

Calcination atmosphere-engineered Cu/SiO₂ catalysts for efficient hydrogenation of dimethyl succinate to 1,4-butanediol

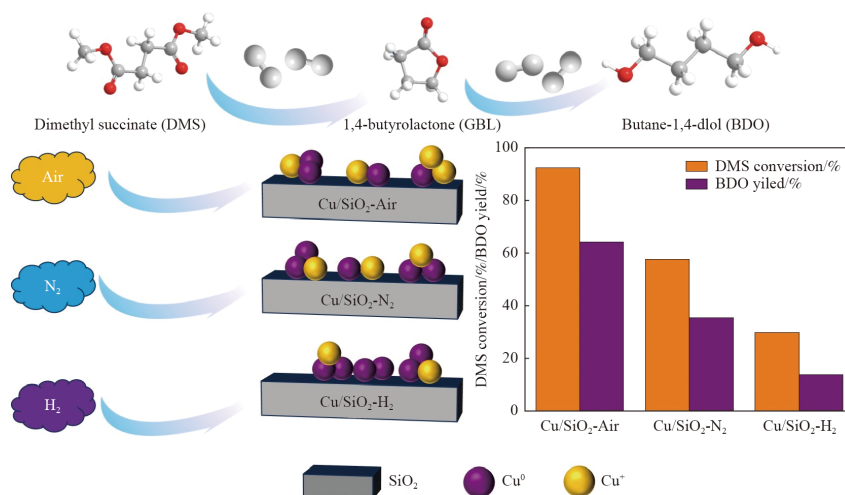
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Abstract: The catalytic hydrogenation of biomass-derived dimethyl succinate (DMS) to 1,4-butanediol (BDO) represents a pivotal route for producing high-value C4 chemicals in the context of green chemistry. Cu/SiO₂ catalysts are known for their high selectivity in hydrogenating ester groups, and their performance is correlated with the microstructure of the copper species. Although calcination is a critical step in defining this



active structure, the systematic influence of the calcination atmosphere remains underexplored. In this study, Cu/SiO₂ catalysts were prepared *via* a urea-assisted hydrothermal method and calcined under different atmospheres to elucidate their effects on catalyst physicochemical properties and subsequent hydrogenation performance. A comprehensive characterization suite (N₂ physisorption, FT-IR, H₂-TPR, XRD, TEM, N₂O pulse chemisorption, XPS and NH₃-TPD) revealed that the calcination atmosphere profoundly alters the metal-support interaction, thereby regulating the dispersion and chemical state of the loaded copper species. Specifically, calcination in air promoted a stronger metal-support interaction, effectively enhancing the dispersion of copper species and increasing the proportion of key active Cu⁺ species. Consequently, the air-calcined catalyst demonstrated superior performance, achieving 92.37% DMS conversion and 64.15% BDO yield under optimized conditions (210 °C, 5.0 MPa, WHSV of 0.6 h⁻¹, H₂/DMS molar ratio of 100). This work underscores calcination atmosphere engineering as a potent strategy for optimizing metal-support interactions in heterogeneous catalysts for efficient hydrogenation processes.

Key words: copper-based catalyst; calcination atmosphere; metal-support interaction; hydrogenation

The global energy and chemical feedstock systems are undergoing a profound transition from fossil-based to renewable resources. This shift represents not only a

necessary response to the depletion of fossil fuels but also a critical pathway to mitigating the greenhouse effect and environmental pollution, thereby facilitating the transition

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toward green, low-carbon development. Against this backdrop, biomass, as the only renewable organic carbon source in nature, has attracted widespread attention from both academia and industry for its valorization^[1–2]. The catalytic conversion of biomass-derived platform molecules into high-value-added chemicals is widely regarded as a cornerstone of sustainable chemical production. Among these molecules, dimethyl succinate (DMS), produced from biomass through fermentation and esterification, serves as an ideal precursor toward this end. DMS can be catalytically hydrogenated to high-value C4 chemicals such as γ -butyrolactone (GBL), 1,4-butanediol (BDO) and tetrahydrofuran (THF), thereby establishing an integrated green value chain from “biomass to platform molecules to high-value chemicals”. This route substantially reduces dependence on traditional petroleum-based pathways (e.g., hydrogenation of maleic anhydride) and significantly lowers overall carbon emissions^[3].

The hydrogenation of DMS to BDO involves a complex tandem reaction network comprising multiple sequential, parallel, and competitive steps^[4]. The generally accepted reaction pathway begins with the stepwise hydrogenation of DMS, accompanied by methanol removal, to form GBL, which subsequently undergoes ring-opening hydrogenation to produce BDO^[5]. However, BDO can be reversibly dehydrogenated back to GBL or dehydrated over acid sites to form the undesired THF by-product^[6–8]. A central challenge in this network is designing an efficient catalyst that steers the reaction pathway toward high DMS conversion and high BDO selectivity. An ideal catalyst should exhibit synergistic bifunctionality: it must efficiently activate and hydrogenate the C=O bond while suppressing over-hydrogenation, and it should also possess suitably moderated acidity to avoid side reactions such as BDO dehydration^[9].

Among various catalytic systems, noble metals (e.g., Pd, Pt, Ru) exhibit high intrinsic activity but are costly and prone to over-hydrogenation, leading to poor economic viability and selectivity. In contrast, non-noble copper-based catalysts have emerged as promising candidates for the selective hydrogenation of DMS, owing to their unique ability to adsorb moderately and selectively hydrogenate carbonyl (C=O) groups, coupled with low activity toward C–C bond hydrogenolysis^[10–11]. In particular, Cu/SiO₂ catalysts have shown exceptional promise. Their performance is strongly influenced by the microstructure of copper species, including nanoparticle size, dispersion, valence distribution (Cu⁰, Cu⁺), and the strength of metal-support interactions^[12–13]. These structural parameters are, in turn, dictated by the catalyst preparation process^[14]. Therefore, refining preparation procedures to optimize the microstructure of Cu/SiO₂ represents a key research direction for enhancing intrinsic activity and selectivity^[15].

