Review

Copper Phyllosilicates-Derived Catalysts in the Production of Alcohols from Hydrogenation of Carboxylates, Carboxylic Acids, Carbonates, Formyls, and CO₂: A Review

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Abstract: Copper phyllosilicates-derived catalysts (CuPS-cats) have been intensively explored in the past two decades due to their promising activity in carbonyls hydrogenation. However, CuPS-cats have not been completely reviewed. This paper focuses on the aspects concerning CuPS-cats from synthesis methods, effects of preparation conditions, and dopant to catalytic applications of CuPS-cats. The applications of CuPS-cats include the hydrogenation of carboxylates, carboxylic acids, carbonates, formyls, and CO₂ to their respective alcohols. Besides, important factors such as the Cu dispersion, Cu⁺ and Cu₀ surface areas, particles size, interaction between Cu and supports and dopants, morphologies, and spatial effect on catalytic performance of CuPS-cats are discussed.

Keywords: copper; hydrogenation; phyllosilicates

1. Introduction

Phyllosilicates are versatile materials with numerous applications such as being carriers of enzymes in the synthesis of chemical and pharmaceutical compounds [1–8], precursors of organo-phyllosilicates nanocomposites [9–15], ferromagnetic [16] and antiferromagnetism materials [17], lithium ion batteries [18,19], pharmaceutical excipients [20–23], adsorbents of heavy metals [24,25], toxic compounds [26,27], industrial dyes [28–32], and CO₂ scrubbers [33–35]. One of its applications is to be the precursor of heterogeneous catalysts. Figure 1 shows the bibliometric analysis of phyllosilicate-related catalysis papers. An exponential trend underlines the emerging interest of phyllosilicate in catalysis applications.

Figure 1. Number of publications concerning “phyllosilicate” (dots) and “phyllosilicate + catal” (bars) over years (compiled from statistical data of Scopus on 8 December 2020).
The burgeoning research of phyllosilicates has been stimulated by its unique physicochemical properties. Phyllosilicate is a laminar-structured silicate mineral which is comprised of one tetrahedral layer of silica (SiO$_4^{4-}$), sharing 3 oxygen atoms together in a planar with another oxygen links with a layer of octahedra units (see Figure 2) [36,37]. The core of the octahedron unit could be occupied by divalent or trivalent metallic cations such as Al, Mg, Zn, Mn, Fe, Cu, Ni, and Co [38,39]. Various phyllosilicates can be formed by assembling different tetrahedral and octahedral layers. For example, chrysocolla (Cu$_2$Si$_2$O$_5$(OH)$_2$) is a lamellar structure consisted of layers of SiO$_4$ tetrahedra sandwiched between discontinuous layers of CuO$_6$ octahedra [40]; kaolinite is an 1:1 aluminum phyllosilicates while pyrophyllite is 2:1 [41], chrysotile is made of 1:1 magnesium phyllosilicates (Mg$_3$Si$_2$O$_5$(OH)$_4$) [37]. The difference between the radius of tetrahedrally coordinated Si and octahedrally coordinated cation can bend the layer-structured phyllosilicates [37,42], resulting in distorted morphologies such as rolling of paper sheets into a tube. Compared to conventional catalysts (metal impregnated on SiO$_2$), the high surface area of laminar structured phyllosilicate allows metal atoms to be finely dispersed. At the same weight loading but higher dispersion, phyllosilicate structure might possess more active sites than the conventional catalysts.

**Figure 2.** Structural scheme of the 2:1 phyllosilicates and 1:1 phyllosilicates (chrysocolla) (reproduced from [36] with permission from Elsevier and from [40] with permission from American Chemical Society).

Structural diversity, compatibility with various transition metals, high surface area, and finely dispersed metallic cations makes phyllosilicates attractive in numerous reactions, such as Fischer–Tropsch [43], esterification [44], cellulose conversion to glucose [45], oxidation of water [46,47], oxidation of CO [48–52], CO or CO$_2$ reforming [34,53–61], hydrogen generation from methanol steam reforming [62–66], and syntheses of valuable alcohols from hydrogenation of CO [67–69], CO$_2$ [53,70–72], and hydrogenolysis of esters [73–92]. Copper [70,71,73,75–84,86–120] and nickel phyllosilicates [53–55,57–61,69,72,121–152] derived catalysts (CuPS-cats and NiPS-cats, respectively) are extensively investigated. NiPS-cats are usually used for the hydrogenation of unsaturated hydrocarbons [120,148], CH$_4$ dry reforming [58,60,129,136,137], CO$_2$ methanation [53], water-gas shift [130,134], deoxygenation [151], steam reforming, [135], and hydrodeoxygenation of biomass [131]. In compari-
son, CuPS-cats are promising in alcohol synthesis through the hydrogenation of carbonyls such as ester, carboxylic acid, carbonate, and CO\textsubscript{2} as well. So far, there are three reviews [153–155] that discuss about the catalytic hydrogenation of C=O bond to produce alcohols using copper-based catalysts. However, only a specific aspect was focused in each review. Watari et al. [153] targeted hydrogenation reactions mediated by using copper-based catalysts, containing limited information about CuPS-cats. Ye et al. [154] aimed to combat the deactivation problem of Cu-based catalysts. Bian and Kawi [155] published an insightful review on the synthesis of CoPS, NiPS, and CuPS, but emphasized the usages of NiPS. In this contribution, we focus solely on CuPS-cats, but all aspects of CuPS-cats including the preparation methods, control factors of morphology, effects of hetero-element addition, and reduction behaviors of CuPS were systematically summarized and in-depth discussed. This is followed by the applications of CuPS-cats in the hydrogenation of carboxylates, carboxylic acids, carbonates, formyls and carbon dioxide. Lastly, the existing challenges and future prospective of CuPS-cat were discussed based on latest updated researches till 2020.

2. Formation of CuPS-Cats

The development of CuPS-cats over the past 20 years was summarized in Figure 3. There are five major approaches in CuPS synthesis, including examination of synthesis criterion, design of preparation method, selection of supports, addition of promoters, and control of PS morphology, and these topics will be discussed in Sections 2.1–2.5, respectively. Since a reduction step is necessary to transform CuPS into CuPS-cat, the reduction behavior of CuPS will be addressed in Section 2.6.

Figure 3. The chronograph of the development of copper phyllosilicates-derived catalysts (CuPS-cats).

2.1. Synthesis Methods

2.1.1. Ammonia Evaporation-Related Approaches

CuPS was firstly synthesized by using the cationic exchange method [93]. The cations of copper tetraamine complex [Cu(NH\textsubscript{3})\textsubscript{4}(H\textsubscript{2}O)\textsubscript{2}]\textsuperscript{2+} were dissolved and then deposited on a silica surface at room temperature. The cationic exchange method is usually accompanied by a deposition-precipitation step because the formation of CuPS was proposed to be a sequential process through the dissolution of silica followed by the precipitation of phyllosilicates. Toupance et al. [40] proposed that the formation mechanism of CuPS is through the selective adsorption of neutral Cu complexes (i.e., Cu(OH)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}) on a silica surface. Therefore, the cationic exchange was renamed as selective adsorption. Later, Chen et al. [73] reported an ammonia evaporation (AE) method for CuPS synthesis. In this process, silica sol was mixed with a copper ammonia complex (initial pH value at about 11–12), followed by the gradual removal of ammonia through evaporation till the solution is neutralized, yielding CuPS as the precipitates. After washing, drying,
and calcination, CuPS-cats can then be obtained. Mostly, octahedrally coordinated Cu$^{2+}$ needs to be activated by the reduction to lower oxidation states such as Cu$^{+}$ or Cu$^{0}$.

