cu species dispersion enables synergistic optimization of catalytic activity, selectivity, and stability.

### 3.3. Metal-support interaction

Metal-support interaction (MSI) refers to a dynamic interdependent system formed between metal active components and support materials through physicochemical interactions such as charge transfer, interfacial bonding, and coating effects during preparation, activation, and reaction processes. The strength and form of MSI directly influence the electronic structure of catalysts, accessibility of active sites, and reaction stability. For example, in the $Cu/SiO_2$ system, the $SiO_2$ support induces electron transfer from the support to Cu species *via* oxygen defects, forming electron-rich $Cu^+$ active centers (XPS characterization shows a $Cu^+$ ratio of 74.8%), significantly enhancing C═O bond activation and increasing ethylene glycol selectivity in DMO hydrogenation to 98% [18–25]. In contrast, the $Cu/Al_2O_3$ system exhibits strong interfacial bonding between $Al^{3+}$ and $Cu^{2+}$ due to electrostatic attraction, reducing the average Cu particle size from 24 nm (conventional impregnation) to 15 nm, while improving high-temperature stability by 4-fold and catalytic activity by 37% [27]. For $TiO_2$ supports, strong interactions between surface oxygen vacancies and Cu not only elevate the $Cu^+/(Cu^0 + Cu^+)$ ratio to 0.85 but also establish electronic channels *via* anatase-rutile heterointerfaces, achieving 100% conversion and 98% EG selectivity in DMO hydrogenation [31]. Such robust MSI also suppresses metal sintering; for instance, the $Cu/TiO_2$ catalyst remains stable for over 100 h at 450 °C [32,33]. However, support coatings can exhibit dual effects: HKUST-1-derived Cu coatings triple $Cu^+$ surface coverage and enhance DMO conversion by 12%, but excessively thick coatings (>5 nm) hinder reactant diffusion, reducing space-time yield by 28% [34,35]. Ordered mesoporous $SiO_2$ regulates $Cu^+$ -reaction intermediate matching *via* 3–5 nm pore sizes, achieving a space-time yield of 2.16 $g \cdot g^{-1} \cdot h^{-1}$ for EG while maintaining 99% selectivity [36]. These studies demonstrate that MSI synergistically determines catalytic performance through multidimensional mechanisms including charge redistribution, geometric effects, and mass transport regulation. Optimization requires balancing electronic coupling strength between the support and metal with active site exposure [30,37–39].

### 3.4. Morphology effect

The morphology of the catalyst, including surface structure, particle shape, size distribution and pore structure, has a significant effect on the catalytic performance. For the key industrial reaction of DMO hydrogenation to EG, Cu-based catalyst has become the focus of research because of its excellent activity and selectivity. Therefore, it is still a hot topic to study how the morphology effect of catalyst acts on the reaction and how to optimize the catalytic performance through morphology regulation.

The results show that the morphology of catalyst has an important effect on the distribution and catalytic performance of supported active Cu species. Due to the Brownian motion of supported Cu particles on the surface of the support, it is easy to lead to particle aggregation and sintering of Cu species on the surface, and then deactivate the catalyst. To solve this problem, various strategies such as Cu-silicate-layered structure [40], core-shell coating structure [34], metal-organic framework structure [41] and molecular sieve pore channel [42] have been used to inhibit the growth and sintering of Cu particles during reduction and reaction by limiting effect. At the same time, the application of structured channel support can effectively promote the diffusion of reactants and products, and further enhance the reaction activity.

In addition, the study also found that under the same distribution of Cu active sites, catalysts with specific morphologies exhibit enhanced catalytic performance. For instance, Ai *et al.* [35] achieved confinement effects by encapsulating copper nanoparticles within the nanochannels of carbon nanotubes (CNTs). Specifically, the researchers employed an ultrasonic-assisted impregnation method to inject copper nitrate solution into the open channels of CNTs, followed by calcination under an inert atmosphere. Due to electronic defects on the inner surface of CNTs (where π-electron density migrates from the inner to outer surface), copper oxides ($CuO/Cu_2O$) formed strong interactions with CNTs during calcination. This allowed for spontaneous reduction to metallic $Cu^0$ or metastable $Cu^+$ without external hydrogen. The dual confinement effects—physical confinement (CNT channels restricting particle size and distribution) and chemical confinement (inner CNT surface modulating reduction kinetics)—resulted in highly dispersed Cu nanoparticles within CNT interiors (TEM analysis revealed 87% of Cu particles were 10–20 nm in size with no external surface loading). These catalysts demonstrated enhanced reduction capacity and catalytic activity, enabling efficient regulation of the selective hydrogenation of dimethyl oxalate. Their activity significantly surpassed that of amorphous silica catalysts. This finding further confirms the important effect of catalyst morphology on catalytic performance. Meanwhile, relevant theoretical calculations and experimental studies have also revealed how catalysts with specific morphologies promote the enrichment and hydrogenation activity of reactants [43].

In summary, the catalyst morphology effect has a significant effect on the performance and stability of Cu-based catalyst for DMO hydrogenation to EG. By precisely controlling the morphology

characteristics of the catalyst, the distribution of supported active Cu species can be optimized, the particle growth and sintering can be inhibited, and the diffusion of reactants and products can be promoted, thus effectively improving the catalytic performance and stability. These studies provide important theoretical basis and practical guidance for the design and optimization of catalysts.

## 4. Catalyst Activity Enhancement Strategy

In terms of improving the performance and stability of DMO-to-EG Cu-based catalyst, researchers have carried out in-depth exploration and practice, and achieved remarkable results, which can be summarized as the three strategies of optimizing support structure, adding promoters and improving the preparation. Table 1 summarizes some representative catalysts.

### 4.1. Optimizing support structure

The support material plays a pivotal role in catalyst design, providing not only physical stability for the active species but also significantly influencing the overall catalytic performance, including specific surface area, number of active sites, catalytic efficiency, selectivity, and stability. This intricate interaction mechanism renders the support a critical component in optimizing catalyst performance. The following sections will elaborate on how these factors impact Cu-based catalysts' efficacy in DMO hydrogenation reactions and discuss recent advancements in this research domain.

Initially, the support offers attachment points for active copper species to ensure their uniform dispersion across its surface [68]. Such uniformity enhances both the specific surface area of the catalyst and substantially increases the number of available active sites, thereby elevating overall catalytic activity [35]. An augmented specific surface area allows more reactant molecules to access the catalyst's surface, thus enhancing reaction probabilities. Concurrently, an increase in active site numbers directly accelerates catalytic reaction rates.

Furthermore, various properties of the support material [26], such as acidity-alkalinity [19] and pore structure [21], profoundly influence the morphology and interactions among active species. These characteristics indirectly modulate catalytic performance by regulating the microenvironment around these species. For instance, variations in acidity can alter reactant adsorption modes and activation levels—thereby affecting selectivity during catalysis [3]. Additionally, pore architecture dictates diffusion pathways for reactants and products while impacting mass transfer efficiency and reaction stability [41].

Moreover, supports can optimize the reaction path and improve the catalytic selectivity and stability by changing the adsorption and desorption properties of the reactants and products [69]. In the reaction of DMO hydrogenation to EG, suitable support can effectively promote the adsorption and activation of DMO, and inhibit the formation of by-products, so as to improve the selectivity of EG. At the same time, the support can also limit the space of Cu nanoparticles by its structural characteristics (such as pore size, pore shape, *etc*.) to prevent agglomeration and sintering, thus improving the stability of the catalyst.

Ordered mesoporous silica materials (such as MCM-41, SBA-15, and HMS) have gained prominence as supports for Cu-based catalysts due to their abundant mesoporous structures with regular channels coupled with high surface area [28—70]. These attributes enable ordered mesoporous silica to enhance Cu dispersion