Among the various steps in catalyst synthesis, calcination serves as a critical bridge between the precursor and the final active structure, playing a decisive role in defining catalytic performance. The calcination atmosphere is a

powerful yet easily adjustable synthesis parameter that directly influences precursor decomposition, copper speciation, and the metal-support interface, enabling precise engineering of metal-support interaction strength. Nevertheless, systematic studies examining the effect of calcination atmosphere on the structure and performance of Cu/SiO₂ catalysts in DMS hydrogenation remain scarce. This gap presents a clear research opportunity: by using calcination atmosphere (oxidizing, inert, reducing) as a “precision switch” powerful and tunable synthesis parameter, it is possible to directionally tailor metal-support interactions strength, optimize copper dispersion and valence distribution, and synergistically modulate surface acidity, thereby significantly enhancing catalytic performance.

In this study, Cu/SiO₂ catalyst precursors were synthesized *via* a urea-assisted hydrothermal method and calcined under different calcination atmospheres (air, N₂, H₂) to systematically investigate their physicochemical properties and performance in DMS hydrogenation. A combination of characterization techniques, including N₂ physisorption, FT-IR, H₂-TPR, XRD, TEM, N₂O pulse chemisorption, XPS and NH₃-TPD, was employed to elucidate the structure-performance relationships linking the calcination atmosphere to metal-support interaction and catalytic performance. This work aims to provide new insights and effective synthesis strategies for the rational design of high-performance copper-based catalysts for DMS hydrogenation to BDO.

1 Experimental

1.1 Experimental reagents and materials

Cu(NO₃)₂·3H₂O ($w \geq 99.5\%$) was purchased from Shanghai Macklin Biochemical Co., Ltd. Urea ($w \geq 99\%$) was purchased from Sigma-Aldrich. Methanol ($\varphi \geq 99.5\%$) and ethanol ($\varphi \geq 99.7\%$) were obtained from Sinopod Chemical Reagent Co., Ltd. All materials were used as received without further purification.

1.2 Preparation of Cu/SiO₂ catalysts with different calcination atmospheres

Copper nitrate trihydrate (2.31 g) was dissolved in 100 mL of distilled water. Urea was then added under stirring with a urea-to-copper molar ratio of 3:1. Subsequently, 13.5 g of silica sol was introduced, and the mixture was stirred continuously for 4 h. The resulting mixture was transferred into a Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 200 °C for 24 h. After the hydrothermal treatment, the solid product was collected by centrifugation and washed with deionized water until the supernatant reached a pH value of 7. The obtained solid was then dried overnight in an oven at 100 °C. The dried precursor

was calcined at 450 °C for 4 h in a muffle furnace or tube furnace to obtain the final Cu/SiO₂ catalyst with a Cu mass fraction of 15% (Cu/SiO₂=15%). The resulting catalysts were designated based on their calcination atmosphere: Cu/SiO₂-A (calcined in air), Cu/SiO₂-N (calcined in nitrogen) and Cu/SiO₂-H (calcined in a 40% H₂/Ar stream).

1.3 Catalyst activity test

Catalyst performance was evaluated using a fixed-bed reactor and a dual-channel reactor system. The system comprised a vaporizer, a three-stage reactor (upper, middle, and lower sections), a back-pressure valve, a gas-liquid separator, a product collection tank, and a quartz reaction tube (6 mm inner diameter). Specifically, 0.2 g of catalyst (40–60 mesh) was loaded into the quartz tube and positioned in the reactor. The system was sealed and pressurized to 5.0 MPa with H₂ using the back-pressure valve. The temperature was then raised to 300 °C at a ramp rate of 2 °C/min and maintained for 3 h for reduction. Finally, the temperature was adjusted to the reaction temperature of 210 °C. Subsequently, the feedstock—a 20% solution of DMS in methanol—was vaporized and introduced into the system at a flow rate of 0.01 mL/min, with a concurrent H₂ flow of 64.00 mL/min. This corresponds to a H₂/DMS molar ratio of 100 and a weight hourly space velocity (WHSV) of 0.6 h⁻¹. The system was stabilized under these conditions for 10 h, during which the liquid products were discarded. After the stabilization period, the reaction products passed through a gas-liquid separator. The liquid phase was directed to a collection tank and sampled at 2–4 h intervals. The main hydrogenation products of DMS were GBL, BDO and THF. For analysis, an internal standard (hexanol) was added to the liquid samples, which were then analyzed by gas chromatography (GC, Shimadzu GC-2014) equipped with a KB-5 column and a flame ionization detector (FID). The GC oven temperature was set at 260 °C, and the injection volume was 0.2 µL.

1.4 Catalyst characterization

N₂ physisorption measurements were performed on a Quantachrome QDS-30 analyzer. A 200 mg sample, prepared by compressing the powder into a tablet at 10 MPa for 1 min and then crushing it, was placed in a degassing tube. The sample was outgassed under vacuum at 200 °C for 4 h. After cooling to room temperature, the sample was transferred to the analyzer for N₂ adsorption-desorption analysis at liquid nitrogen.

X-ray diffraction (XRD) analysis was performed on a Rigaku Smart Lab diffractometer to determine the phase composition of the samples. The catalyst was reduced with the same reduction conditions as before the reaction. Data were collected using Cu Kα radiation (40 kV, 40 mA) over a 2θ range of 5° to 85° at a scanning rate of 4(°)/min.

H₂-temperature-programmed reduction (H₂-TPR) analysis was conducted using a TP-5080 instrument (Tianjin Xianquan). Approximately 50 mg of the prepared sample was loaded into the reactor. Prior to analysis, the sample was purged with a N₂ stream at 150 °C for 60 min. After cooling to 50 °C under N₂, the gas was switched to a 5% H₂/Ar mixture. The temperature was then raised from 50 to 700 °C at a heating rate of 10 °C/min. Hydrogen consumption was monitored online using a thermal conductivity detector.

NH₃ temperature-programmed desorption mass spectrometry (NH₃-TPD-MS) was performed using a fully automated TP-5080 multifunctional adsorption apparatus (Tianjin Xianquan). The catalyst was reduced with the same reduction conditions as before the reaction. Approximately 100 mg of the sample was first purged with a He stream at 150 °C for 60 min. After cooling to 50 °C, the sample was exposed to NH₃ until saturation adsorption was achieved. Subsequently, physically adsorbed NH₃ was removed by purging with He. Finally, the temperature was programmed to increase from 50 to 600 °C at a rate of 10 °C/min under He flow. The desorbed NH₃ was monitored online by mass spectrometry.