Besides the AE method, an ammonia evaporation hydrothermal (AEH) method which integrated an additional hydrothermal treatment step to ammonia evaporation process was developed by Gong et al. [96]. The major difference between AE and AEH method is that the latter had a follow-up hydrothermal treatment for the resultant solid after AE. The difference of CuPS-cats synthesized from AE and AEH has not been fully understood. Another related synthesis method was ammonia hydrothermal (AH). The AH method was firstly described by Yue et al. [97] for synthesizing copper phyllosilicate nanotubes (CuPSNTs). Briefly, by excluding the AE step, the mixture of silica, copper nitrate, and ammonia was treated under hydrothermal conditions (200 °C and 10 MPa), resulting in nanotube-shaped CuPS structure. Excess ammonium by adding NH$_4$Cl [107,113] or NH$_4$NO$_3$ [156] in the mixture is required.

2.1.2. Precipitation

Precipitation methods such as co-precipitation (CP) and deposition-precipitation method were developed to synthesize CuPS-cats. Typically, a mixture of copper and silica sol was precipitated by dropwise adding basic agents such as (NH$_4$)$_2$CO$_3$ [79,92], NH$_4$HCO$_3$ [104], Na$_2$CO$_3$ [117,157], or ammonia solution [158]. Unlike the AE method, the pH value of the aqueous solution in precipitation methods was maintained at 6–7. When using tetraethyl orthosilicate (TEOS) as the silica source, CuPS-cats would be produced through a hydrolysis precipitation by using (NH$_4$)$_2$CO$_3$ as a precipitation agent [81,116]. Zhang et al. [78] invented urea hydrolysis deposition-precipitation (UHDP) method by using urea as the precipitant. Briefly, hydrolysis of urea increased the pH value, and thereby induced precipitation of CuPS. The UHDP method was also named as “urea-assisted gelation” [76,85,90,95,159].

2.1.3. Other Methods

The pioneer study of sol-gel method was developed by He et al. [94]. At the outset, ammonia solution was added into the mixture of copper and silica sol until the pH value of the solution increased to 11–12. The gelation was subsequently conducted at 50 °C. Weight loading of copper can be maximized at 45%. Abbas et al. [84] synthesized CuPS-cats by using novel methods such as sonochemical and stirring-enhanced hydrothermal. Systems such as a pulse-mode ultrasonic reactor and agitation-enhanced hydrothermal bomb were applied to improve intermolecular collision. A combinative method of ultrasound-treated and agitation-enhanced hydrothermal method was also reported [160].

In sum, several methods can be used in CuPS-cats synthesis. Among them, the laminar structure of phyllosilicate is usually prepared by using the AE method, as confirmed by various techniques such as TEM, XRD, and FTIR (Figure 4). Besides, AE-made CuPS-cats had several advantages compared to those made by other methods, including high surface area [99,104,158], good structural regularity [158], strong thermal stability [104], and great reproducibility. All these features render AE method the most effective to fabricate CuPS.

One drawback of using the AE method for CuPS preparation is the emission of waste ammonia. This inspires Popa et al. [79] and Ding et al. [92] to invent ammonia emission-free process, i.e., the ammonium carbonate deposition precipitation (AC) method, through which CuCO$_3$ was precipitated on SiO$_2$ followed by a calcination step to decompose CuCO$_3$. AC-made Cu/SiO$_2$ had a lower surface area and a less phyllosilicate crystallinity than those of AE-made counterparts; however, they had comparable dimethyl oxalate (DMO) hydrogenation activities. More Cu$^{+}$ species were formed (the content of Cu$^{+}$ over the total Cu species is greater than 60%) by using AC method [79,92].
Figure 4. Characterization of Cu/SiO$_2$ catalysts synthesized by impregnation (IM), deposition-precipitation (DP) and ammonia evaporation (AE) (reproduced from [117] with permission from MDPI).

| Catalysts          | $S_{\text{BET}}$ (m$^2$·g$^{-1}$) | $D_{\text{pore}}$ (nm) | $V_{\text{pore}}$ (cm$^3$·g$^{-1}$) | Grain Size $a$ (nm) |
|--------------------|----------------------------------|------------------------|-----------------------------------|---------------------|
| CuO/SiO$_2$(IM)    | 231                              | 17.4                   | 1.07                              | 16.2                |
| CuO/SiO$_2$(DP)    | 304                              | 7.1                    | 0.69                              | 7.6                 |
| CuO/SiO$_2$(AE)    | 457                              | 4.6                    | 0.67                              | –                   |
| SiO$_2$            | 328                              | 9.3                    | 0.77                              | –                   |

*a Calculated according to the formula $D = K \lambda /\beta \cos \theta$.

2.2. Effect of Synthesis Criteria

2.2.1. Temperature for Ammonia Evaporation

The effect of ammonia evaporation temperature was investigated in the range of 60 to 100 °C [73]. Morphologies of CuPS (sphere-like or slit-like structure) depends heavily on the temperature used in AE. An optimal crystallinity was achieved at 90 °C (see Figure 5). A maximal fraction mole of Cu$^+$ (Cu$^+$–(Cu$^0$ + Cu$^+$) = 0.55) and the highest DMO hydrogenation activity was evidenced on the CuPS-cat made by using 90 °C as the evaporation temperature.

Figure 5. Phyllosilicate crystallinity degree of calcined samples at evaporation temperatures, the crystallinity degree was estimated from $I_{663}/I_{800}$ of FTIR (adapted from [73]).
2.2.2. Aging Time

The effect of aging time of CuPS precursors was investigated \[100\]. The mixture of silica sol and $[\text{Cu(NH}_4\text{)}^2\text{]}^{2+}$ was stirred for different times (4, 16, 24, and 40 h) at room temperature before ammonia evaporation. Aging time does not significantly influence the surface area and porosity of CuPS-cats. By contrast, the $\text{Cu}^+/\text{Cu}^0+\text{Cu}^+ \text{)}$ ratio of 20 wt % CuPS-cats were 0.30, 0.48, and 0.39, with respect to the aging time of 4, 24, and 40 h. An explanation for the effect of aging time on the distribution of $\text{Cu}^+$ and $\text{Cu}^0$ was still absent. Presumably, the crystallization behaviors of CuPS may vary depending on the aging time \[92\].

2.2.3. Calcination and Reduction Temperature

Ding et al. \[102\] investigated the effect of calcination temperatures on AE-synthesized CuPS-cats in the hydrogenation of diethyl malonate (DEM) to 1,3-propanediol (PDO). Elevating the calcination temperature above 623 K may partially damage the structure of CuPS. The decreasing order of $\text{Cu}^+$ concentration corresponding to the calcination temperature is estimated to be 47.6% (1023 K) > 45.5% (723 K) > 41.3% (623 K) > 36.9% (823 K) > 35.1% (923 K). However, the hydrogenation rate did not follow the same trend as that of the $\text{Cu}^+$ concentration. This indicated that the activity of CuPS-cat depends not only on $\text{Cu}^+$ concentration, but also on the nature (such as crystallite size and intimacy of $\text{Cu}^0$ and $\text{Cu}^+$) of derived Cu species.

Sun et al. \[87\] systematically investigated the structure-activity correlation of CuPS-cats reduced at different temperatures and their DMO hydrogenation activities. The DMO conversion and ethylene glycol (EG) selectivity showed a volcano-like trend, while $\text{Cu}^+/(\text{Cu}^0+\text{Cu}^+)$ ratio, surface area, pore volume, Cu dispersion, and Cu particles size did not have a strong correlation with the reduction temperature (Figure 6). The interaction of Cu and the support with a proper reduction treatment may improve the catalytic performances of CuPS-cats, as discussed vide infra.