**Table 1**
Summary of the representative catalysts for the hydrogenation of DMO to EG.

| Catalyst | $T$/°C | $P$/MPa | $(H_2/DMO)$/mol·mol$^{-1}$ | LHSV/h$^{-1}$ | WHSV/h$^{-1}$ | $Conv_{DMO}$/% | $Selec_{EG}$/% | Ref. |
|---|---|---|---|---|---|---|---|---|
| $Cu/SiO_2$-$CH_3$ | 200 | 2.5 | 80 | 2 | – | 100 | 97 | [3] |
| 2.0-Zn-$Cu/SiO_2$ | 200 | 1.5 | 130 | – | 1 | 99.6 | 96.7 | [5] |
| $10Cu_{0.5}In/SiO_2$ | 190 | 2.5 | 95 | – | 0.5 | 100 | 96.5 | [6] |
| Cu/MMO-S3 | 165 | 2 | 50 | – | 1 | 98.2 | 96.1 | [8] |
| 30Cu-TEOS | 190 | 2.5 | 80 | 1.75 | – | 100 | 97 | [20] |
| $Cu/SiO_2$ | 180 | 3 | 80 | 0.5 | – | 100 | 95.2 | [44] |
| MOF-CmS | 200 | 2 | 50 | – | 0.82 | 100 | 98.81 | [25] |
| $Cu/SiO_2$-MOF | 200 | 2 | 50 | – | 0.82 | 99.9 | 98.6 | [41] |
| 20Cu/OMS | 180 | 2.5 | 80 | – | 1 | 100 | 98.2 | [28] |
| Cu/MS-3 | 180 | 2.5 | 100 | – | 0.4 | 99.96 | 97.9 | [45] |
| 50CZ | 220 | 2.4 | 80 | – | 2 | 96.8 | 97.4 | [46] |
| Cu/FMS | 245 | 2.5 | 100 | – | 0.4 | 99.62 | 96.95 | [38] |
| Ce-Cu-Si-AE | 185 | 2 | 100 | – | 1.2 | 100 | 95.3 | [47] |
| $Cu/SiO_2$-5 | 200 | 2.5 | 80 | – | – | 100 | 95 | [48] |
| 1.2Ce-Cu/HMS | 200 | 2 | 100 | 1.2 | – | 99.6 | 96.3 | [49] |
| $Cu1In/SiO_2$ | 180 | 2.5 | 80 | 0.6 | – | 100 | 96 | [50] |
| Cu-0.6%$Sn/SiO_2$ | 200 | 2.5 | 90 | – | 1 | 100 | 96 | [51] |
| Cu-4Mg/ZnO | 220 | 2.5 | 100 | 2 | – | 100 | 95 | [52] |
| 2.0βCD-CuSiMS | 180 | 2 | 50 | – | 1 | 99.9 | 97.5 | [53] |
| 0.08E-$Cu/SiO_2$ | 180 | 2 | 100 | – | 1 | 99.9 | 97.7 | [54] |
| 0.1CDCu-$SiO_2$ | 210 | 2 | 50 | – | 0.72 | 99.9 | 95 | [55] |
| 0.05D-Cu-$SiO_2$ | 190 | 2 | 50 | – | 2 | 99.8 | 92.3 | [56] |
| 0.2CD-Cu-$SiO_2$ | 190 | 2 | 50 | – | 1 | 99.9 | 97.4 | [57] |
| Cu/0.1B-CA | 230 | 2.4 | 180 | 1 | – | 100 | 68.4 | [58] |
| $Cu/SiO_2$-1.3$NH_2$ | 200 | 2.5 | 80 | 1.5 | – | 100 | 95.5 | [59] |
| Cu-$SiO_2$-24 h | 180 | 2 | 50 | – | 1 | 98.6 | 81.9 | [60] |
| Cu-$Ag_x/SiO_2$(B) | 190 | 2 | 50 | 0.2 | – | 100 | 97.4 | [61] |
| Cu-Ni/$ZrO_2$-DBD | 200 | 2.5 | 120 | – | 0.3 | 100 | 96 | [62] |
| $CuSi_3$ | 175 | 2 | 120 | 0.5 | – | 99.9 | 96.7 | [63] |
| O-IE-$Cu/SiO_2$ | 180 | 2 | 100 | – | 1 | 99.9 | 94.7 | [33] |
| Cu/ZSM-5-24 | 175 | 2 | 120 | – | 0.5 | 100 | 93.04 | [64] |
| 32CLZ700 | 220 | 2.4 | 80 | – | 1.2 | 97 | 98 | [65] |
| CZ-600 | 200 | 2.5 | 200 | – | 0.4 | 100 | 95.09 | [66] |
| R-50 | 210 | 2.5 | 100 | 2 | – | 100 | 98 | [67] |

effectively while mitigating nanoparticle agglomeration through spatial confinement mechanisms. However, in practical applications, these supports also face some challenges. Most of the traditional ordered mesoporous silica supports have cylindrical channels, which may lead to inefficient utilization of active sites. Due to the limitation of channel shape, some of the active sites may not be fully utilized, thus reducing the overall activity of the catalyst. In addition, when Cu nanoparticles are highly dispersed within the channel, they may block the channel, resulting in poor transfer of reactants and products, affecting catalytic efficiency. To address these issues researchers have implemented several optimization strategies. For example, Ma *et al.* [42] selected MCM-41 with a high specific surface area and ordered mesoporous structure as the support, and employed the ammonia evaporation method to regulate copper dispersion, achieving optimized carrier structure. At a copper loading of 20% (mass), copper nanoparticles were uniformly dispersed within MCM-41 channels, forming small particles with an average size of ~4.5 nm while maintaining a large copper-specific surface area of 34 $m^2 \cdot g^{-1}$. This approach effectively prevented pore blockage and aggregation issues caused by high loadings. Furthermore, the mesoporous structure of MCM-41 (initial pore diameter ~2.5 nm) partially transformed into secondary pores (~5 nm) after copper loading, significantly enhancing reactant and intermediate diffusion while reducing mass transfer resistance. The optimized carrier structure not only provided abundant active sites but also stabilized the coexistence of $Cu^+$ and $Cu^0$ through strong metal-support interactions (SMSI), thereby substantially improving the catalytic performance for DMO hydrogenation to EG. This system achieved 100% DMO conversion and 92% EG selectivity. Yet limitations regarding potential channel blockage at elevated loadings still exist.

To further improve the performance of ordered mesoporous silica support, Zhang *et al.* [45] achieved optimization by designing an MS-3 support with a unique hexagonal prism structure. This structure, prepared *via* a room-temperature stirring method, endowed MS-3 with a higher specific surface area (1846.3 $m^2 \cdot g^{-1}$) and narrower pore size distribution (~2.5 nm). The design not only provided ample diffusion space for copper ammine complexes, enabling their uniform dispersion within the pores, but also suppressed excessive growth of copper nanoparticles (Cu NPs) through spatial confinement effects. TEM and XRD results revealed that the average Cu NP size in Cu/MS-3 was only 8.2 nm, significantly smaller than those on other supports (*e.g.*, Cu/MS-1 with 6.4 nm but poor stability), demonstrating the critical role of pore structure in particle size control.

Secondly, strong metal-support interactions (SMSI) are key to stabilizing copper species. During catalyst preparation, copper ammine complexes reacted with the MS-3 silica matrix, forming a copper phyllosilicate structure. This structure anchored copper atoms firmly onto the support surface *via* Si-O-Cu bonds, maintaining a high $Cu^+$ proportion ($Cu^+/(Cu^+ + Cu^0)$ ratio reached 67.9% in Cu/MS-3) even after high-temperature reduction and prolonged reaction. XPS and XAES analyses confirmed that $Cu^+$ acted as the active center to activate the ester group of DMO, while $Cu^0$ facilitated $H_2$ dissociation. The synergistic interplay between $Cu^+$ and $Cu^0$ enhanced reaction efficiency.

Furthermore, thermal stability and anti-sintering mechanisms were optimized through structural design. The high specific surface area and ordered pores of MS-3 reduced local copper concentration, decreasing particle collision probability at elevated temperatures. $H_2$-TPR results showed that Cu/MS-3 exhibited a higher reduction peak temperature (340 °C) compared to Cu/MS-1 (328 °C), indicating stronger metal-support interactions that further suppressed Cu NP migration and aggregation. After 400 h of reaction, Cu/MS-3 retained 97.9% EG selectivity, with XRD and TEM showing minimal particle growth (+1.5 nm), confirming its anti-sintering capability.

Finally, enhanced mass and heat transfer efficiencies optimized reaction kinetics. The large specific surface area and mesoporous structure of MS-3 accelerated reactant diffusion to active sites while promoting timely product desorption, preventing carbon deposition and side reactions. In the highly exothermic DMO hydrogenation, this structural feature effectively dispersed reaction heat, mitigating localized overheating-induced catalyst deactivation. This finding suggests that the dispersion and stability of Cu nanoparticles can be optimized by adjusting the structure and morphology of the support, thereby improving the overall performance of the catalyst. Fibrous mesoporous silica (FMS) has a unique center-radial conical pore structure, which gives its loaded Cu NPs high exposure and accessibility. As the pore size gradually increases from the center to the surface, the FMS support can effectively promote the diffusion of reactants and products, and improve the catalytic efficiency. At the same time, the independent conical channel can also play a certain spatial constraint on Cu species, preventing their agglomeration and sintering, so as to improve the stability of the catalyst. Ai *et al.* [38] achieved multi-dimensional optimization of Cu-based catalysts by designing a FMS support with a unique centrally radiating conical pore structure, combined with liquid-phase deposition technology. The distinctive pore architecture of FMS not only delivered a high specific surface area (269.08 $m^2 \cdot g^{-1}$) and tailored pore size distribution (~3 nm) but also enhanced spatial confinement effects for copper species through its fibrous morphology, enabling high dispersion even under high-temperature reaction conditions (TEM showed an average Cu particle size of only 16 nm). During liquid-phase deposition, Cu precursors reacted with surface silanol groups on FMS to form Si-O-Cu chemical bonds, significantly strengthening metal-support interactions to suppress Cu nanoparticle migration and aggregation. These strong interactions promoted the formation of $Cu^+$ species ($Cu^+/(Cu^0+Cu^+)$ ratio reached 0.70), with high $Cu^+$ surface area confirmed by CO chemisorption (34.39 $m^2 \cdot g^{-1}$), providing active sites for selective activation of C═O bonds in DMO hydrogenation. Furthermore, FMS's ordered pore structure accelerated reactant diffusion while reducing mass transfer resistance, and the thermal stability of Si-O-Cu bonds maintained the original crystal phase even after 450 °C heat treatment. This design ultimately enabled ultra-stable operation for 1000 h at 245 °C with 99.62% DMO conversion and 96.95% EG selectivity.