Fourier-transform infrared (FT-IR) spectra of the samples were recorded on a Bruker INVENION S spectrometer. The potassium bromide (KBr) used for tablet pressing was dried in an oven at 150 °C overnight to remove moisture and minimize its interference with the measurements. Subsequently, approximately 0.1 g of dried KBr was thoroughly mixed and ground with a small amount of the sample in an agate mortar. The mixture was then pressed into a transparent flake at 10 MPa for 1 min. The resulting KBr flake was placed in the spectrometer, and the spectrum was acquired by averaging 32 scans over a wavenumber range of 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Shimadzu AXIS SUPRA instrument. The catalyst was reduced with the same reduction conditions as before the reaction. The analysis utilized an Al Kα X-ray source. The binding energy scale was calibrated by setting the C 1s peak to 284.8 eV. The surface elemental composition (Cu, Si, O) was analyzed and Cu LMM Auger spectra were collected to facilitate the quantification of different copper valence states (Cu⁰, Cu⁺).

TEM characterization was performed using a JEOL JEM-2000F high-resolution transmission electron microscope at 200 kV during the tests. The catalyst was reduced with the same reduction conditions as before the reaction. The samples were first pretreated by dispersing in ethanol, then placed in an ultrasonic bath for 5 min. Finally, the mixtures were placed on a microgrid for detection using a transmission electron microscope. The histogram statistics are 209 for Cu/SiO₂-A, 205 for Cu/SiO₂-N and 223 for Cu/SiO₂-H.

The copper surface area and dispersion were determined by N₂O pulse chemisorption using a TP-5080 analyzer (Tianjin Xianquan). Approximately 50 mg of catalyst was

loaded into a U-shaped quartz tube. The sample was first purged with N₂ (30 mL/min) at 150 °C for 30 min. After cooling to 50 °C under N₂, the gas was switched to a 10% H₂/N₂ mixture (30 mL/min). The temperature was then ramped to 500 °C at 10 °C/min and held for 15 min for reduction. After reduction, the sample was purged with Ar and cooled to 50 °C. It was then exposed to a 10% N₂O/Ar flow (30 mL/min) at 50 °C for 30 min to oxidize surface Cu⁰ atoms. Subsequently, the system was purged with N₂ for 30 min to remove physisorbed species. Finally, the gas was switched to a 10% H₂/Ar mixture (30 mL/min), and the temperature was increased to 500 °C at 10 °C/min, then maintained for 15 min to reduce surface-oxidized copper.

2 Results and discussion

2.1 Characterization of Cu/SiO₂ with different calcination atmospheres

Metal-support interaction is a critical factor governing catalytic performance, as it regulates the anchoring of metal species on the support surface, thereby directly dictating their dispersion and thermal stability. The calcination atmosphere serves as a powerful synthetic parameter for establishing initial metal-support interactions, as it controls precursor decomposition and the chemical state of the support surface. To elucidate the structure-property-performance relationships, Cu/SiO₂ catalyst precursors were calcined under three distinct atmospheres: oxidizing (Air), inert (N₂) and reducing (H₂). This approach enabled precise tuning of the metal-support interactions, ultimately leading to the development of a highly active and selective catalyst

for DMS hydrogenation.

Initially, N₂ physisorption was used to assess whether the calcination atmosphere significantly altered the catalysts' physical structure. As shown in Figure 1, all catalysts exhibited type IV isotherms with H II (b)-type hysteresis loops, suggesting the presence of similar mesoporous structures. The textural properties summarized in Table 1 further demonstrate only marginal variations across catalysts prepared under different calcination atmospheres, confirming that the calcination atmosphere has a negligible impact on the catalyst's physical structure.

As shown in Figure 2(a), all catalysts exhibit absorption bands at approximately 800 and 1110 cm⁻¹, corresponding to the symmetric and asymmetric stretching vibrations of Si–O bonds, respectively, confirming the presence of the amorphous SiO₂ support^[16–18]. The band around 500 cm⁻¹ is associated with the Si–O bending vibration. A noticeable shift in this band is observed for the Cu/SiO₂-A and Cu/SiO₂-N catalysts compared to pure SiO₂ (466 cm⁻¹), providing direct evidence for the formation of strong metal-support interactions between copper species and the silica support. H₂-TPR results further corroborate this finding. The Cu/SiO₂-H catalyst exhibits a single symmetric reduction peak at 181 °C, assigned to the reduction of Cu⁺ species to Cu⁰^[19–20]. In contrast, the Cu/SiO₂-A and Cu/SiO₂-N catalysts display asymmetric reduction profiles, indicating the presence of multiple copper species with distinct reducibility. For these catalysts, the lower-temperature reduction peaks (252 and 259 °C, respectively) are attributed to the highly dispersed CuO nanoparticles. In comparison, the higher-temperature peaks (298 and 311 °C) correspond to copper species strongly interacting with the SiO₂ support, likely in a Cu–O–Si structure^[21–24].