![Figure 6. The correlation of reduction temperature and physicochemical properties of CuPS-cats (adapted from \[87\]).](image)

Calcination and reduction temperatures are important in tailoring the ratio of $\text{Cu}^+–\text{Cu}^0$ of CuPS-cats. Different calcination and reduction temperatures were used since a proper $\text{Cu}^+–\text{Cu}^0$ ratio can be varied with respect to the reaction per se. For example, a ratio of $\text{Cu}^+–(\text{Cu}^0+\text{Cu}^+)$ close to unity is claimed to be effective in $\text{CO}_2$ hydrogenation \[70\] (see Figure 7); while 0.5 is a more proper ratio for hydrogenation of dimethyl malonate \[102\]. The varying preferred values of $\text{Cu}^+–(\text{Cu}^0+\text{Cu}^+)$ ratios with respect to different reactions complicate the developing, preparation, and optimization of CuPS-cats.
2.2.4. Cu Weight Loading

Dong et al. [106] found that agglomeration of CuO particles were formed when the percentage of Cu was higher than 43% in CuPS preparation. They claimed that a maximal loading of Cu for phyllosilicate is at 39%, corresponding to the Cu–Si molar ratio of approximately 0.75. The favorable weight loading of Cu to synthesize CuPS-cats is in line with the content of Cu in chrysocolla (Cu$_2$Si$_2$O$_5$(OH)$_2$). However, the relation of Cu loading and activity of CuPS-cat varies in different systems. Li et al. [108] found that 10% of Cu showed the best performance for hydrogenation of ethylene carbonate (EC) to EG. Jiang et al. [111] reported the 20% CuPS-cats could maximize the conversion of adipic acid (AA) and the yield of its hydrogenated product, i.e., 1,6-hexanediol (HDOL). For the conversion of furfural (FFAL) to 2-methyl furan, 25% of Cu was reported to be appropriate [106]. Much remains to be learned about the correlation between a proper Cu content and different hydrogenation reactions.

2.2.5. Ammonium Cation Concentration

Apart from Cu and Si concentrations, the amount of ammonium cation can tune the crystallization of CuPS. Toupance et al. [40] found that the crystallinity of CuPS showed a 4-fold decrease when the pH value increases from 10 to 11 by using ammonia to control the pH value in the deposition-precipitation process. If the [NH$_4^+$]–[Cu$^{2+}$] ratio surpassed 10, CuPS structure cannot be formed due to excess [Cu(NH$_3$)$_4$]$^{2+}$ complexes. Di et al. [80] also supported this claim: excess ammonia inhibits crystallization of CuPS. CuPS-cats synthesized by using CP with an abundance of ammonia could be reduced easier than that without adding excess ammonia. They also discovered that adding a trace of Zn cations with ammonium can change the morphology of CuPS from 2:1 to 1:1.

2.3. Effect of Supports

2.3.1. Silica Support

Ultra-fine silica produced from in situ hydrolysis of TEOS was proved to enhance the dispersion of copper and to induce the formation of Cu$^+$ [81]. No diffraction of CuO was observed by XRD even at a high copper loading (40 wt % Cu). A volcano trend of the ratio of CuPS phase to amorphous silica was discovered with its apex at a 30% Cu loading. The concentration of Cu$^+$ in the 30 wt % Cu sample was doubled than that of the 30% CuPS-cats synthesized by using the AE method.

Qi et al. [112] disclosed that Cu precipitated on nanosized silica showed a high dispersion (>69%), regardless with silica particle sizes. In contrast, Wang et al. [88] synthesized CuPS-cats at a 20 wt % Cu by using fine silica particles with varying sizes (5 to 25 nm)
through the AE method. They found that the Cu dispersion depends on the particle size of silica: the smaller the size of silica, the higher the Cu dispersion can be. Although the correlation between Cu dispersion and silica particle size is still elusive, the aforementioned groups agreed that the interaction between Cu and SiO$_2$ became stronger by reducing SiO$_2$ particle size. The hydroxyl-enriched surface of silica with small particle size was proposed to enhance the concentration of Cu$^+$ and CuPS crystallinity (Figure 8).

Figure 8. The correlation between surface hydroxyl groups, CuPS phase and Cu$^+$ surface area (adapted from [88]). Surface hydroxyl groups and CuPS phase were, respectively, defined from $I_{960}/I_{800}$ and $I_{670}/I_{800}$ relative intensity of FTIR peaks. Cu$^+$ surface area was estimated from XPS and N$_2$O titration.

In order to increase the contact intimacy of silica and copper, mesoporous silica was adopted. Zhao et al. [82] investigated the effect of different silica sources by using mesoporous silica and silica sol in the synthesis of CuPS-cats by using the AE method. They claimed that the high surface area of mesoporous silica ($S_{BET} = 1019$ m$^2$/g) produced higher concentration of Cu$^+$ than the silica sol did. The different dissolution rates of silica sources were attributed to the varying concentration of yielded Cu$^+$. Other mesoporous silica such as SBA-15, KIT-6, and MCM-41, were used to prepare CuPS-cats, and their influences in Cu dispersion was noticeable [105,161]. A high dispersion of Cu was obtained by using SBA-15 (26.2%) as the silica source, much higher than those made by using KIT-6 (8.2%) and MCM-41 (6.8%). [105]. Ciotonea et al. [161] claimed that Cu nanoparticles can be finely anchored on SBA-15 without sintering. After reduction, the sheet-like structure of phyllosilicate is intact with small metallic Cu particles (~5 nm).

In sum, ultra-fine silica or mesoporous silica with the large surface area and high surface hydroxyl groups might cause a stronger interaction between Cu and SiO$_2$. The stronger interaction can increase the dispersion of Cu and Cu$^+$ concentration as well. Moreover, sintering of Cu can be eased due to the strong interaction with silica.

2.3.2. Binary Oxides Support

Besides pure silica, AE-synthesized binary oxides such as SiO$_2$-TiO$_2$ [162], SiO$_2$-MgO [163], or SiO$_2$-CeO$_2$ [164] was developed to enhance Cu dispersion. Introducing TiO$_2$, MgO, or CeO$_2$ in silica leads to a high Cu$^0$ concentration due to exchanged electrons between Cu and dopant [162–164]. Mixing MgO and CeO$_2$ with silica sources could enhance Cu$^+$ concentration. Nevertheless, the formation mechanism of binary oxides phyllosilicate phases has not yet been studied.
2.3.3. Interaction between Silica and Copper

Most studies suggest the performances of CuPS-cats depend heavily on the ratio of \( \text{Cu}^+ \text{-Cu}^0 \). A different viewpoint was claimed by Xu et al. [113], indicating that silica can promote molecular hydrogen dissociation for the hydrogenolysis of esters. In comparison to bare copper particles, a dramatic jump in the hydrogenation rate of the carbonyl group was found in copper particles coated by mesoporous silica. DFT calculation showed that higher partially positive charged Cu cations were formed on silica-coated Cu than its uncoated counterpart. Moreover, the negative charged intermediates, such as \( \text{CH}_3\text{O(O\text{-})C–H}^{\delta^-} \), and \( \text{H}^{\delta^-} \), can be stabilized due to the presence of \( \text{SiO–H}^{\delta^+} \) species at the interfaces between copper oxide and silica. Therefore, the Cu–O–SiO\(_x\) interface is concluded to be active in hydrogen dissociation and to stabilize the intermediates. In comparison to other oxides such as TiO\(_2\), Al\(_2\)O\(_3\), and ZrO\(_2\), silica showed a much stronger interaction with copper [96]. Cu dispersion and Cu surface area of the SiO\(_2\) supported CuPS-cats were 5 to 10 times higher than those of TiO\(_2\), Al\(_2\)O\(_3\), and ZrO\(_2\) supported counterparts. The descending order of the strength of support-copper interaction was SiO\(_2\) > Al\(_2\)O\(_3\) > ZrO\(_2\) > TiO\(_2\) [96].