In addition, catalytic stability can be successfully improved by confining or embedding Cu species into morphologically well-defined inorganic cavities or channels. This constraint effect effectively improves the stability of the catalyst by increasing the surface area of Cu and limiting its migration. On this basis, various types of confinement structures have been formed, including core-shell [34], metal-organic frame structures [41], mesoporous and lamellar structures [40,42,71]. Wang *et al.* [34] successfully constructed a $Cu@CeO_2$ core-shell structured catalyst through a simple sol-gel method, where the unique core-shell design enhanced catalytic performance *via* dual mechanisms: (1) the $CeO_2$ shell acted as a physical barrier to effectively prevent Cu nanoparticle aggregation, and (2) the enhanced metal-support interactions at the core-shell interface promoted the generation of more $Cu^+$ species. TEM characterization revealed that the Cu particles in this catalyst exhibited a size of only 16 nm, significantly smaller than the 50 nm particles prepared by traditional impregnation methods. XRD results further indicated lower crystallinity, suggesting smaller crystallite sizes and higher dispersion. In the methylethanoate hydrogenation reaction, $Cu@CeO_2$ maintained 100% methylethanoate conversion and 100% ethanol selectivity over

160 h of sustained reaction at 215 °C, whereas the conventional impregnation catalyst experienced a sharp decline in activity within just 10 h due to Cu particle sintering. This remarkable stability enhancement was attributed to the dynamic stabilization of Cu species by the core-shell structure and the synergistic effects between $Cu^0$ and $Cu^+$ at the interface—their spatial proximity optimized the synergistic efficiency of hydrogen dissociation and C—O bond activation. Another innovative study developed a Cu@CNTs-500 catalyst by confining Cu nanoparticles within the nanochannels of carbon nanotubes (CNTs) [35]. This strategy leveraged the self-reduction behavior of Cu species during high-temperature calcination, driven by interactions between the electron-deficient inner surfaces of CNTs and CuO. XRD and TPR analyses revealed an optimized synergistic exposure of $Cu^0$ and $Cu^+$ in Cu@CNTs-500, with specific surface areas of 18.8 $m^2 \cdot g^{-1}$ ($Cu^0$) and 3.4 $m^2 \cdot g^{-1}$ ($Cu^+$). The $H_2$-TPR profile demonstrated a reduction peak temperature >150 °C lower than conventional supported catalysts. In dimethyl ether hydrogenolysis to ethanol, Cu@CNTs-500 achieved 99.5% methylethanoate conversion and 77.9% ethanol selectivity at 270 °C, significantly outperforming traditional $Cu/SiO_2$ catalysts. Notably, under an ultrahigh space velocity of 1.6 $h^{-1}$, the catalyst maintained 99.9% conversion and 96.0% ethanol selectivity, attributed to the confinement effect of CNT nanochannels that prevented Cu over-reduction at high temperatures while stabilizing $Cu^+$ active sites *via* strong interactions with channel walls. This structural design not only expands the application scope of Cu-based catalysts in complex tandem reactions but also provides a novel approach for synergistically modulating catalytic performance through geometric/electronic effects. Shi *et al.* [36] successfully constructed a CuMgAl layered double hydroxide (LDH) catalyst system through a simple co-precipitation strategy, where Cu active sites were effectively confined within the interlayer structure. Studies revealed that when the Mg/Al molar ratio was 1.25, the catalyst exhibited a unique well-ordered layered stacking morphology, with highly dispersed copper active sites distributed on the surface. This structure created a synergistic microenvironment combining weakly alkaline sites (originating from interlayer hydroxyl groups and M—O bonds) and moderate-strength acidic sites (Lewis acid centers derived from $Al_2O_3$). This cooperative acid-base microenvironment efficiently activated DMO molecules: (1) copper species promoted hydrogen dissociation and adsorption, providing active hydrogen for subsequent hydrogen transfer steps; (2) moderate Lewis acidity polarized the carbonyl oxygen atoms in DMO, reducing the activation energy barrier for C═O bond cleavage; while (3) the physical confinement effect of the layered structure suppressed Cu nanoparticle migration and aggregation at elevated temperatures. Experimental results demonstrated that under reaction conditions at 553 K, the catalyst achieved nearly complete DMO conversion (~100%) with ethanol selectivity exceeding 83%. The exceptional performance was attributed to the synergistic mechanisms of active sites and the strong anchoring effect of LDH layers for stabilizing metal nanoparticles. Ding *et al.* [46] successfully exfoliated $Cu/ZrO_2$ catalysts into nanolayered structures by precisely tuning the Cu loading. This unique layered configuration significantly increased the exposure of Cu active sites and Cu-$ZrO_2$ heterointerfaces, enhancing the adsorption-activation efficiency of reactant molecules (*e.g.*, DMO) and intermediates (*e.g.*, $CO_2$, $H_2O$). Studies revealed that when the Cu content reached 50% (mass), the catalyst formed a well-defined nanolayered structure with a thickness of approximately 100 nm. Although the specific surface area ($S_{BET}$ = 4.5 $m^2 \cdot g^{-1}$) showed limited increase, the Cu-$ZrO_2$ interfacial area expanded by over three times compared to conventional particulate catalysts, resulting in a turnover frequency (TOF) surge to 134.1 $h^{-1}$—nearly an order of magnitude higher than reported $Cu/SiO_2$ systems (TOF ≈ 18–82 $h^{-1}$) [14,17]. Notably, the catalyst maintained 94.5% EG selectivity after 200 h of continuous reaction at 220 °C, demonstrating excellent industrial potential. Further $H_2$-TPR and XRD characterizations revealed that the strong interfacial interactions between 16.8 nm CuO crystallites and the tetragonal $ZrO_2$ support synergistically optimized hydrogen dissociation and oxygen migration capabilities. However, excessive Cu loading (*e.g.*, 58CZ) led to structural collapse and active site aggregation. This discovery provides a critical structural design paradigm for developing high-activity, long-lifespan Cu-based hydrogenation catalysts.

In the field of copper-based catalysts, the influence of different crystalline phase of supports on catalytic performance has also attracted much attention. Therefore, crystal phase engineering represents another critical direction in catalyst support modification. Wang *et al.* [31] synthesized a $Cu/TiO_2$ catalyst using an ammonia evaporation method, innovatively employing P25 $TiO_2$ (composed of 80% anatase and 20% rutile phases) as the support. Characterization *via* XRD, TEM, and XPS revealed that the crystal phase synergy of P25 significantly enhanced copper species dispersion: the anatase-rutile interface formed unique $Cu^0/Cu^+$ synergistic sites, where $Cu^+$ predominantly resided on the rutile phase, while $Cu^0$ was enriched on the anatase phase. This heterointerfacial effect not only optimized the $Cu^0/Cu^+$ ratio (approximately 0.85) but also suppressed copper nanoparticle aggregation through strong metal-support interactions (SMSI). In the DMO hydrogenation to EG reaction, the catalyst exhibited 100% DMO conversion and 99% EG selectivity while maintaining stability over 96 h of continuous reaction. This study demonstrates the potential of polycrystalline-phase supports to regulate active site distribution *via* interfacial engineering, providing a novel strategy for designing heterogeneous catalyst architectures. Fang *et al.* [37] developed a crystallization inhibition strategy whereby $K^+$ induces the formation of granular and dense foliated copper silicate to prepare copper-based catalysts with abundant Cu species and oxygen vacancies (Fig. 3). The surface of $Cu/SiO_2$ contains more abundant oxygen vacancies, which is more conducive to the process of methanol dehydrogenation and DMO adsorption. A large amount of $K^+$ blocked the hydroxyl group on the surface of $SiO_2$, inhibited the nucleation of lamellar foliated copper silicate, and formed granular foliated copper silicate with poor crystallinity. The space between $SiO_2$ particles is filled by a dense $CuSiO_3/SiO_2$ material, which is reduced to a more abundant and stable $Cu^+/Cu^0$ site located at the interface of $CuSiO_3$ and $SiO_2$.

In contrast, Yue *et al.* [72] designed a monolithic catalyst based on $Cu/SiO_2$ to achieve high dispersion and stable anchoring of copper through the formation of layered copper silicate and regular channel structure. This monolithic catalyst also shows high catalytic performance in DMO hydrogenation reaction (DMO conversion rate of 100%, EG selectivity of 95% or more), and has advantages in reaction efficiency, thermal stability and industrial application potential. This study not only validates the importance of layered structures and regular channels in catalyst design, but also provides strong support for the industrial application of whole catalysts.

In order to further improve the selectivity and stability of $Cu/SiO_2$ catalyst in DMO hydrogenation to EG reaction, the researchers adopted a surface modification strategy. Wang *et al.* [3] employed a silane coupling agent to graft-modify the catalyst, selectively covering surface hydroxyl groups with amino or alkyl functional groups to reduce the density of strong basic sites. The modified catalyst exhibited a twofold increase in MG desorption rate, a 70% reduction in byproduct $C_3$–$C_4OH$ selectivity, while the strong adsorption of MG intermediates on the modified surface was weakened, effectively suppressing copper particle agglomeration.

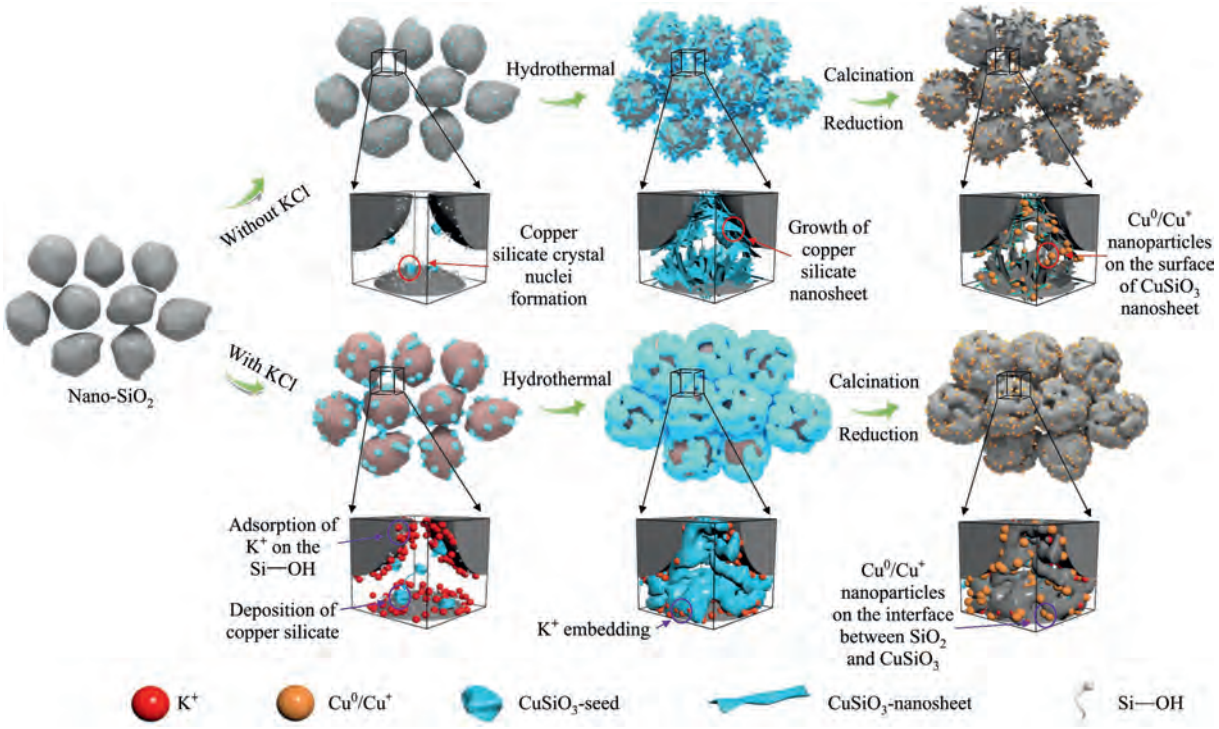



**Fig. 3.** Two copper phyllosilicate formation processes with and without KCl addition [37]. Copyright 2021 Elsevier Inc.