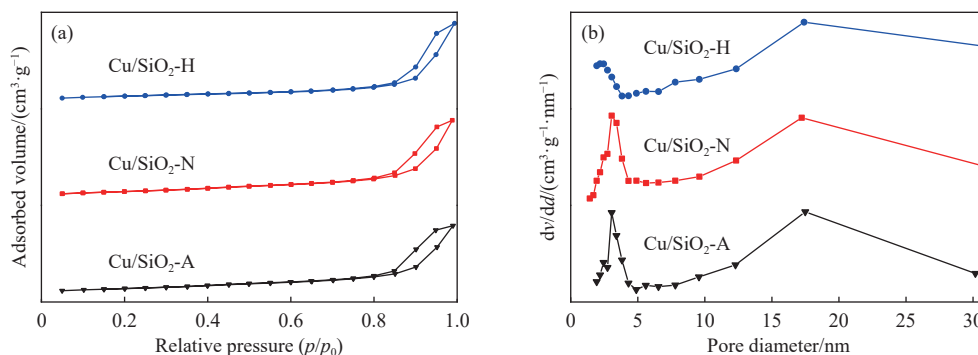
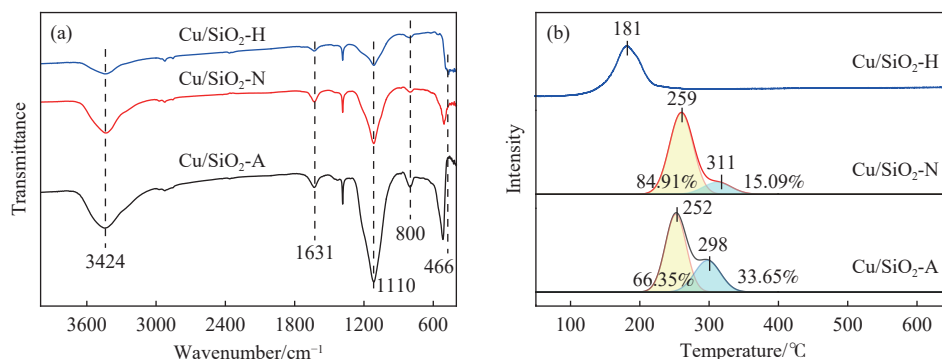


Fig. 1 N₂ adsorption and desorption curves (a) and pore size distribution curves (b) for catalysts with different calcination atmospheres

Table 1 Physicochemical properties of catalysts with different calcination atmospheres

Catalyst	$S_{\text{BET}}^a/(\text{m}^2 \cdot \text{g}^{-1})$	$v_p^a/(\text{cm}^3 \cdot \text{g}^{-1})$	d_p^a/nm	$d_{\text{cu}}^b/\%$	$S_{\text{Cu}}^b/(\text{m}^2 \cdot \text{g}^{-1})$	Average size ^c /nm	Acidic sites ^d /($\mu\text{mol} \cdot \text{g}^{-1}$)		
							weak	medium	total
Cu/SiO ₂ -A	146.79	0.54	14.7	1.13	48.25	5.28	10.51	6.56	17.07
Cu/SiO ₂ -N	155.23	0.60	15.6	0.74	46.35	5.54	5.61	4.40	10.01
Cu/SiO ₂ -H	132.20	0.61	18.5	0.61	35.518	6.94	4.14	5.51	9.65

^a: Determined by N₂ adsorption-desorption; ^b: Determined by N₂O titration; ^c: Determined by TEM; ^d: Determined by NH₃-TPD.


 Fig. 2 FT-IR (a) and H₂-TPR (b) spectra of catalysts with different calcination atmospheres

The significantly higher reduction temperatures for Cu/SiO₂-A and Cu/SiO₂-N underscore their stronger metal-support interactions compared to Cu/SiO₂-H. Such strong interactions are known to enhance catalytic activity and stability by anchoring metal species and inhibiting sintering. Furthermore, deconvolution of the TPR profiles reveals that the high-temperature reduction peak constitutes 33.65% of the total area for Cu/SiO₂-A, substantially greater than the 15.09% for Cu/SiO₂-N. This quantitative difference indicates a higher population of strongly interacting copper species in the Cu/SiO₂-A catalyst.

The distinct metal-support interactions induced by different calcination atmospheres critically govern the dispersion and valence distribution of the loaded copper species, which are decisive factors for the catalytic activity, selectivity, and stability. XRD analysis was used to determine the phase composition of the catalysts. As shown in Figure 3(a), all catalysts exhibit a broad diffraction peak at approximately 21.5°, characteristic of amorphous SiO₂^[25–26]. For catalysts calcined under inert (N₂) and oxidative (Air) atmospheres, weak diffraction peaks appear around 35.04°, corresponding to CuO species. This observation, combined with the low intensity of these peaks, suggests a strong metal-support interaction that promotes the uniform dispersion of copper. In contrast, the Cu/SiO₂-H catalyst displays distinct diffraction peaks assignable to Cu₂O and Cu⁰ species. This indicates that precursor decomposition and its simultaneous reduction to metallic and cationic copper occurred during H₂ calcination. Consequently, the opportunity for forming a strong Cu-O-Si interaction with the support was diminished, leading to

significant copper agglomeration, as evidenced by the relatively sharp and intense copper diffraction peaks in Cu/SiO₂-H^[24].

After hydrogen reduction, the XRD pattern of the Cu/SiO₂-H catalyst remained unchanged, whereas significant transformations were observed for the Cu/SiO₂-N and Cu/SiO₂-A catalysts. The CuO diffraction peaks disappeared, and new characteristic peaks for Cu₂O and Cu⁰ emerged, confirming the complete reduction of CuO to lower-valence species, accompanied by particle agglomeration. The broad nature of the Cu₂O diffraction peaks implies a high dispersion of Cu₂O species. The stability of these Cu₂O species is attributed to strong metal-support interactions, which effectively stabilize the cationic copper and suppress its over-reduction and aggregation into large metallic particles^[27–29]. The crystallite sizes of the copper species in the reduced catalysts were estimated using the Scherrer equation (Table 2), yielding values between 3–7 nm. The reduced Cu/SiO₂-A catalyst possessed the smallest crystallite size, indicating superior copper dispersion. TEM analysis (Figure 4) showed that the average copper particle sizes followed the order: Cu/SiO₂-A (5.28 nm) < Cu/SiO₂-N (5.54 nm) < Cu/SiO₂-H (6.94 nm). This consistent trend from both techniques conclusively demonstrates that calcination in air achieves the highest metal dispersion, followed by nitrogen and hydrogen atmospheres.

The copper dispersion and surface area were further quantified by N₂O chemisorption. As summarized in Table 1, the Cu/SiO₂-A catalyst exhibits superior copper dispersion and a larger copper surface area than its N₂- and H₂-calcined counterparts.