2.4. Effect of Promoters—Interaction in a Bimetallic System

Introducing a secondary metal such as B [95,165], Ag [159], Ni [119,120,135,136,157,166], In [90,115], Zn [86,109,116], La [114,167], Sn [110], Ce [85], or Mo [168] in CuPS allows the activity and stability of CuPS-cat to be enhanced because of the inhibition of Cu sintering and the presence of electron transfer between Cu and dopant. Smaller Cu crystalline and higher dispersion of Cu can be obtained by doping the promoters than those of pristine CuPS after reduction. The average particles size of Cu promoted by adding 1% cerium can be reduced to be about 3–4 nm [85]. In the case of Zn- [109,116] and La-doped-CuPS-cats [167], Cu particles were at approximately 3 nm. Moreover, the Cu particles size in Ni\(_3\)-Cu\(_{36}\)PS rose slightly from 4.0 to 4.7 nm, much less than that of its counterpart of Cu\(_{41}\)PS [119]. Note that the high dispersion of Cu particles can be reached at a very low amount of additives, usually 1–2 wt % [85,110,115,159,167] but the aggregation of Cu will be substantial when doping excess amount of additives (as demonstrated in Figure 9). For activity enhancement, electron transfer between dopants and neighboring Cu species can tailor the \( \text{Cu}^+ \text{-Cu}^0 \) ratio. For example, boron [95,165] has a higher electrophilicity than that of copper, and the tandem Cu/B site allows electron transfer from Cu to B, elevating the Cu\(^+\) concentration. Conversely, Cu\(^+\) concentration is suppressed by forming tandem In/Cu or Sn/Cu sites [90,115]. The electronegativity of the elements might give a rough estimation of \( \text{Cu}^+ \text{-Cu}^0 \) proportion based on electron donating and accepting (Figure 10); however, inconsistent trends were reported [85,86,110,114,167]. Beside the electron interaction, the acidity and basicity of CuPS-cats was influenced by heteroelements. The \( \text{NH}_3\)-TPD and \( \text{CO}_2\)-TPD profiles (Figure 11) indicated that acid sites of B-doped CuPS-cats increased following the trend of increased boron content [95,165]. Sometimes, the alloy of copper and promoters may be formed such as InCu [90], NiCu [120] and AgCu [159].
Figure 9. Sinter of Cu particles when absence of Ni (a), adding trace Ni (b), adding a proper amount of Ni (c), and adding excess Ni (d) into the CuPS (adapted from [157]).

Figure 10. A prediction of the interaction of Cu and other metals based on electronegativity by Pauling scale.

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2.5. Non-Planar CuPS-Cats

CuPS nanotubes (CuPSNTs) can be formed from rolling CuPS sheets into a tubular shape under hydrothermal condition [97]. The CuPSNTs of approximately 200–300 nm of length and 15 nm of thickness were successfully synthesized by using hydrothermal treatment. Similarly, the CuPSNTs with hundreds nm of length and 1–2 nm in thickness were synthesized [107,113] by replacing basic ammonia solution with mild acidic ammonia chloride solution. A hybrid type of tubular- and spherical-shaped phyllosilicate–nanotube-assembled hollow spheres (NAHS) (Figure 12) was designed as well [156]. Moreover, synthesize CuPSNTs by the AEH method using a copolymer of ethylene oxide and propylene oxide (P123) as a template was reported [169].

Figure 11. NH$_3$-TPD and CO$_2$ TPD profiles of xB-Cu-SiO$_2$ catalysts. (reproduced from [95] with permission from Elsevier)

Figure 12. Scheme of nanotube-assembled hollow-sphere nanoreactor formation. (reproduced from [156] with permission from American Chemical Society).

To evaluate the confinement effect of CuPSNTs on DMO conversion to ethanol (EtOH), Yue et al. [97] impregnated Cu nanoparticles in the inner space of CuPSNTs (Cu/CuPSNTs-in), and a higher thermal stability and activity were found than those made by anchoring Cu on the outer surface (Cu/CuPSNTs-out) did. The Cu particles of the reduced Cu/CuPSNTs-in were twice less than those of the reduced Cu/CuPSNTs-out. Moreover, the concentration of Cu$^+$ was much greater of Cu/CuPSNTs-in (90% of the overall Cu content) than that of
Cu/CuPSNTs-out. The curvature effect-induced Cu-support interaction of CuPSNTs-in was proposed [70,73,106].

An excellent thermal stability of CuPSNTs after a 24-h thermal treatment at 350 °C was reported [107]. The space time yield (STY) of CuPSNTs in dimethyl 1,4-cyclohexanedicarboxylate (DMCD) conversion to 1,4-cyclohexane dimethanol (CHDM) was unaltered while that of CuPS-cats prepared by the AE method showed a 7.4% decreasing rate. Cu sintering seemed to be hindered by CuPSNTs with ignorable changes of Cu particle size before and after reaction. The great activity and stability were attributed to the strong Cu-O-Si bond and the confinement effect. Xu et al. [113] claimed that the high percentage of Cu$^+$ in CuPSNTs was related to the enriched Cu-O-SiO$_x$ interface, which is highly active in DMO hydrogenation. To demonstrate the metal-support interaction and the confinement effect, a thin layer of mesoporous silica was coated on CuPSNTs (CuPSNTs@m-SiO$_2$) (Figure 13). The ratio of Cu$^+$/Cu$^0$ in CuPSNTs@m-SiO$_2$ dramatically increased, which was approximately 2-fold higher than those of CuPSNTs and CuPS-cats.

![Figure 13. Scheme of CuPSNTs coated mesoporous silica (reproduced from [113] with permission from Springer Nature).](image)

The relationship between morphologies of CuPS-cats (laminar, nanotubes, and nanotube-assembled hollow spheres (NAHS)) and their activities of DMO hydrogenation was investigated [156,170]. The laminar-, nanotubes- and NAHS-type have similar surface areas, Cu$^+$–Cu$^0$ ratios, and distributions of active sites. However, the NAHS showed the highest turnover frequency in DMO hydrogenation to EG and a high yield of EG (95%) and stability (>300 h) at a H$_2$–DMO molar ratio as low as 20 while using NTs and laminar CuPS needed to be operated at the H$_2$–DMO ratios greater than 50 to obtain the equivalent amount of EG. Noting that the H$_2$–DMO molar ratio of the feed is usually at 80 to 200 (Table 1). They demonstrated that hydrogen can be preferentially adsorbed on the concave surface of nanotubes and hollow spheres, resulting in the high TOF for the NAHS. The design of NAHS opens a new window of low hydrogen consumption in DMO hydrogenation.

### 2.6. Reduction in CuPS-Cats

To transform CuPS precursors into CuPS-cats, a designed temperature-programmed reduction in H$_2$ atmosphere (H$_2$-TPR) is needed. The H$_2$-TPR profiles of CuPS-cats show a main reduction peak at around 240–250 °C [70,73,96,111,119,171] and the reduction peak ends at around 300 °C. The reduction peak may vary depending on the crystallinity of CuPS, calcination treatment, and interaction with supports or with promoters. From the H$_2$-TPR profiles, different reduction temperatures were selected depending on reduction degrees. Mostly, CuPS-cats are reduced at 300 or 350 °C to completely deconstruct Cu octahedral, to yield Cu$^+$ and Cu$^0$ species for catalysis applications. In some cases, lower reduction temperatures such as 200 [105], 220 [78], 250 [87,172], 260 [157], 270 [104,106], and 280 °C [84] were also selected for lower reduction degrees. The reduction temperatures and time are listed in Table 1.
Table 1. The CuPS-cats and their catalytic performance for hydrogenation reactions.