After 44 h of continuous reaction testing, EG selectivity remained above 92%, significantly extending the catalyst's lifespan.

The carrier size effect is also significant in the $Cu/SiO_2$ system. Wang *et al.* [48] utilized ultrafine silica sol (5 nm) as a carrier precursor, optimizing copper silicate formation pathways by regulating surface hydroxyl density. The high specific surface area ($522\ m^2 \cdot g^{-1}$) and abundant hydroxyl groups of the silica sol promoted uniform nucleation of $Cu^{2+}$ during the sol-gel process, forming highly dispersed layered copper silicate structures. After reduction, the $Cu^+$ surface coverage increased to 62% (*vs.* 20% for conventional catalysts), with $Cu^0$ particle size controlled at 2.8 nm. In DMO hydrogenation, the catalyst demonstrated a spatial-temporal yield of $1.85\ g \cdot g^{-1} \cdot h^{-1}$, representing a 3.5-fold improvement over conventional large-particle silica sol catalysts ($0.53\ g \cdot g^{-1} \cdot h^{-1}$). Mechanistic studies revealed that the quantum confinement effect of ultrafine silica sol reduced the electron transfer barrier for $Cu^+/Cu^0$ redox cycles, while high-density hydroxyl groups accelerated $H_2$ dissociation. This research confirms the enhanced accessibility of active sites and reaction kinetics through carrier nanoscaling, providing new perspectives for designing high-performance catalysts.

In summary, optimizing the carrier structure significantly enhances the performance of copper-based catalysts through multiple mechanisms, including enhanced dispersion of active components, regulation of the microenvironment, and improved mass transfer efficiency. The carrier provides uniform anchoring sites to promote copper species dispersion, increases effective specific surface area and the number of active sites, thereby improving catalytic activity. Its acid-base properties, pore structure, and surface chemical characteristics optimize reaction pathway selectivity and product inhibition effects by regulating reactant adsorption/desorption behavior, intermediate stability, and electronic interactions. For example, the pore size restriction of mesoporous silica suppresses byproduct formation and promotes selective hydrogenation of DMO. Three-dimensionally ordered pores and special morphologies (*e.g.*, fibrous and core-shell structures) restrict nanoparticle migration and sintering *via* spatial confinement effects, while metal-support strong interactions (SMSI) stabilize $Cu^+/Cu^0$ synergistic active centers, enhancing resistance to carbon deposition and sintering. High specific surface area and hierarchical pore structures accelerate mass transfer, alleviating deactivation caused by local heat accumulation at high temperatures. Experimental results demonstrate that optimized carriers (*e.g.*, MS-3, FMS) achieve 100% DMO conversion, over 96% EG selectivity, and significantly extended stability to a thousand-hour scale, confirming that carrier structure design is a key strategy for enhancing the comprehensive performance of copper-based catalysts.

### 4.2. Adding promoters

The additive is a very effective way to improve the catalytic activity, selectivity and stability of copper-based catalysts. The addition of promoters may regulate the electron density of copper, improve the reduction degree of metal copper, affect the interaction between the metal and the support, and form an alloy with the metal and other active species. The types of auxiliaries can be mainly divided into metal auxiliaries and non-metal auxiliaries. Among them, rare earth elements in metal auxiliaries, especially lanthanum [73] and cerium [47], have shown unique advantages in the field of catalysis as co-catalysts. They are widely used to optimize various catalytic reactions [74,75] because of their paramagnetism, high lattice oxygen mobility, valence state variability, and ability to significantly improve the electron transfer characteristics of catalysts [76]. In the copper-based catalyst system, lanthanum is often used as an accelerator or additive, which enhances the anti-sintering performance of the catalyst to

improve the catalytic efficiency through a series of complex mechanisms.

In particular, the addition of lanthanum can create synergies between special active sites and La participating sites by increasing metal dispersion. Alternatively, the electron density of Cu can be reduced through electron transfer to stabilize the active site in the optimal valence state, thus leading to positive changes in the catalyst structure [77]. For example, Han *et al.* [78] modified the Cu-fiber-structured PdAu alloy-$CuO_x$ catalyst by introducing $La_2O_3$, significantly enhancing its low-temperature activity and stability in the gas-phase hydrogenation of DMO to EG. The strong Lewis acidity of $La_2O_3$ promoted hydrogen spillover effects, while its surface acidic sites accelerated the migration of $H^+$ from the support to $CuO_x$, reducing the reduction temperature of $CuO_x$ (as evidenced by the left-shifted TPR peak), thereby improving $H_2$ activation capability. Additionally, $La_2O_3$ formed electronic interactions with the PdAu alloy, further enriching the electron density of Pd's 3d orbitals *via* electron-withdrawing effects, weakening the H—H bond strength. The synergistic contribution of Au optimized the alloy's electronic structure, enhancing $H_2$ dissociation efficiency. Furthermore, partial reduction of $La_2O_3$ to $LaO_x$ during the reaction generated oxygen vacancies on its surface, effectively activating the C═O and C—O bonds in DMO molecules and facilitating intermediate conversion. Finally, the incorporation of $La_2O_3$ suppressed excessive reduction of $Cu^+$, maintained the $Cu^+/Cu^0$ synergy active sites, and stabilized $Cu^+$ species to reduce sintering, prolonging catalyst lifespan. These synergistic effects enabled the 2% (mass) $La_2O_3$-modified catalyst to achieve 93.4% EG selectivity at 230 °C while maintaining high activity for 500 h, overcoming the limitations of traditional Cu-based catalysts that require high-temperature operation.

The addition of La to Cu/$ZrO_2$ catalysts can also reduce the copper particle size, enhance copper dispersion, promote the formation of Cu-La interactions, and stabilize the tetragonal structure of $ZrO_2$, exerting a significant influence on optimizing the catalyst's activity and selectivity. Its underlying mechanism bears similarity to the role of $La_2O_3$ introduction in modifying the Cu-fiber-structured PdAu alloy-$CuO_x$ catalyst. At the same time, La doping also enhanced the transport and diffusion of reactant molecules in the catalyst matrix. Although this increased the surface acid/base site to a certain extent with a slight decrease in EG selectivity, the conversion rate of DMO was improved in general [46].

Cerium is another important rare earth element, and its modified Cu/HMS catalyst also performs well in DMO hydrogenation to EG reaction. The introduction of cerium significantly enhances catalytic performance through multidimensional optimization of the microstructure and electronic properties of the catalyst. Wu *et al.* [49] demonstrated that: (1) Cerium incorporation effectively suppresses high-temperature sintering of copper nanoparticles by strengthening metal-support interactions (*e.g.*, forming Cu-O-Si bonds and copper phyllosilicate phases), reducing the average particle size from 3.1 nm (pure Cu/HMS) to 2.2 nm (1.2Ce-Cu/HMS). This substantially improves copper dispersion (D_Cu increases from 31.8% to 45.5%) and surface active site density. (2) Cerium doping modulates Cu valence state distribution. XPS and $N_2O$ titration revealed that optimal cerium content increases the surface $Cu^+/(Cu^0+Cu^+)$ ratio from 32.83% (Ce-free) to 48.03% (1.2Ce-Cu/HMS). This arises because cerium's basicity promotes partial reduction of $Cu^{2+}$ to $Cu^+$, where $Cu^+$ acts as Lewis acid sites to polarize DMO molecules, synergizing with $Cu^0$'s hydrogen dissociation sites to accelerate selective C—O bond cleavage. Additionally, cerium optimizes pore structure - although specific surface area slightly decreases, average pore size expands from 2.68 nm to 5.08 nm, alleviating product diffusion limitations. However, excessive cerium (>1.2%) causes Cu active site coverage, reduces $Cu^+$ proportion, and triggers particle size rebound, ultimately degrading performance. Thus, 1.2% Ce doping achieves optimal balance among dispersion, electronic structure, and pore regulation, achieving 99.6% DMO conversion and 96.3% EG selectivity.