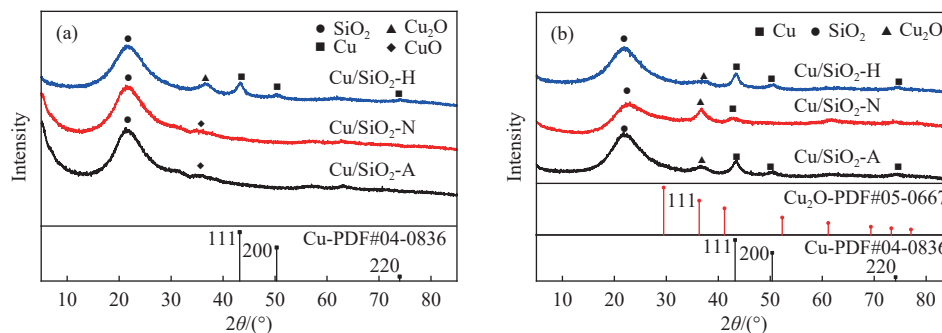
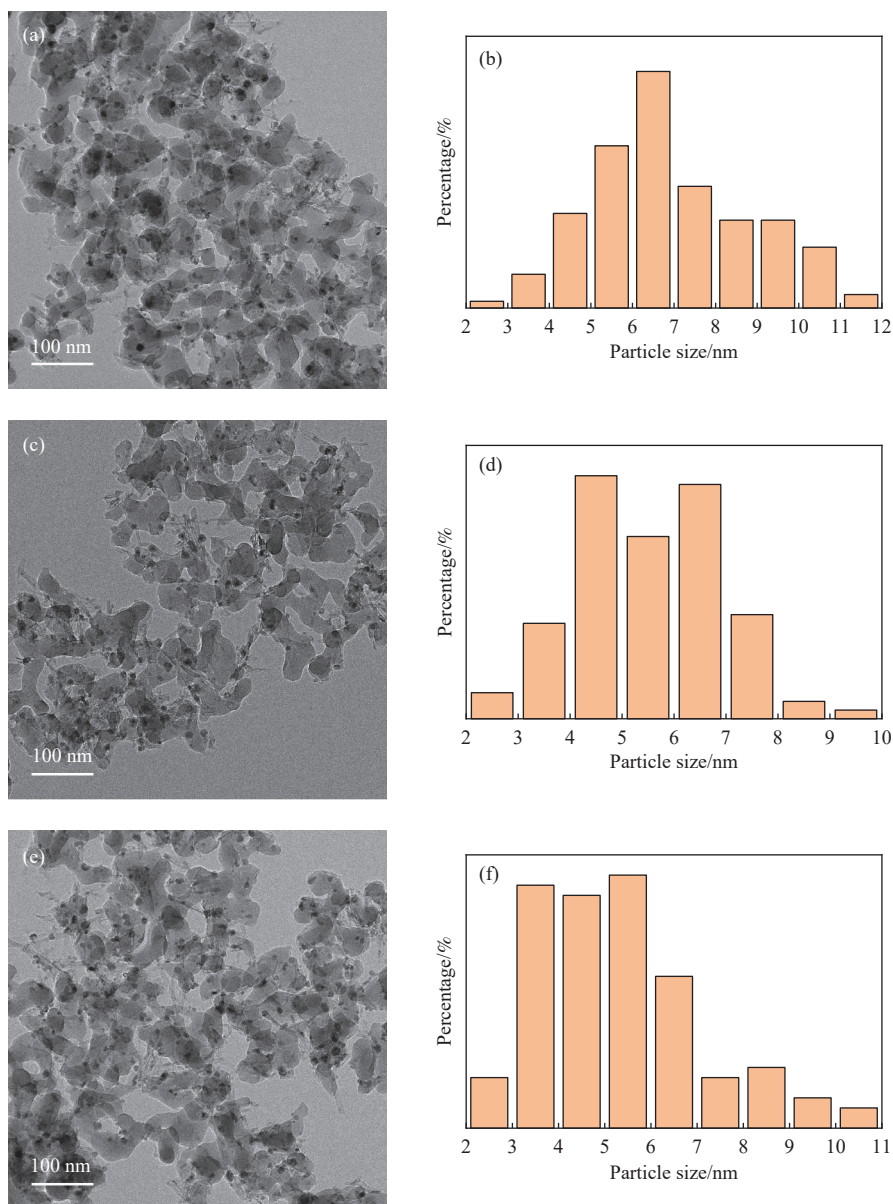


Fig. 3 XRD spectra of calcined catalysts (a) and reduced catalysts (b)

Table 2 Cu crystal size based on XRD results of reduced catalysts

Catalyst	Crystalline size/nm		
	Cu(111)	Cu ₂ O(111)	Cu(200)
Cu/SiO ₂ -A	5.1	3.6	3.6
Cu/SiO ₂ -N	5.3	5.1	—
Cu/SiO ₂ -H	6.1	3.9	6.5



(a), (b): Cu/SiO₂-H; (c), (d): Cu/SiO₂-N; (e), (f): Cu/SiO₂-A.

Fig. 4 TEM images of the reduced catalysts

These results, collectively with the XRD and TEM findings, confirm that the strength of the metal-support interaction directly governs the dispersion of the loaded metal. Enhanced copper dispersion provides a higher population of accessible active sites, which is crucial for the hydrogenation of DMS to BDO. These abundant sites facilitate efficient hydrogen activation and reactant adsorption, while precisely regulating the hydrogenation

depth to suppress over-hydrogenation and undesired side reactions, thereby leading to superior catalytic activity.

The metal-support interactions govern not only the dispersion of the loaded metal but also its chemical state. Since the surface chemical state of the reduced catalysts is critical to hydrogenation performance, the catalysts were analyzed by X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger electron spectroscopy (XAES). The

survey spectra confirm that all catalysts consist of Cu, Si and O, indicating a consistent bulk composition. In the high-resolution Cu 2*p* spectra (Figure 5(b)), all catalysts exhibit only two characteristic peaks at approximately 932.6 eV (Cu 2*p*_{3/2}) and 952.5 eV (Cu 2*p*_{1/2}) with no satellite features in the 941–945 eV region that are characteristic of Cu²⁺ species. This confirms the complete reduction of Cu²⁺ to Cu⁰ and/or Cu⁺, consistent with the XRD results. Notably, the Cu 2*p* peaks for Cu/SiO₂-A and Cu/SiO₂-N are slightly shifted to lower binding energies compared to those of Cu/SiO₂-H, with the shift being most pronounced for the Cu/SiO₂-A catalyst^[30]. This suggests the strongest metal-support interaction in Cu/SiO₂-A, aligning with the H₂-TPR and FT-IR findings.