| Reactions          | Reaction Conditions | Performance | Catalysts (prep. Method) | Activation b | Activity                  | Ref.       |
|--------------------|---------------------|-------------|--------------------------|--------------|---------------------------|-----------|
|                    | T (°C)       | P H₂ (MPa) | H₂/Reactant | (L/W/G) HSV (h⁻¹) | Conv. (%) | Sel. (%) | TOS (h) | T calc. (°C) | T red. (°C) | XCu⁺ |       |               |
| DMO to EG          | 200       | 2.5        | 50         | (L) 0.25                         | 100         | 98       | -       | 450          | 4            | 0.55  | Cu⁺       | Chen 2008 [73] |
|                    | 200       | 2.5        | 50         | (L) 1.2                          | 100         | 95       | -       | -            | 4            | 0.14  | Cu⁰       | Yin 2011 [75]  |
|                    | 180       | 3.0        | 80         | (L) 0.5                          | 100         | 95       | -       | 450          | 250          | 0.40  | Cu⁰ and Cu⁺ | Sun 2018 [87] |
|                    | 200       | 2.0        | 80         | (L) 1.0                          | 100         | 95       | -       | 450          | 220          | 0.62  | Cu⁰ and Cu⁺ | Zhang 2012 [78]|
|                    | 190       | 2.5        | 80         | (L) 3.25                         | 100         | 91       | -       | 400          | 350          | 0.52  | Cu⁰ and Cu⁺ | Zhao 2017 [81]|
|                    | 210       | 2.0        | 80         | (W) 0.8                          | 100         | 86       | -200    | 400          | 300          | 0.60  | Cu dispersion | Popa 2015 [79]|
|                    | 180       | 2.5        | 80         | (L) 0.3                          | 100         | 98       | 250     | 400          | 350          | 0.53  | Formation of more CuPS | Zhao 2017 [82]|
|                    | 200       | 2.5        | 80         | (L) 3.5                          | 100         | 95       | 200     | 200          | 4            | 0.66  | Increase in specific surface area | Wang 2020 [88]|
|                    | 190       | 3.0        | 80         | (W) 2.0                          | 100         | 95       | 300     | 350          | 350          | 0.66  | Ti-Cu interaction | Lin 2012 [76]|
|                    | 200       | 3.0        | 100        | (L) 0.6                          | 100         | 90       | 70      | 450          | 300          | 0.66  | Cu dispersion | Wen 2013 [162]|
|                    | 190       | 2.0        | 50         | (W) 1.0                          | 99.8        | 97       | 200     | 450          | 350          | 0.84  | Cu dispersion | Ye 2017 [83]  |
|                    | 190       | 3.0        | 80         | (W) 3.5                          | 99.7        | 93       | 300     | 350          | 350          | 0.64  | B-Cu interaction | He 2011 [95]  |
|                    | 190       | 3.0        | 80         | (L) 0.6                          | 100         | 86       | 150     | 350          | 350          | 0.53  | Ag-Cu alloys | Huang 2013 [159]|
|                    | 215       | 3.0        | 100        | (L) 0.5                          | 100         | 97       | 2000    | 400          | 260          | -     | Cu dispersion | Zhu 2016 [157]|
|                    | 200       | 2.5        | 90         | (L) 1.0                          | 100         | 96       | 180     | 450          | 300          | 0.49  | Sn-Cu interaction | Zhang 2017 [110]|
|                    | 200       | 3.0        | 80         | (L) 0.4                          | 99.5        | 92       | -       | 450          | 300          | 0.53  | Cu dispersion | Qi 2018 [86]  |
|                    | 190       | 2.5        | 95         | (W) 1.0                          | >95         | >70      | 100     | 400          | 350          | -     | In-Cu alloys | Yu 2019 [90]  |
|                    | 200       | 3.0        | 80         | (L) 4.2                          | 100         | 98       | -       | CuPSNTs (AH) | -            | 0.39  | Xu 2018 [113] |
Table 1. Cont.

| Reactions    | Reaction Conditions | Performance | Catalysts (prep. Method) | Activation a | Activity                  | Ref.               |
|--------------|---------------------|-------------|--------------------------|--------------|---------------------------|--------------------|
|              | T (°C) P H₂ (MPa) H₂/Reactant (L/W/G) HSV (h⁻¹) | Conv. (%) Sel. (%) |                         | T_{calc.} (°C) Time (h) | T_{red.} (°C) Time (h) | X_{Cu⁺} c          |
|              |                     | TOS (h)     |                          |               |                           |                    |
| DMO to MG    | 220 2.5 200 (W) 0.3 | 86 94       | -                        | 400 4        | 280 4                    | 0.54 Cu⁺ and Cu⁺  | Abbas 2018 [84]    |
| DMO to EtOH  | 280 2.5 200 (G) 6500 | -96 -88     | <5                       | 450 5        | 300 5                    | -                  | He 2010 [94]       |
|              | 200 2.0 440 (L) 1.8 | 97 30       | -                        | 450 4        | 300 4                    | 0.33 Cu⁺ and Cu⁺  | Ding 2016 [102]    |
| DEM to PDO   | 200 2.0 440 (L) 1.8 | 91 32       | 100                      | 450 4        | 300 4                    | 0.45 Dispersion of | Ding 2016 [102]    |

Note: a) Activation conditions; b) Activity conditions.
| Reactions         | Reaction Conditions    | Performance | Catalysts (prep. Method) | Activation $^b$ | Activity                                                                 | Ref. |
|-------------------|------------------------|-------------|--------------------------|-----------------|---------------------------------------------------------------------------|------|
|                   | T ($^\circ$C) | P H$_2$ (MPa) | H$_2$/Reactant | (L/W/G) | HSV (h$^{-1}$) | Conv. (%) | Sel. (%) | TOS (h) | $T_{\text{calc.}}$ ($^\circ$C) | $T_{\text{red.}}$ ($^\circ$C) | Time (h) | $X_{\text{Cu}^+}$ | |
| MA to EtOH        | 220       | 1.0         | 40 (W)    | 1.0   | 81       | 51       | -         | -         | 20Cu/SiO$_2$ (AE) | 450     | 4       | 350     | 3       | -       | Dong 2016 [158] |
|                   | 340       | 3.0         | 10 (L)    | 2.0   | -80      | -95      | 50        | -         | Cu/9MgO-SiO$_2$ (AE) | 450     | 3       | 350     | 4       | 0.64    | Qin 2015 [163] |
|                   | 250       | 3.0         | 15 (L)    | 2.0   | -97      | -96      | 100       | -         | Cu/30%CeO$_2$-SiO$_2$ (AE) | 450     | 4       | 350     | 4       | 0.42    | Ye 2016 [164]  |
|                   | 250       | 3.0         | 15 (L)    | 2.0   | 98       | 98       | 100       | -         | 1%In$_2$O$_3$-30%Cu/SiO$_2$ (AE) | 450     | 4       | 350     | 4       | 0.57    | Zhang 2018 [115] |
|                   | 220       | 2.0         | 20 (L)    | 2.0   | 92       | 89       | -         | -         | 1Zn-9Cu/SiO$_2$ (AC) | 400     | 4       | 300     | -       | 0.41    | Zhao 2018 [116] |
| EA to EtOH        | 250       | 3.0         | 29 (L)    | 1.24  | 100      | 99       | -         | -         | Zn, NH$_4$ modified Cu/SiO$_2$ (CP) | 450     | 4       | 300     | 1       | 0.95    | Di 2016 [80]   |
| DMCD to CHDM      | 220       | 5           | 260 (L)   | 1.0   | -99      | -95      | 1000      | -         | CuPSNTs | 450     | 4       | 350     | 4       | 0.65    | Gong 2017 [107] |
| DMM to THF        | 240       | 5           | 60 (L)    | 0.9   | 84       | 100      | -         | -         | Cu/SiO$_2$ (AE) | 450     | 4       | 300     | 4       | 0.61    | Han 2015 [99]  |
| EC to EG          | 200       | 5           | -         | (Batch reactor) | 100 | 95       | -         | -         | 10Cu/SBA-15 (AE) | 400     | 4       | 200     | 4       | 0.65    | Li 2016 [105] |
|                   | 180       | 5           | -         | (Batch reactor) | 100 | 98       | -         | -         | 10Cu/SiO$_2$ (AE) | 400     | 4       | 350     | 4       | 0.51    | Li 2017 [108] |
Table 1. Cont.