Chen *et al.* [47] conducted in-depth studies on cerium promoters. By synchronously introducing $Ce^{3+}$ and $Cu^{2+}$ during the mixing stage of the ammonia evaporation method, they constructed a Cu-Ce composite oxide structure (Fig. 4) with synergistically enhanced effects, significantly improving catalytic performance. The mechanisms include: (1) Homogeneous mixing of free $Cu^{2+}$ and $Ce^{3+}$ ions in solution forms solid-solution composites, increasing active site density ($Cu^0/Cu^+$ ratio reaches 79.7%) while $Ce^{3+}$ stabilizes $Cu^+$ species through electronic regulation, suppressing copper nanoparticle sintering. (2) HAADF-STEM and XPS analyses revealed strong electronic interactions at $Cu^+/Ce^{3+}$

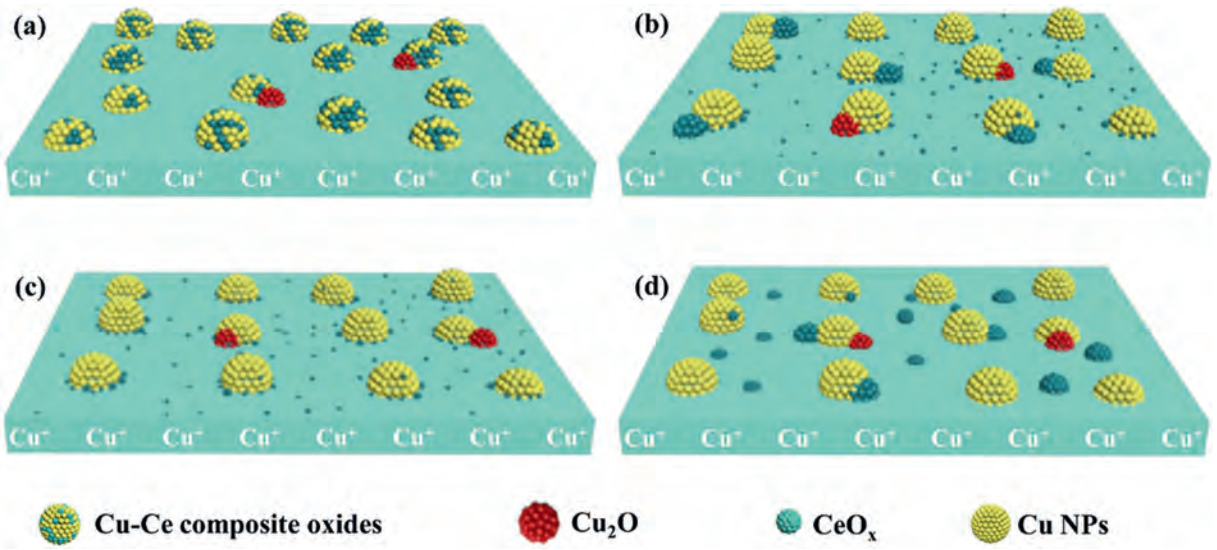



**Fig. 4.** The distribution of surface species over the reduced Ce-Cu-Si-T catalysts, (a) Ce-Cu-Si-AE, (b) Ce-Cu-Si-Evap, (c) Ce-Cu-Si-Dry, (d) Ce-Cu-Si-Cal [47]. Copyright 2021 Elsevier.

interfaces in the composite oxide, optimizing hydrogen activation and oxalate intermediate adsorption synergy. $Cu^0$ provides hydrogen dissociation sites, $Cu^+$ acts as Lewis acid for carbonyl activation, while $Ce^{3+}$ maintains $Cu^+$ stability *via* redox cycling. In contrast, post-introduction methods (post-evaporation/drying) cause Ce segregation on copper surfaces or active site blocking, reducing $Cu^+$ proportion and activity. Therefore, the synchronous introduction strategy achieves comprehensive improvements through structural regulation and electronic synergy, attaining 100% DMO conversion, 95.3% EG selectivity, and 480-h operational stability without performance decay.

In summary, rare earth elements enhance the catalytic performance of copper-based catalysts primarily by modulating the electronic structure of copper, optimizing the distribution of active sites, and strengthening interfacial synergy. Their mechanisms of action include: (1) reducing copper's electron density through electron transfer, stabilizing intermediate oxidation states (*e.g.*, $Cu^+$), and enhancing metal-support interactions to suppress sintering and improve reduction efficiency; (2) leveraging high lattice oxygen mobility, redox versatility, and Lewis acidity of elements like La and Ce to form alloy or oxide interfaces, promote hydrogen spillover, activate reactant molecules (*e.g.*, C═O bonds), and optimize intermediate conversion pathways. For instance, $La_2O_3$ enhances $H_2$ dissociation efficiency of PdAu alloys *via* electronic interactions while its surface acidic sites accelerate proton migration to lower the reduction temperature of $CuO_x$; (3) Ce stabilizes $Cu^+$ species, regulates pore structures, and inhibits high-temperature sintering, significantly improving copper dispersion and active site density. Experimental results demonstrate that a Cu fiber-PdAu/$CuO_x$ catalyst with 2% (mass) $La_2O_3$ achieves 93.4% selectivity for ethylene glycol (EG) in dimethyl oxalate (DMO) hydrogenation with stable operation over 500 h, while 1.2% Ce-doped Cu/HMS catalyst attains 99.6% DMO conversion by synergistically optimizing electronic structure and pore size distribution. These findings confirm that rare earth promoters synergistically enhance catalytic activity, selectivity, and stability through multidimensional mechanisms, overcoming the limitations of traditional copper-based catalysts requiring high-temperature operation.

In recent years, indium oxide ($In_2O_3$) catalyst has attracted wide attention in the field of catalysis, especially its remarkable effect in promoting the performance improvement of copper-based catalysts [79]. Studies have shown that the strong interaction between copper and indium can modulate the electronic structure of copper, enhance the adsorption capacity of hydrogen, inhibit the formation of adverse intermediates, and optimize the dispersion and surface concentration of copper [80]. In the reaction of DMO hydrogenation to EG, the synergistic effect of $Cu^0$ and indium significantly promoted the activation of hydrogen, thus improving the catalytic efficiency. In addition, indium-promoted Cu/$SiO_2$ catalysts prepared by different methods reveal that the amount of indium has a profound effect on the chemical properties and catalytic performance of catalysts. In particular, the formation of CuIn alloy not only increases the surface content of $Cu^0$ and the adsorption amount of hydrogen, but also promotes the activation and conversion of carbon-oxygen bonds (Fig. 5), thus significantly improving the spatio-temporal yield of the target product EG and the conversion frequency of copper, and reducing the activation energy of the reaction [50]. These findings highlight the key role of $Cu^0$, $Cu^+$ and CuIn alloys in DMO hydrogenation reactions and provide important guidance for the optimization of catalyst design.

Tin, as an effective catalyst promoter, has also shown its unique advantages in various catalytic systems. It significantly enhances the dispersion of the active metal to improve the overall stability

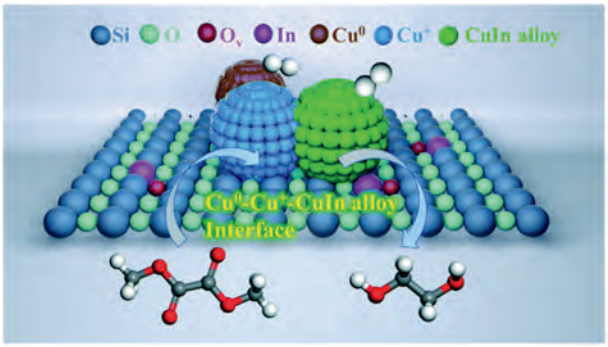



**Fig. 5.** The structural model and surface configuration of indium-promoted Cu/$SiO_2$ [50]. Copyright 2019 Elsevier.

of the catalyst, which has been verified in several research cases. Specifically, tin doping can effectively reduce the size of metal particles in the active center and effectively inhibit carbon deposition through the presence of SnO*x*, thus extending the lifetime of the catalyst [81].

In addition, tin plays a regulating role in the process of DMO hydrogenation of EG with its strong reducing ability, affecting the catalytic effect by adjusting the ratio of $Cu^0/Cu^+$. The study by Zhang *et al.* [51] systematically revealed the profound influence of $Sn^{2+}$ doping on the structure and properties of silica-supported copper catalysts. They found that the appropriate introduction of $Sn^{2+}$ can significantly improve the catalytic activity and stability of Cu/$SiO_2$ catalyst in the synthesis of glycol from dimethyl oxalate. The $Cu^0/Cu^+$ ratio is changed by the increase of $Sn^{2+}$ content, which was revealed by various characterization methods. Transmission electron microscopy directly proved that the introduction of $Sn^{2+}$ reduced the size of active copper particles, showing an effective role in separating and stabilizing active copper. These combined effects inhibit the accumulation of copper in the catalyst, thus prolonging the service life of the catalyst.

In general, tin, as a catalyst accelerator, has shown significant promoting effects in various catalytic reactions through various mechanisms such as promoting metal dispersion, inhibiting carbon deposition and migration, adjusting metal valence ratio and stabilizing active components, to provide new ideas and methods for the development of catalytic science.

In addition, the influence of Mg doping on the catalyst is also quite significant, especially when the Mg element is introduced into the Cu-ZnO-based catalyst, the texture, structural properties and catalytic behavior of the catalyst can be significantly optimized through fine regulation of the doping amount of $Mg^{2+}$ [82]. Studies have shown that an appropriate amount (such as 1% (mass)) of MgO loading can effectively promote the dispersion of Cu, increase the surface $Cu^0$ active site, and thus improve the catalytic activity and selectivity of DMO hydrogenation to EG [82]. However, too high concentration of $Mg^{2+}$ doping may lead to the aggregation of Cu nanoparticles, reduce the active site, and reduce the catalytic efficiency. Notably, at specific MgO loads (*e.g* 4.0% (mass)), the catalyst exhibits a high surface density of $Cu^+$ sites and $O^{2-}$ centers, promoting excellent hydrogenation activity, achieving near-complete DMO conversion and high EG yield with long-term stability. This performance improvement can be attributed to the close contact between $Mg^{2+}$ doping and Cu-ZnO matrix, which promotes the formation of Cu and oxygen vacancy on the surface, and enhances the dissociation adsorption capacity of DMO molecules. In addition, $Mg^{2+}$ modification also enhanced the metal-support interaction (MSI), further improving the stability of the catalyst [52]. In another study, a ZnO-doped Cu/MgO

catalyst synthesized by an innovative acoustochemical method demonstrated excellent catalytic performance in DMO hydrogenation reactions. The introduction of Zn improves the dispersion, crystal defects, surface segregation and the synergistic effect between $Cu^0/Cu^+$, thus improving the catalytic efficiency. The catalyst maintained a high DMO conversion rate during a long-term reaction, showing good long-term stability [82]. These findings not only reveal the effect of Mg and Zn doping on the performance of Cu-based catalysts but also demonstrate the potential of sonochemical synthesis of highly efficient heterogeneous catalysts under green, surfactant-free conditions, providing new ideas for catalyst design and optimization.