Due to the nearly overlapping binding energies of Cu⁺ and Cu⁰ in the Cu 2*p* spectra, Cu LMM Auger spectroscopy was employed to distinguish these species. The deconvoluted Cu LMM spectra confirm the coexistence of both Cu⁺ and Cu⁰ in all reduced catalysts, with binding energy typically around 572 and 568 eV, respectively. Quantitative analysis reveals that the relative proportion of Cu⁺ (Cu⁺/(Cu⁺+Cu⁰)) follows the order: Cu/SiO₂-A (47.18%) > Cu/SiO₂-N (32.45%) > Cu/SiO₂-H (26.41%). The observed order of Cu⁺ proportion (Cu⁺/(Cu⁺+Cu⁰)) can be attributed to the varying strength of the metal-support interaction, as indicated by H₂-TPR and FT-IR results. Specifically, the Cu/SiO₂-A catalyst exhibits the strongest Cu-O-Si interaction, which helps stabilize Cu⁺ species and allows more Cu₂O to remain after reduction. Although Cu/SiO₂-N shows the most intense Cu₂O diffraction peak in Figure 3(b), this likely reflects the presence of larger and better-crystallized Cu₂O particles in its bulk phase. In contrast, the weaker diffraction signal from Cu/SiO₂-A does

not imply a lower amount of Cu₂O, but instead suggests that Cu₂O is highly dispersed on the support surface, which is consistent with its higher Cu⁺ proportion derived from XPS analysis. This quantitative trend is significant, as a synergistic interaction between Cu⁺ and Cu⁰ sites is crucial for the hydrogenation reaction. The Cu⁺ sites are primarily responsible for activating and adsorbing the carbonyl group of DMS, while also contributing to the catalyst's thermal stability. Consequently, a higher concentration of Cu⁺ sites enhances both the activity and stability of copper-based catalysts.

The surface acidity of the catalysts calcined under different atmospheres was characterized by NH₃-TPD. As shown in Figure 6, all reduced catalysts exhibit NH₃ desorption peaks in the range of 150–400 °C, corresponding to the presence of both weak and medium-strong acid sites. Quantitative analysis *via* peak deconvolution reveals that the total acid amounts of the Cu/SiO₂-N and Cu/SiO₂-H catalysts are similar, whereas the Cu/SiO₂-A catalyst exhibits a significantly higher total acid amount. Specifically, the weak acid amount reaches 10.51 μmol/g for Cu/SiO₂-A, which is considerably higher than that of Cu/SiO₂-N (5.61 μmol/g) and Cu/SiO₂-H (4.14 μmol/g). In the hydrogenation of DMS to BDO, weak acid sites are believed to facilitate the reaction by adsorbing and polarizing the carbonyl oxygen atom of the ester group. This polarization weakens the C=O bond, thereby enhancing its reactivity toward nucleophilic attack by hydrogen species activated on adjacent metallic copper sites^[31]. In contrast, medium-strength acid sites catalyze the intramolecular dehydration and cyclization of BDO, leading to the formation of the THF by-product.

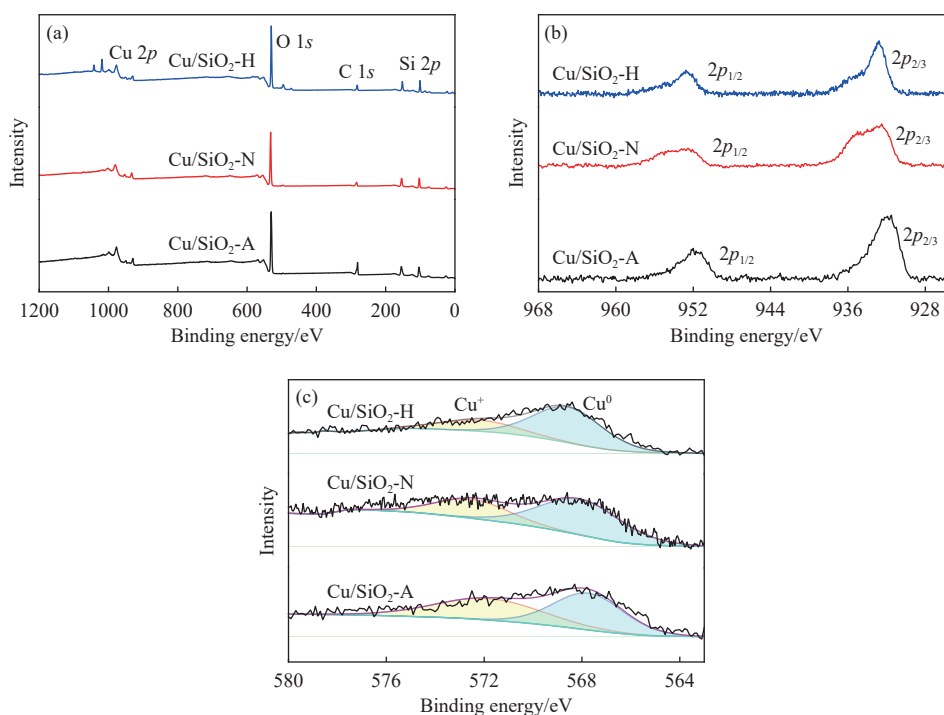
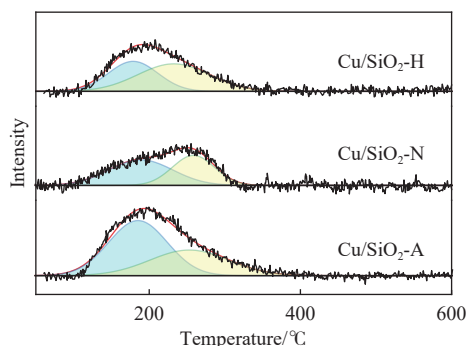