| Reactions       | Reaction Conditions | Performance | Catalysts (prep. Method) | Activation b | Activity | Ref.       |
|-----------------|---------------------|-------------|--------------------------|--------------|----------|------------|
|                 | T (°C)              | P H₂ (MPa)  | H₂/Reactant (L/W/G)      | HSV (h⁻¹)   | Conv. (%) | Sel. (%)   | TOS (h)   | Tcalc. (°C) | Time (h) | Tred. (°C) | Time (h) | X_{Cu⁺} c |           |
| AA to HDOL      | 240                 | 6           | -                        | (Batch reactor) | 100       | 97         | -         | 20Cu/SiO₂ (AEH) | 400       | 350       | 3         | 0.19      | Cu⁺ and Cu⁺ | Jiang 2018 [111] |
|                 | 240                 | 6           | -                        | (Batch reactor) | 100       | 95         | -         | 5Ni-36Cu/SiO₂ (AEH) | 400       | 350       | 3         | -         | Ni-Cu interaction | Tu 2019 [119] |
| LA to GVL       | 130                 | 12          | -                        | (Batch reactor) | 95.7      | 85.2       | -         | OTS-grafted Cu/SiO₂ (AEH) | 400       | 350       | 3         | -         | Cu⁺ and Cu⁺ | Tsou 2020 [173] |
| FFAL to FFOH    | 140                 | 0.1         | 17                       | (W) 2.0      | 95        | 88         | -         | 24Cu/SiO₂ (AEH) | 450       | 270       | -         | -         | Phyllosilicates formation | Dong 2016 [104] |
|                 | 140                 | 0.1         | 17                       | (W) 7.0      | 39        | 99.5       | -         | 24Cu/SiO₂ (AEH) | 450       | 270       | 16        | -         | Cu⁺/Si ratio at 0.75 for Phyllosilicates formation | Dong 2017 [106] |
| HMF to DHMF     | 80                  | 5           | -                        | (Batch reactor) | 80        | 100        | -         | 15Cu/SiO₂ (UH)  | 450       | 250       | 2         | -         | SiO₂-Cu interaction | Zhu 2017 [172] |
| CO₂ to MeOH     | 320                 | 3           | 4                        | (W) 16       | -28       | -21        | 120       | 11Cu/SiO₂ (AE) | 500       | 300       | 2         | 1         | Cu⁺       | Wang 2015, 2016 [70,71] |

a Catalysts and preparation methods. The prefix represents the weight loading of copper and the characters between parenthesis represents the preparation method. For example: 20CuPS-cats (AE) means the copper phyllosilicate-derived catalysts with 20 wt % of Cu dispersing on SiO₂ was prepared by ammonia evaporation method. b Activation treatment includes calcination and reduction at different temperatures and time (Tcalc: calcination temperature, Tred: reduction temperature). c After activation, the active sites are supposed to the ratio of Cu⁺ and Cu⁰. The ratio of Cu⁺ over total surface area of copper was calculated from XAES data by the following formula X_{Cu⁺} = Cu⁺/(Cu⁰ + Cu⁺).
The exsolution of Cu particles from CuPS-cats was disclosed by van den Berg et al. [174] by using in situ TEM. In this study, kinetic models such as nucleation-and-growth, diffusion- and reaction-limited autocatalytic reduction were established to describe the formation and growth of Cu particles. In accordance with the TPR results, the TEM images observed Cu particles at 250 °C (see Figure 14C). To ensure the TEM images reflect for the whole sample, different regions of a sample were picked up to monitor the particle growth (Figure 14E). Time-resolved TEM images indicated the mechanism of the autocatalytic reduction is controlled by the diffusion of mobile copper species and the Cu particles size has a strong correlation with the time of isothermal treatment (Figure 14E).

![Figure 14](image-url)

**Figure 14.** The in situ mannered reduction in CuPS-cats under hydrogen atmosphere monitored by TEM at different temperatures (A–D) and isothermal (E) with 3 subregions. (Reprinted with permission from [174]. Copyright (2016) American Chemical Society).

The influences by using different reducing agents on derived Cu species were investigated by our group using in situ XANES analysis in H\(_2\) and CO environments. Composition of Cu\(^{2+}\) (in CuPS), Cu\(^+\) and Cu\(^0\) of XANES spectra were analyzed by using the linear combination method (see Figure 15). The results showed that the evolution of Cu\(^+\) and Cu\(^0\) species in hydrogen and CO environments are different. H\(_2\) is a stronger reducing agent than that of CO, facilitating Cu\(^{2+}\) reduction to Cu\(^0\) and yielding a limited amount of Cu\(^+\) in the whole temperature range. In contrast, using CO as the reducing agent produced a
higher composition of Cu\(^+\) even at temperature higher than 400 °C. This indicated that CO is a more suitable reducing agent than H\(_2\) to control Cu\(^0\) and Cu\(^+\) distribution of CuPS-cats.

![Graphs showing X-ray adsorption spectra and temperature programed reduction](image)

**Figure 15.** The non-isothermal reduction (X-ray adsorption spectra and temperature programed reduction) of CuPS-cats under H\(_2\) ([upper]) and CO ([lower]) as reductive agents (our group’s results).

### 3. Hydrogenation Activity of CuPS-Cats

CuPS-cats are widely used in the synthesis of alcohol from carbonyl groups hydrogenation. In this review, hydrogenation of esters, carbonates, carboxylic acids, aldehydes, and carbon dioxide are included (Figure 16).

![Diagram showing alcohol production](image)

**Figure 16.** Scheme of alcohol production from the hydrogenation of carboxylate, carbonate, carboxylic, aldehyde, and CO\(_2\) by using CuPS-cats.
3.1. Esters to Alcohols

3.1.1. Hydrogenation of DMO and DEO

CuPS-cats exhibited an extremely high activity for the hydrogenolysis of DMO and diethyl oxalate (DEO) because many studies claimed that both Cu$^0$ and Cu$^+$ mediate the reduction in carbonyl group [116]: Cu$^+$ polarizes the carbonyl, facilitating the subsequent hydride insertion of dissociated hydrogen on Cu$^0$ [78,84,87,92,94,96]. Conversion of DMO and DEO were operated at approximately 200 °C and H$_2$ pressure of 2 to 3 MPa by using CuPS-cats. The distribution of products derived from DMO and DEO hydrogenation, i.e., methyl glycolate (MG), EG, or EtOH (Figure 17), can be controlled by varying synthesis approaches, adding promoter, and varying morphologies of CuPS-cat. EG is the most favorable product because of its essential application as an antifreeze and a coolant [175].

![Figure 17. Reaction pathway of hydrogenation of DMO and DEO to MG, EG, and EtOH (adapted from [73,97,159] and [91,92]).](image)

- EG as the hydrogenated product

Different synthesis methods, such as AE, AC, and sol-gel, were used in CuPS-cats preparation for EG production (EG yields > 90%). Ding and co-workers [92] reported EG production from DEO catalyzed by CuPS-cats prepared by using deposition precipitation method using ammonium carbonate (CuPS-cats-AC) and ammonia evaporation method (CuPS-cats-AE). Although the CuPS-cats-AE and CuPS-cats-AC have the same conversion of DEO (>95%), the EG selectivity of the CuPS-cats-AE is always 5–10% less than that of the CuPS-cats-AC did [92]. Furthermore, the CuPS-cats-AC showed a higher thermal stability than that of CuPS-cats-AE [79]. The durability tests of CuPS-cats-AC lasted for more than 200 h. The higher activity and stability were correlated to the formation of Cu$_2$O, which is more stable than Cu$^+$ of CuPS-cats-AE. The CuPS-cats prepared by sol-gel method also exhibited a relatively high DEO conversion and EG selectivity (96 and 88%, respectively) [94].