To optimize the performance of Cu-based catalysts in the hydrogenation of DMO to EG, some researchers have also achieved significant catalytic improvement by introducing a variety of non-metallic promoters, such as $\beta$-cyclodextrin ($\beta$-CD) [53], ethylenediamine tetraacetic acid (EDTA) [54] and low-cost polysaccharide [83,84]. Huang *et al.* [53] introduced β-CD *via* a hydrothermal method. By leveraging the stable complex formed between $\beta$-CD and copper ions, they effectively regulated the concentration of copper-ammonia complexes and reaction pathways. Under alkaline conditions, this approach promoted the interaction between the $Cu(OH)_2(H_2O)_4$ precursor generated from silicate dissolution and $\beta$-CD, thereby inducing the oriented growth of copper-layered silicates. This process not only suppressed heterogeneous adsorption of copper species on silica surfaces but also restricted the local enrichment of copper-ammonia complexes, leading to the formation of smaller $Cu^0$ nanoparticles (approximately 4.1 nm) with uniform dispersion after reduction. Additionally, it retained a high proportion of active $Cu^+$ sites ($Cu^+/(Cu^+ + Cu^0)$ ratio reached 67.1%), significantly enhancing the synergistic catalytic efficiency between $Cu^+$ and $Cu^0$. Consequently, DMO conversion exceeded 99.9% at a low temperature of 453 K. Ye *et al.* [55–57] also employed β-CD and dextrin to modify Cu-$SiO_2$ through sol-gel and ammonia evaporation methods, respectively, successfully enhancing copper loading capacity and dispersion (Fig. 6). The introduction of $\beta$-CD inhibited copper particle agglomeration by forming an ordered Cu-O-Si structure. Its unique molecular framework not only acted as a structure-directing agent to regulate the distribution of copper species but also stabilized highly dispersed $Cu^+$ active sites *via* weak interactions, thereby optimizing the $Cu^0/Cu^+$ ratio and significantly improving catalytic activity and selectivity. Meanwhile, the hydroxyl network of dextrin modulated the hydrolysis pathway of copper precursors through hydrogen bonding, facilitating the formation of a compact copper core-shell structure during ammonia evaporation and reducing the generation of large copper particles. Further studies revealed that the catalytic performance could be fine-tuned by adjusting the doping levels of $\beta$-CD or dextrin, demonstrating an intrinsic relationship between nano-copper crystal structure and catalytic activity: moderate doping balanced copper dispersion and support interactions, while excessive amounts led to active site coverage. In contrast, Li *et al.* [54] demonstrated that EDTA, through strong chelation, preferentially bound $Cu^{2+}$, reducing the concentration of $Cu(NH_3)_4^{2+}$ in solution and weakening its promoting effect on copper-layered silicate formation. However, an optimal amount of EDTA regulated the dissociation equilibrium of copper-ammonia complexes, enabling the formation of more uniformly dispersed CuO precursors during ammonia evaporation. After reduction, these small-sized (3.5–4.3 nm) and highly dispersed $Cu^0$ nanoparticles (specific surface area of 12.8 $m^2 \cdot g^{-1}$) maintained a moderate $Cu^+$ ratio while effectively suppressing sintering aggregation due to increased interparticle distances. This resulted in 99.9% DMO conversion and 97.7% ethylene glycol selectivity at 180 °C, along with exceptional stability over 1200 h. Both studies enhanced $Cu^+$–$Cu^0$ synergy by tailoring the microstructure and valence distribution of copper species. However, $\beta$-CD primarily focused on silicate structural directionality, whereas EDTA emphasized precursor dispersion optimization, highlighting distinct molecular-level mechanisms for catalytic activity modulation by different additives.

Numerous research teams have made innovative explorations in the field of non-metallic additives. For instance, Lu *et al.* [58] innovatively utilized boron-doped carbon aerogel supports to optimize copper (Cu) particle size, dispersion, and surface acidity/basicity by tuning boron content. The electron-deficient nature of boron enhanced metal-support electron transfer, exposing more $Cu^+$ species. Simultaneously, the graphite-like structure formed by boron doping reduced loss in specific surface area, maintaining high-temperature stability. Notably, Wang *et al.* [59] introduced amino groups onto the surface of Cu/$SiO_2$ *via* grafting, significantly improving ethylene glycol (EG) selectivity through synergistic effects of the electron-donating capability of amines and moderate basic sites. The incorporation of amino groups not only reduced Cu oxidation state *via* electron transfer, promoting hydrogen dissociation, but also effectively suppressed condensation side reactions between ethylene glycol and methanol/ethanol due to their weak basicity, leading to a substantial decrease in $C_3$–$C_4$ alcohol byproducts.

In summary, non-metallic additives optimize the synergistic catalytic performance of Cu-based catalysts in the hydrogenation of dimethyl oxalate (DMO) to ethylene glycol (EG) by regulating the morphology, dispersion, and valence state distribution of copper

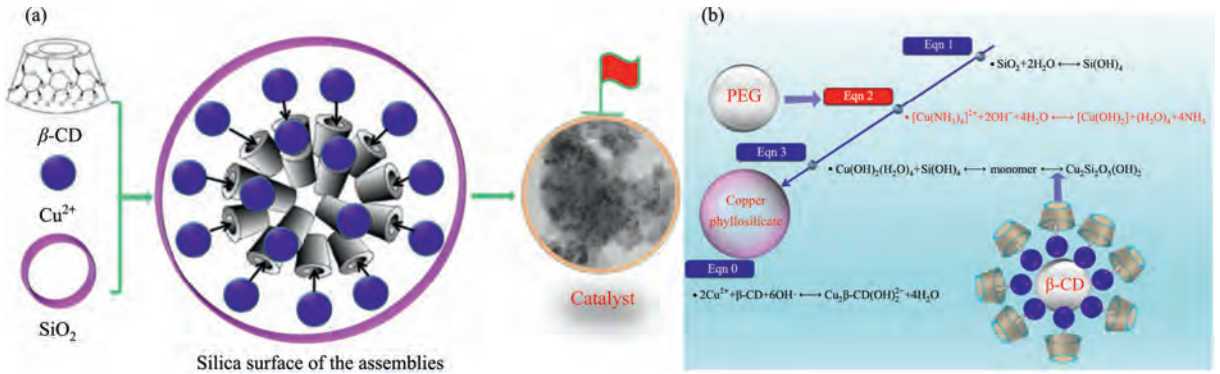



**Fig. 6.** (a) A possible schematic mechanism for formation of β-CD doped Cu-$SiO_2$ catalysts [55]; (b)Plausible formation mechanism of copper phyllosilicate with Eq.(1) to Eq.(3) under β-CD and PEG [57]. Copyright 2019 Elsevier.

species. For instance, $\beta$-CD stabilizes the coordination interactions between copper-ammonia complexes and copper ions, guiding the oriented growth of copper silicate layers under alkaline conditions. This suppresses copper particle aggregation, forming small-sized ($\approx$4.1 nm) highly dispersed $Cu^0$ nanoparticles while preserving a high proportion of active $Cu^+$ sites ($Cu^+/(Cu^+ + Cu^0) = 67.1\%$). The enhanced $Cu^+/Cu^0$ synergy achieves over 99.9% DMO conversion. Ethylenediaminetetraacetic acid (EDTA), through strong chelation, modulates the dissociation equilibrium of copper-ammonia complexes, optimizing CuO precursor dispersion and promoting the formation of small-sized (3.5–4.3 nm) $Cu^0$ particles after reduction. Coupled with its ability to maintain moderate $Cu^+$ ratios, this achieves 99.9% DMO conversion and 97.7% EG selectivity at 180 °C with over 1200 h of stability. Polysaccharide-based additives regulate hydrolysis pathways of copper precursors *via* hydroxyl hydrogen bonding to form dense core-shell structures, while boron-doped carbon aerogels enhance metal-support interactions through electronic defects to expose more $Cu^+$ sites. Amino-functionalized supports reduce copper oxidation states and suppress side reactions *via* electron-donor effects. These additives precisely tailor the microenvironment of copper species through molecular-level structural directing, electron transfer, or coordination effects, revealing a structure-activity relationship between additive types and catalytic activity. Moderate addition balances dispersion and support interactions, whereas excess additives lead to active site coverage, demonstrating the multi-dimensional mechanisms by which non-metallic additives optimize Cu-based catalyst performance.

### 4.3. Optimizing synthesis methods

Exploring the optimized catalyst preparation method is also one of the key ways to improve the performance of Cu-based catalysts. In recent years, remarkable progress has been made in optimizing the preparation process of catalysts. On the one hand, the improvement of traditional preparation methods such as uniform precipitation deposition, hydrothermal method and sol-gel method [85,86] has significantly improved the dispersion of Cu species on the support to elevate the activity of the catalyst. Studies have shown that the ion exchange between cuprammonia and SiOH occurs in the aging stage, and the hydrothermal aging time can significantly improve the performance of Cu-$SiO_2$ catalyst in the hydrogenation of DMO to EG [39]. Hydrothermal aging promoted the accumulation of $Cu^0$ species on the catalyst surface, weakened the coverage of $Cu^+$, and enhanced the synergistic effect of $Cu^+$ and $Cu^0$. It is also found that the high $Cu^0$ density is not conducive to the adsorption and polarization of the C=O bond at the $Cu^+$ active site. Cu-$SiO_2$ catalyst with moderate $Cu^0$ dispersion can obtain the best performance by optimizing the hydrothermal aging time to 24 h (Fig. 7) [60].