Fig. 5 (a) XPS survey scan, (b) Cu 2*p* and (c) Cu LMM spectra of reduced catalysts


 Fig. 6 NH₃-TPD spectra of reduced catalysts

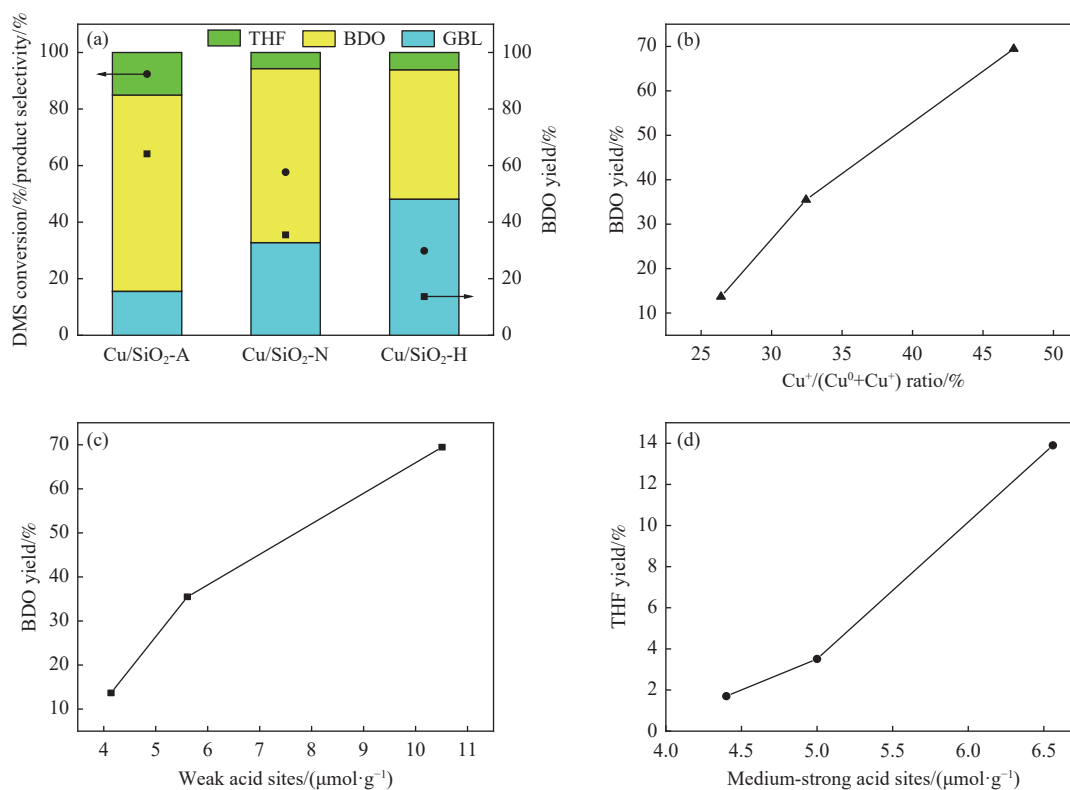
Compared with Cu/SiO₂-N and Cu/SiO₂-H, the Cu/SiO₂-A catalyst possesses a notably higher density of medium-strength acid sites. Therefore, while the highest density of weak acid sites in Cu/SiO₂-A contributes to its superior DMS conversion, the concurrent high density of medium-strength acid sites also promotes THF formation.

2.2 Performance evaluation of catalysts with different calcination atmospheres

The catalytic performance of the Cu/SiO₂ catalysts calcined under different atmospheres was evaluated for DMS hydrogenation to BDO at 210 °C, 5.0 MPa, a WHSV of 0.6 h⁻¹ and an H₂/DMS molar ratio of 100. As summarized in Figure 7(a), the Cu/SiO₂-A catalyst

demonstrated superior activity, achieving a DMS conversion of 92.37%, which is substantially higher than that of the Cu/SiO₂-N (57.67%) and Cu/SiO₂-H (29.86%) catalysts. Notably, the Cu/SiO₂-A catalyst also exhibited the highest BDO selectivity of 69.45% at this high conversion level. In contrast, the Cu/SiO₂-N catalyst showed moderate conversion with comparable BDO selectivity, while the Cu/SiO₂-H catalyst performed poorly in both activity and selectivity.

To further elucidate the key active sites in the catalyst that influence activity and selectivity, we correlated the yield of BDO with both the Cu⁺/(Cu⁰+Cu⁺) ratio and the weak acid site density, and separately linked the formation of the THF to the medium-strong acid site density. As shown in Figure 7(b) and (c), the BDO yield exhibits a positive correlation with both the Cu⁺/(Cu⁰+Cu⁺) ratio and the weak acid amount. This suggests that achieving a high BDO yield is governed by a synergistic and competitive interplay among different types of active sites on the catalyst surface. Specifically, the Cu⁺-Cu⁰ dual site serves as the core active center for the sequential hydrogenation of DMS to BDO, with Cu⁺ activating the carbonyl group and Cu⁰ facilitating H₂ dissociation. Their proximity ensures efficient hydrogenation. Meanwhile, weak acid sites stabilize polar intermediates through weak adsorption, aiding the hydrogenation process and thereby enhancing the BDO yield.



(a): Catalytic performance of catalysts with different calcination atmospheres; (b): BDO yield versus Cu⁺/(Cu⁰+Cu⁺) ratio; (c): BDO yield versus weak acid sites; (d): THF yield versus medium-strong acid sites.

Fig. 7 Performance of catalysts and correlation with Cu⁺/(Cu⁰+Cu⁺) ratio and acid sites

Conversely, once formed, BDO molecules can interact with medium-strong acid sites, where intramolecular dehydration and cyclization occur, leading to the formation of the THF. Thus, the high performance of the optimal catalyst, Cu/SiO₂-A, stems from its combination of a high density of Cu⁺-Cu⁰ dual sites and a suitable weak-acid environment, which together maximize BDO production efficiency. However, its relatively higher density of medium-strong acid sites also results in increased THF selectivity. Notably, Cu/SiO₂-A possesses the highest density of weak acid sites and the largest Cu⁺/(Cu⁰+Cu⁺) ratio. This optimized configuration delivers outstanding performance, achieving a DMS conversion of 92.37% and a BDO selectivity of 69.45%.