A proper Cu$^+$–Cu$^0$ ratio to maximize the EG yield is a popular hypothesis of CuPS-cats in DMO hydrogenation [78,87]. Sun et al. [87] discovered a strong dependence of DMO hydrogenation performance and the Cu$^+$–Cu$^0$ ratio by controlling the reduction temperature of CuPS-cats. At a reduction temperature of 250 °C, the Cu$^+$–(Cu$^+$ + Cu$^0$) ratio was 0.4, implying the amounts of Cu$^+$ and Cu$^0$ were similar. The CuPS-cats reduced at 250 °C showed the highest hydrogenation activity of DMO to EG with a complete conversion and 95.2% selectivity at 180 °C with a 16 h durability. The selectivity of EG from DMO hydrogenation can be tailored by controlled reduction temperatures. However, the effect of reduction temperature on the physicochemical properties of CuPS is unclear. It is likely that different reduction treatments of CuPS can create various degrees of Cu–Si interaction.
Besides, the use of high surface area of silica such as mesoporous silica [82], nanosphere-shaped silica [88], or foam framework of zeolite [76] demonstrated a significant improvement of catalytic performance of CuPS-cats. The high surface area of silica possesses a large amount of surface hydroxyl groups which were supposed to increase the crystallinity of CuPS and surface Cu dispersion. The relationship between surface hydroxyl groups, CuPS phase, and Cu\(^+\) surface area were indicated in Section 2.3.1. Silica Support. The higher dispersion, the better catalytic performance because more active sites are produced. A 98% yield of EG was obtained for 250 h reaction at 180 °C when a mesoporous silica was applied to produce the highest surface areas of Cu\(^0\) (36.9 m\(^2\)/g) and Cu\(^+\) (41.6 m\(^2\)/g) [82].

The reactivity of CuPS-cats for the hydrogenation of DMO to EG was investigated by doping boron [95], silver [159], nickel [157], tin [110], zinc [86], or indium [90]. Adding other metals into CuPS-cats was able to improve the activity and stability of the CuPS-cats due to electron donating or accepting between Cu and the additional dopant or formation of Cu-dopant alloy.

Another factor that needs to be combated with is the need of excess hydrogen in DMO hydrogenation. Normally, the molar ratio of H\(_2\)–DMO in the feed is greater than 50. Yao et al. [156] proposed a novel design—CuPS-cats based nanotube-assembled hollow spheres, which enrich hydrogen concentration inside the spheres so that the molar ratio of H\(_2\)–DMO of the feed could be reduced to 20 with similar performances as those of conventional CuPS-cats. An improved EG productivity was conducted by Yue et al. [77] when cylindrical cordierite monoliths with micro-tunnels were dip-coated by CuPS-cats. The operating LHSV of their system can be as high as 16 h\(^{-1}\), more than 5 times higher than those used in other studies (2–3 h\(^{-1}\)). That is, the space time yield of EG can be substantially magnified.

- **MG as the hydrogenated product**

Sometimes, MG is a desired product of DMO hydrogenation. Partial inhibition of DMO hydrogenation to produce high yield of MG using CuPS-cats was proposed [84,89]. Since Cu\(^0\) is supposed to be hydrogenation-active, suppressing Cu\(^0\) concentration should improve the selectivity of MG. Thus, sodium silicate was impregnated into CuPS-cats powder prepared by AE method, intentionally to increase the formation of Si-O-Cu bonds, to limit surface concentration of Cu\(^0\) [89]. As expected, the reducibility of Cu cations was decreased with additional sodium silicate. Coherently, the surface area of Cu\(^0\) decreased along with the increase in Cu\(^+\) surface area (the ratio of Cu\(^0\)–Cu\(^+\) = 0.50–0.54). The selectivity of MG increased from 0.8 to, approximately, 100% at 84% of DMO conversion by doping 0.5 wt % of sodium silicate. This highlighted the strong correlation between DMO-derived products and surface Cu species.

- **EtOH as the hydrogenated product**

In general, the high Cu surface area (Cu\(^+\) and Cu\(^0\) active sites) and the high dispersion of Cu are the two key factors to increase the yield of EtOH. By introducing Ce to CuPS-cats, the dispersion and electron density of copper could be enhanced [85]. The 1Ce-Cu/SiO\(_2\) [85] can produce 92% of EtOH within 200 h constantly, the highest yield and stability compared to other works [96,97]. Besides, a large amount of H\(_2\) (H\(_2\)/DMO = 200) and higher reaction temperature (280 °C) are required (Table 1) to further hydrogenate EG to EtOH. Hydrogen concentration could be enhanced from the feed-in stream or from an increase in local partial pressure. In the case of CuPSNTs, due to the confinement effect of CuPSNTs, hydrogen pressure inside the tubes is higher than that outside [156]. Moreover, longer contacting time of reactants and catalytic sites inside the tubes allows the deep hydrogenation goes further to EtOH [97]. However, too long a reaction time may decrease the EtOH selectivity and increase by-products such as PDO and 1,2-butanediol [97].

### 3.1.2. DEM to PDO

The reactivity of CuPS-cats for DEM hydrogenolysis to PDO was investigated [102,103]. Because PDO is an intermediate product between 3-hydroxyl ethyl propionate and n-propanol (see Figure 18), the catalytic activity of CuPS-cats should be tuned to moderate
in order to increase the productivity of PDO. For example, the PDO productivity of the CuPS-cats can be controlled by calcination temperature. Calcination temperature at 450 °C was found to be the most appropriate to achieve the highest Cu dispersion of CuPS-cat, which showed the highest selectivity of PDO at around 30%, and over 90% of DEM converted for a duration time of 100 h [102]. Increasing calcination temperature of CuPS will lead to deep hydrogenation of DEM to n-propanol due to the increase in Cu crystallite size.

![Figure 18. Reaction pathway of hydrogenolysis of DEM to 3-hydroxy ethyl propionate, PDO, and n-propanol (adapted from [103]).](image)

Another way to improve PDO yield is using promoters to tune the rate of Cu\(^{+}\) and Cu\(^{0}\). Depending on the electron interaction between Cu and the additional elements, Cu\(^{+}\) or Cu\(^{0}\) will be promoted (see effect of promoters in Section 2.4). Taking B, Ag, Zn, Al, Ni, or Mo as examples, productivity of hydrogenation of DEM can be manipulated by doping these elements into CuPS-cats [103]. Incorporating Zn, Al, and Mo into CuPS-cats enhanced the selectivity of 3-hydroxyl ethyl propionate. Meanwhile, doping Ag and Ni into CuPS-cats enhanced deep hydrogenation to n-propanol. Introducing B was found to be favorable for PDO production because of the enriched Cu\(^{0}\) surface (mole fraction of Cu\(^{0}\) = 0.67). A close to balance ratio of Cu\(^{0}\) and Cu\(^{+}\) is good enough for production of an intermediate product like PDO.

### 3.1.3. Methyl Acetate (MA), Ethyl Acetate (EA) to EtOH

CuPS-cats prepared by the AE method exhibited a higher hydrogenation activity for MA conversion than those prepared by ion exchange and deposition precipitation due to the high dispersion of Cu [158]. Nevertheless, EtOH accounted for half of the yield of total products. Additional dopant can tune the product distribution.

The support effect on EtOH yield was investigated [163,164]. The Cu supported on MgO-SiO\(_2\) system (30 wt % of Cu and MgO–SiO\(_2\) mass ratio of 9) showed extremely high selectivity of EtOH (80.3% conversion and 99% selectivity) due to a strong interaction between MgO and Cu, which retarded the reduction in Cu\(^{+}\) to Cu\(^{0}\) and improved the surface area of Cu\(^{+}\) (about 65% of Cu\(^{+}\)–(Cu\(^{+}\)+Cu\(^{0}\)) fraction) [163]. Ye et al. [164] indicated that adding 30 wt % of cerium to CuPS-cats enhanced interaction of Cu and support, improved copper dispersion and enriched Cu\(^{+}\) concentration. More than 90% yield of EtOH was obtained with a full conversion during the 100-h test. Moreover, Cu\(^{+}\) was stabilized in the Cu/30%CeO\(_2\)–SiO\(_2\) after the reaction (Cu\(^{+}\)–Cu\(^{0}\) ratio was 0.72 and 0.65 before and after the reaction).