To solve the problem of insufficient activity and poor stability of Cu/$SiO_2$ catalyst, researchers have proposed the introduction of an appropriate amount of accelerator or additive is an effective strategy, which is also described in detail in the previous content of this paper, but the introduction stage of the accelerator also has a significant impact on the catalytic performance. Yang *et al.* [61] prepared two Cu-Ag/$SiO_2$ catalysts by changing the addition sequence of Ag accelerators by the sol-gel method and impregnation method. The results showed that the introduction stage of the accelerator had a significant effect on the catalytic performance. In particular, the introduction of Ag accelerators at specific preparation stages can inhibit the growth of Cu particles and improve the dispersion of Cu components, resulting in more active sites, and strengthen the interaction between metals by forming CuAg alloys, thereby optimizing the catalytic activity of Cu/$SiO_2$ catalysts (Fig. 8). The optimized Cu-$Ag_{0.04}/SiO_2$ (B) catalyst showed an EG selectivity of up to 97.4% at 463 K, implying that the performance of Cu/$SiO_2$ catalysts can be significantly improved with a well-designed accelerator introduction strategy.

Lin *et al.* [87] studied in detail the effects of different copper loads on sol-gel preparation methods. Under the same experimental conditions, the main factors affecting the activity of sol-gel catalysts are encapsulation and agglomeration when the copper load increases. When $w(Cu) \leqq 10\%$, the coating property of silica is strong, which becomes the main influencing factor of the catalyst surface. When $w(Cu)$ is more than 10%, the agglomeration phenomenon between copper species is more serious, which becomes the main influence factor on the catalyst surface. These two factors affect the surface structure of the catalyst, the form of the copper, and the chemicals around the catalyst, thus affecting the performance of the catalyst. Zhang *et al.* [32] compared the effects of the ammonia evaporation method and sol-gel method on the structure, size, dispersion and surface chemical state of copper nanoparticles and other catalyst structures and the corresponding catalytic properties. The results show that under the optimized reaction conditions, the average size of copper nanoparticles

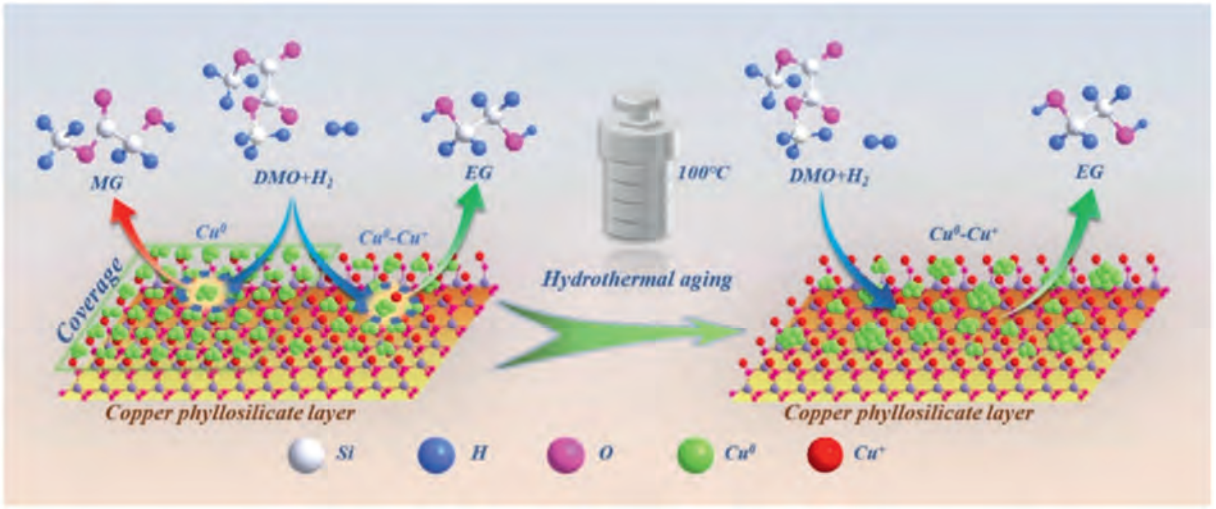



**Fig. 7.** The structure-effect of the Cu-$SiO_2$ catalysts with hydrothermal aging [60]. Copyright 2023 Springer Link.

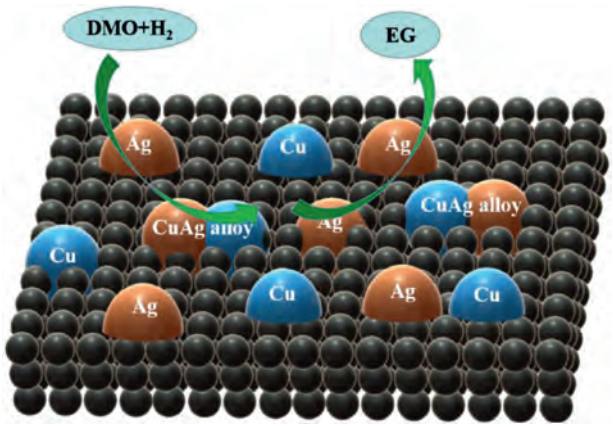



**Fig. 8.** Reasonable schematic diagram of interaction between cooper and silver species on the surface of Cu-$Ag_{0.04}/SiO_2$ (B) catalyst in DMO hydrogenation process [61]. Copyright 2022 Elsevier.

prepared by sol-gel method is smaller (about 3–4 nm), with better copper dispersion is, higher $Cu^+/Cu^0$ ratio, and larger BET surface area, all of which contribute to the higher DMO conversion rate and EG selectivity.

In addition, some researchers have made innovative improvements on the basis of traditional catalyst preparation methods and achieved remarkable results. Among them, Zhang *et al.* [62] prepared Cu-Ni/$ZrO_2$ catalyst by plasma-treated deposition-precipitation method, which effectively improved the dispersion of Cu in the catalyst, greatly improved the selectivity and long-term stability and high selectivity of ethylene glycol. Guo *et al.* [18] prepared mesoporous Cu/SBA-15 catalyst with high-content and high-dispersion copper content through ammonia-driven deposition-precipitation method. The catalyst showed excellent performance in selective hydrogenation of dimethyl oxalate to ethylene glycol, which was much better than the catalyst prepared by the traditional impregnation method. Zhao *et al.* [28] used the modified ammonia evaporation method and hydrolytic precipitation method [20] to prepare well-dispersed copper-based catalysts and Cu/$SiO_2$ catalysts with highly active copper types, respectively, and both achieved high ethylene glycol selectivity and catalytic activity. In addition, Zhao *et al.* [63] also prepared Cu-O-Si catalyst materials with large specific surface area and highly dispersed metal components by an improved precipitation method, showing excellent catalytic activity and stability. Yang *et al.* [33] found that the layered copper silicate could form rich Cu-O-Si units through simple thermal pretreatment before ion exchange. In addition, ion exchange significantly enhanced the metal-support interaction, inhibited the growth of copper species, and ultimately improved the $Cu^0$ dispersion and $Cu^+/(Cu^0+Cu^+)$ ratio (Fig. 9), resulting in significantly improved catalytic performance and long-term stability, providing a simple and low-cost method for the design of stable copper-based catalysts.

In order to explore the influence of key parameters in traditional preparation methods on catalyst activity, the researchers also conducted in-depth studies. The optimization of these parameters helps to improve the dispersion of Cu, enhance the interaction between metal and support, and optimize the microstructure of the catalyst, thus further improving the catalytic performance. Using ZSM-5 molecular sieve with a high Si/Al ratio as the support, it was found that the hydroxyl group on the surface of the support had a significant effect on the structure and performance of the catalyst by adjusting the pretreatment conditions. Optimization of pretreatment conditions can improve the dispersion and surface properties of copper, and thus increase the activity of catalyst. For example, by precisely controlling the drying time, Cu/ZSM-5 catalyst with superior catalytic performance at a low reaction temperature can be obtained to achieve high conversion and selectivity, and the catalytic activity remains stable after a long reaction [64].

In addition, the calcination temperature has also been shown to be a key factor affecting the catalyst performance. In the CuO–$La_2O_3/ZrO_2$ [65] and CuZnAl [88] catalyst systems, with the increase of calcination temperature, the specific surface area, pore volume and copper dispersion of the catalyst will change, which are highly correlated to the catalytic performance. Appropriately increasing the calcination temperature can enhance the interaction between the metal and the support, promote the adsorption and activation of hydrogen, while reducing the surface pH and inhibiting the generation of by-products [28]. However, too high calcination temperature will cause the support structure to collapse or sintering, reducing the dispersion and catalytic properties of copper. In another study, self-assembled Cu catalysts obtained by thermal decomposition of oxalate precursors showed excellent catalytic performance and stability at optimized calcination temperatures. This is attributed to the largest surface-Cu site and appropriate surface acid characteristics on the catalyst, as well as the chemical interaction between Cu and Al that enhances the stability of the catalyst [66].