Based on the characterization results and catalytic performance data, we propose a potential synergistic mechanism between Cu⁺ and Cu⁰ species. Specifically, Cu⁺ sites tend to adsorb and activate the C=O bond of dimethyl succinate (DMS), thereby polarizing it, while Cu⁰ sites

facilitate the dissociation of H₂ to provide active hydrogen species (H*). Building on this, a plausible reaction pathway for the hydrogenation of DMS to BDO is proposed (Figure 8). H₂ first undergoes dissociative adsorption on Cu⁰ sites, forming surface adsorbed H atoms. With the cooperative assistance of acidic sites, Cu⁺ then adsorbs and activates the C=O/C=O bonds of DMS. Then, C–O bond cleavage occurs, after which the activated C=O bond reacts with H*, breaking the double bond to yield the intermediate methyl 4-hydroxybutyrate (4-HBM) and methanol. Subsequently, 4-HBM undergoes intramolecular transesterification to form GBL, releasing another methanol molecule^[32]. Next, GBL undergoes ring-opening in the presence of H* to form the intermediate 4-hydroxybutyraldehyde (4-HB), whose C=O bond is then activated by Cu⁺ and further hydrogenated to produce the target product BDO. Furthermore, when medium-strength acid sites are present on the catalyst, BDO can undergo intramolecular cyclodehydration to form THF as a byproduct.

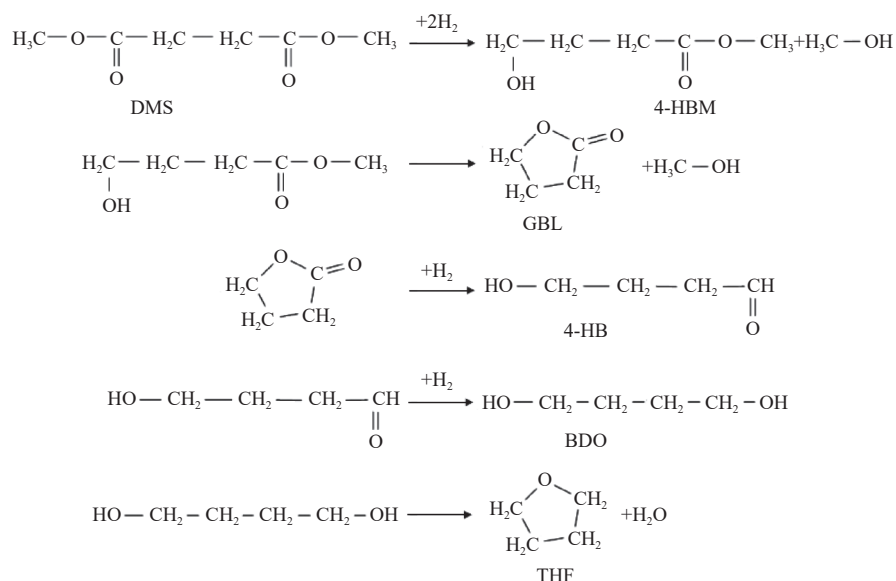


Fig. 8 Reaction pathways for DMS hydrogenation to BDO catalyzed by Cu/SiO₂

3 Conclusion

In summary, the calcination atmosphere is demonstrated to be an effective strategy for engineering the properties of Cu/SiO₂ catalysts, precisely tuning the metal-support interaction and surface acidity. The catalyst calcined in air (Cu/SiO₂-A) exhibited optimal characteristics, including the strongest metal-support interactions, the highest copper dispersion, an abundant surface acidity, and the largest population of stabilized Cu⁺ species. These properties synergistically contributed to its superior performance in the hydrogenation of DMS to BDO. The high dispersion and Cu⁺ sites facilitated hydrogen activation and carbonyl adsorption, while the acid sites promoted C=O polarization. This synergistic cooperation resulted in outstanding catalytic metrics under optimal conditions (210 °C, 5.0 MPa, WHSV of 0.6 h⁻¹, H₂/DMS molar ratio of 100), achieving a

DMS conversion of 92.37% and a BDO yield of 64.15%. This work highlights calcination atmosphere engineering as a pivotal strategy for designing efficient heterogeneous catalysts reliant on metal-acid synergy.

Declaration of Competing Interest

The authors declare no conflict of interest.

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焙烧气氛精准调控的 Cu/SiO₂ 催化剂用于高效催化 丁二酸二甲酯加氢制 1,4-丁二醇

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摘 要: 生物质衍生的丁二酸二甲酯催化加氢制备 1,4-丁二醇, 是绿色化学背景下生产高附加值 C4 化学品的一条关键路径。Cu/SiO₂ 催化剂虽以酯加氢高选择性著称, 但其性能本质上与铜物种的微观结构密切相关。尽管焙烧是形成催化剂活性结构的关键步骤, 但焙烧气氛对其影响的系统性研究尚不充分。本研究采用尿素辅助水热法制备了 Cu/SiO₂ 催化剂, 并在不同气氛下进行焙烧, 以阐明焙烧气氛对催化剂理化性质及其后续加氢性能的影响。通过 N₂ 物理吸附脱附、FT-IR、H₂-TRR、XRD、TEM、N₂O 化学吸附、XPS 和 NH₃-TPD 表征发现, 焙烧气氛能显著改变金属-载体间相互作用, 进而有效调控负载铜物种的分散度和化学状态。尤其是, 在空气中焙烧后的催化剂, 其金属-载体间相互作用较强, 有效提高了铜物种的分散度, 并增加了关键活性位 Cu⁺ 的占比。在优化的反应条件下, Cu/SiO₂-A 催化剂展现了优异的催化性能, 丁二酸二甲酯转化率达 92.37%, 1,4-丁二醇收率达 64.15%。本工作证实了焙烧气氛工程是一种优化多相催化剂中金属-载体相互作用, 从而实现高效加氢过程的强效策略。

关键词: 铜基催化剂; 焙烧气氛; 金属-载体相互作用; 加氢

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