Finally, the evaporation temperature in the ammonia evaporation process has a profound effect on the texture, composition and structure of Cu/$SiO_2$ catalysts. By adjusting the ammonia

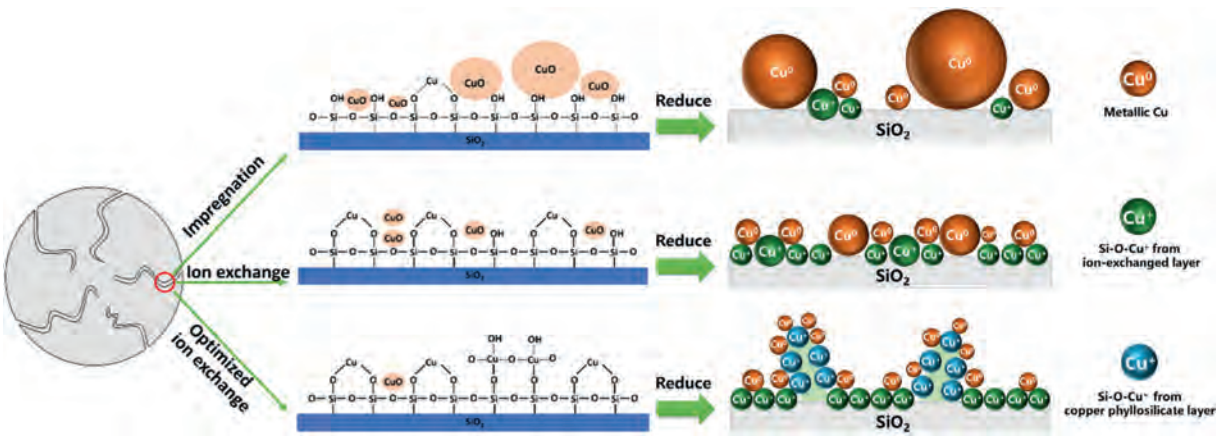



**Fig. 9.** Schematic illustration of the distribution of copper species on three different Cu/$SiO_2$ catalysts [33]. Copyright 2023 American chemical society.

evaporation temperature, the type and surface area of copper on the catalyst can be optimized to achieve efficient catalytic performance [21].

In summary, by precisely controlling the key parameters of traditional preparation methods (such as drying time, calcination temperature, and evaporation temperature), the structure and performance of the catalyst can be significantly optimized, and its catalytic activity and stability in a specific reaction can be improved. These research results provide important theoretical guidance and practical basis for the design and preparation of catalysts.

In addition to the traditional methods, researchers have successfully developed a series of new and environmentally friendly preparation methods. Popa *et al.* [89] used $(NH_4)_2CO_3$ instead of the ammonia water to synthesize nanostructured $Cu/SiO_2$ catalysts. This method improves the temperature stability and high-selective DMO-to-EG conversion performance, mainly due to the better thermal stability, size control and higher $Cu_2O$ content of the catalyst and the improved topography of the supported copper particles.

In another study, San *et al.* [25] reported the highly dispersed $Cu/SiO_2$-MOF catalyst was successfully prepared by guiding the growth of MOF (metal-organic framework) around $SiO_2$ microspheres. The specific surface area and metal load of this catalyst are increased with more uniform film growth, which significantly improves the catalytic performance. Compared with ordinary MOF and $SiO_2$ microspheres, the copper dispersion in the catalyst is more uniform without any copper aggregation, thus improving the activity.

In addition, Kong *et al.* [67] systematically studied the selective leaching of Cu-Al alloy pellets in sodium hydroxide solution to prepare Raney Cu catalyst. It was found that the leaching temperature had an important effect on the microstructure, physicochemical properties and surface properties of the catalyst. The Raney Cu catalyst prepared at a higher leaching temperature showed excellent stability during DMO gas phase hydrogenation, while the catalyst prepared at mild leaching conditions was prone to rapid deactivation. These new preparation methods not only provide more options for the preparation of Cu-based catalysts for DMO hydrogenation of EG but also improve the catalytic efficiency and product selectivity by optimizing the structure and performance of the catalyst, laying a solid foundation for further research and application in related fields.

In conclusion, by optimizing preparation process parameters such as hydrothermal aging time, additive introduction stage, copper loading amount, calcination temperature, and evaporation temperature, significant improvements in the dispersion of active components, regulation of surface chemical states (*e.g.*, $Cu^+/Cu^0$ ratio), enhancement of metal-support interactions, and optimization of catalyst microstructures (*e.g.*, suppression of particle agglomeration, formation of alloys or specific crystal phases) can be achieved. These optimizations collectively enhance catalytic activity, selectivity, and stability. For instance, prolonging hydrothermal aging time promotes the enrichment of $Cu^0$ species on the support surface while reducing $Cu^+$ coverage, thereby strengthening the synergistic effect between $Cu^+$ and $Cu^0$. Introducing additives *via* specific stages suppresses copper particle growth through steric hindrance or alloying effects while increasing active sites. Adjusting calcination temperature balances pore structure development of the support with metal dispersion, avoiding structural collapse at high temperatures. Novel approaches such as plasma treatment, MOF-derived support construction, and alloy dealloying methods further overcome limitations of traditional processes by enhancing component dispersion and regulating surface acidity and electronic properties. Overall, these strategies systematically optimize the structure-performance relationships of catalysts, achieving high activity (*e.g.*, 97.4% EG selectivity in the hydrogenation of DMO to EG), high stability, and low energy consumption. This provides robust theoretical guidance and technical support for designing efficient copper-based catalysts.

## 5. Summary and Prospect

In summary, the copper-based catalyst has great potential in the hydrogenation of dimethyl oxalate (DMO) to ethylene glycol (EG) due to its selective activation of C═O/C—O bond. The results show that the valence equilibrium of copper species, especially the co-catalytic effect between $Cu^0$ and $Cu^+$, has an important effect on the performance of the catalyst. $Cu^0$ species are used to dissociate $H_2$, and $Cu^+$ species are used to adsorb carbonyl and methoxy groups. The synergistic effect of the two groups promotes the formation of an efficient reaction interface. In addition, the surface dispersion of copper species, the interaction between metal and support, and the morphology and structure of the catalyst have also been proved to be the key factors influencing the catalytic activity and stability.

To improve the catalytic performance, researchers have adopted a variety of strategies, including optimizing the structure of the support to increase the number of active sites and improve catalytic selectivity, adding promoters (such as rare earth elements, other metal and non-metal elements, *etc.*) to regulate the electron density of copper species and enhance the interaction between the metal and the support. The preparation methods (such as ammonia evaporation, hydrothermal aging, sol-gel method, and ion exchange method, *etc.*) were improved to optimize the dispersion, valence distribution and support structure of copper species. These measures significantly boosted the conversion rate of DMO, selectivity of EG and stability of catalyst.

Despite the remarkable progress, existing copper-based catalysts still face some challenges, such as the aggregation and sintering of copper nanoparticles at high temperatures, carbon deposition, support collapse, and the dynamic change of copper valence state during the reaction process. Therefore, future research should continue to focus on the relationship between catalyst structure and performance aiming for the development of new high-efficiency and high-stability catalysts.

## 6. Future Development Challenges and Prospects

To enhance the performance of Cu-based catalysts for DMO hydrogenation to EG, extensive research efforts have been made, yet significant core challenges persist in industrial applications. In the industrialization of DMO hydrogenation, the harsh reaction conditions of high temperature (200–300 °C) and high pressure (5–10 MPa) create a dilemma in simultaneously optimizing the stability and activity of Cu-based catalysts: Cu nanoparticles tend to aggregate and grow under dynamic hydrogen environments (particle size growth rate up to 1.2 $nm \cdot h^{-1}$), resulting in a 30% to 50% reduction in active site exposure and a sharp decrease in catalytic surface area, which diminishes selective hydrogenation efficiency. Concurrently, intermediates such as CO and formic acid generated during the reaction adsorb strongly on active sites (adsorption energy as high as −1.8 eV), leading to a catalyst poisoning rate of 0.15 $\mu mol \cdot g^{-1} \cdot h^{-1}$. Furthermore, unconverted DMO undergoes deep cracking at elevated temperatures, producing carbon deposits (up to 8% of catalyst mass) that block pores and accelerate deactivation.

Traditional preparation methods (*e.g.*, coprecipitation) suffer from poor particle size control (dispersity coefficient >25%) and difficulties in tuning metal-support interactions (large fluctuations

in $Cu^0/Cu^+$ ratios), resulting in high production costs (40% to 60% higher than non-noble metal catalysts). The current Research and Development (R&D) model overly relies on trial-and-error methods and empirical accumulation, requiring over five years on average to progress from lab-scale to industrialization, with poor reproducibility (batch-to-batch activity variation >15%).

Future development necessitates integrated multi-scale strategies: achieving atomic-level precision in Cu nanoparticle sizing *via* ion sputtering (error <±2 nm), constructing CNT-confined carriers through ultrasonic-assisted technology (sintering resistance up to 350 °C), and optimizing metal-support interfacial electronic structures *via* plasma treatment (d-band center shift $\Delta E_d$ = 0.6 eV). Simultaneously, breakthroughs are needed to overcome the limitations of traditional trial-and-error approaches. Leveraging multi-dimensional *in-situ* characterization techniques (*e.g.*, operando XRD for phase transition tracking, operando Raman for adsorbate evolution analysis) and artificial intelligence models (*e.g.*, graph neural networks for catalyst structure-performance mapping), quantitative structure-performance models with prediction errors <8% can be established, enabling closed-loop optimization of catalyst design and validation.

Looking ahead, three key directions will dominate next-generation Cu-based catalyst R&D: (1) fabricating sintering-resistant nanoparticles (10–20 nm) with high-density active sites ($>5 \times 10^{-4}$ mol·m$^{-2}$) *via in-situ* confined growth (*e.g.*, CNT cavity assembly); (2) screening support materials using machine learning (database covering >50000 oxide structures) to develop bifunctional catalysts (*e.g.*, Cu@ZnO/CNT for selective C—O bond cleavage); and (3) innovating green preparation processes (*e.g.*, supercritical fluid drying to reduce energy consumption by 30%), driving DMO hydrogenation technology toward efficiency, low-carbon, and sustainability.

## CRediT Authorship Contribution Statement

Hansheng Wang: Writing – original draft. Xintian Luo: Data curation. Kaixuan Chen: Investigation. Benduan Xiao: Validation. Xu Zhang: Investigation. Qingjun Meng: Supervision. Huibing He: Writing – review & editing. Jing Xu: Methodology. Yong Jin: Supervision.

## Declaration of Competing Interest

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

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