Besides, indium and zinc exhibited as an effective promoter for CuPS-cats in conversion of MA to EtOH reaction. About 98% of MA was converted steadily over the course of 100 h reaction by 1% In\(_2\)O\(_3\) addition [115] while 92% of conversion and approximately 90% of selectivity can be obtained when adding Zn into CuPS-cats (Zn–Cu ratio = 1:9) [116]. However, if silica was substituted by alumina, the synergy of Cu and Zn will vanish.

Instead of MA, ethyl acetate (EA) was also a reactant for EtOH synthesis. Incorporating ammonium and zinc ions during the CP method to transform 2:1 CuPS to 1:1 CuPS can greatly enhanced the reactivity of the catalyst [80]. Most of EA was converted to EtOH, and space-time yield of 1.23 g EtOH/(g\(_{\text{cat}}\)h) were achieved using the CuPS-cats prepared by Zn-NH\(_4\)–CP method.
3.1.4. DMCD to CHDM

By using CuPSNTs, an excellent stability for more than 1000 h was found with unaltered space time yield of CHDM in DMCD hydrogenation (Figure 19) [107]. In contrast, CuPS-cat synthesized by using the AE method showed a 7.4% decreasing rate. The cooperative influence caused by the strong Cu-O-Si bonding and the confinement effect was thereby proposed.

Figure 19. Scheme of CHDM synthesis from DMCD (adapted from [107]).

3.1.5. Dimethyl Maleate (DMM) to Tetrahydrofuran (THF)

For the selective hydrogenation of DMM to THF (Figure 20), Han et al. [99] consolidated the synergic role of Cu\(^{+}\) and Cu\(^{0}\). The CuPS-cat prepared by AE method with both Cu\(^{+}\) and Cu\(^{0}\) exhibited an 8-fold yield of THF than that prepared by wet impregnation made counterpart containing mostly Cu\(^{0}\). Although Cu\(^{0}\) species could promote the hydrogenation of DMM with 100% of THF selectivity, conversion of DMM was trivial (approximately 10%). Cu\(^{+}\) was considered as an oxophilic, Lewis acidic site for the adsorption of carboxyl group of DMM.

Figure 20. Scheme of THF synthesis from DMM (reproduced from [99] with permission from Elsevier).

3.2. EC to MeOH and EG

Hydrogenation of EC is a potential way to synthesize MeOH because of its thermodynamic favorability [105]. Moreover, not only MeOH but also EG could be synthesized concurrently (Figure 21).

Figure 21. EC hydrogenolysis reaction to EG and MeOH (adapted from [105]).

Li et al. [108] investigated different weight loadings of Cu (2–30%) in CuPS-cats for the hydrogenation of EC. They found that the conversion of EC was proportional to the increase in Cu content and the surface area of Cu\(^{0}\), while maximized selectivities of MeOH and EG were obtained by using 10 wt % of Cu. An optimal Cu\(^{+}\)–(Cu\(^{0}\) + Cu\(^{+}\)) ratio was proposed at 0.51.
In another study of Li and coworkers [105], the dispersion of Cu on different types of mesoporous silica such as SBA-15, KIT-6, and MCM-41 were investigated. By using the same weight loading of Cu (10 wt %), they found that the dispersion of Cu on SBA-15 (26.2%), was much higher than those on KIT-6 (8.2%) and MCM-41 (6.8%). Although the ratio of Cu$^+$(Cu$^{0}$ + Cu$^+$) in the SBA-15 supported CuPS-cats was far away from the optimal ratio (0.51), the higher surface area of Cu (170 m$^2$/g) likely played a more important role. After a 4 h reaction at 200 °C of temperature and 5 MPa of H$_2$ pressure, EC was completely converted to 94.7% of EG in yield.

3.3. Carboxylic Acid to Alcohol

CuPS-cats were firstly deployed in the hydrogenation of AA to HDOL by our group [111]. CuPS-cats showed better performances in the hydrogenation of dicarboxylic than that of an impregnation-made Cu/SiO$_2$ catalyst. Approximately 90% of HDOL yield together with an improved recyclability were achieved by using CuPS-cats. The follow-up work [119] demonstrated that the addition of nickel can stabilize Cu catalysts derived from hybrid phyllosilicates containing Cu and Ni in their octahedral units (Figure 22). The catalyst derived from Ni-doped CuPS is proposed to induce electron transfer from Cu cations to Ni cations due to a higher electronegativity of Ni than Cu, resulting in an improved activity and stability of hydrogenation. Introducing nickel seems to stabilize copper and to prevent copper leaching in acidic media. Furthermore, Ni-doped CuPS-cat showed an outstanding performance in hydrogenation of several carboxylic acids such as succinic (SUC), glutaric (GLU), hexanoic (HXA), pentanoic acid (PTA), and butyric acid (BTA) as well (Figure 23).

Figure 22. Illustration of conversion AA to HDOL via CuPS-cats and Ni-CuPS-cats (reproduced from [119] by permission of American Chemical Society).
Figure 23. Conversion (X%) of different acids and turnover frequency (TOF h\(^{-1}\)) of the Cu\(_{41}\)PS-cats and Cu\(_{36}\)Ni\(_5\)PS-cats (adapted from Table S2 of [119] by permission of American Chemical Society).

In another work of our group, CuPS-cats demonstrated an application in hydrogenation of levulinic acid (LA) to \(\gamma\)-valerolactone (GVL) [173]. A new strategy was applied to synthesize hydrophobic CuPS-cats: reduction−silylation−reduction. CuPS-cats grafted octyl triethoxysilane (OTS) on the surface showed a high LA conversion (95.7%) and GVL yield (85.2%) at a mild reaction condition (130 °C with a H\(_2\) pressure of 12 bar). The hydrophobic surface of OTS-grafted CuPS-cats was supposed to suppress Cu and Si leaching (Figure 24) and stability of OTS-grafted CuPS-cats, thus, was significantly improved (3 cycles with a 7.5% loss of initial activity). The reduction temperature may influence the activity of the catalyst. The optimal condition was to reduce at 350 °C then graft with OTS and repeat the reduction treatment again at 350 °C.

Figure 24. OTS-grafted CuPS-cats with a hydrophobic surface was protected from water incursion (reproduced from [173] by permission of American Chemical Society).

3.4. Aldehyde to Alcohol

Beside the hydrogenation of carboxylates and carboxylic acids, alcohol can be produced from the hydrogenation of aldehyde catalyzed by CuPS-cats. Taking FFAL [104,106] hydrogenation to FFOH for example, with proper catalyst design and operating condition, FFOH can be maximized as the desired product with limited extent of deep hydrogenation to 2-methylfuran (MF) [104,106] (Figure 25). In case of 5-hydroxymethylfurfural (HMF) [172] (Figure 25), the high conversion of HMF and 2,5-dihydroxymethylfuran (DHMF) yield can be obtained when UDP prepared CuPS-cats was applied.
3.5. CO₂ Hydrogenation to Methanol (MeOH)

Many catalysts have been developed for conversion of CO₂ into valuable chemicals such as CO [176,177], DME [178–183], CH₄ [184–186] or higher hydrocarbons [187], especially, MeOH [72,188–197]. Copper-based catalysts were highly prospective in MeOH synthesis [188–191,193,196–199]. Wang et al. [70,71] proposed a simple and high-performance catalyst derived from CuPS. They claimed that tuning calcination and reduction temperatures can enhance Cu⁺–(Cu⁰ + Cu⁺) ratio of the reduced CuPS-cats usher in an improved hydrogenation activity. They indicated that Cu⁺ is the active site for the CO₂ hydrogenation and the concentration of Cu⁺ can be maximized at 500 °C of calcination and at 300 °C of reduction (see figure). At Cu⁺–(Cu⁰ + Cu⁺) ratio close to 1, the CO₂ conversion and MeOH selectivity reached 25–28% and about 21%, respectively, at 320 °C, 3.0 MPa, weight hour space velocity (WHSV) = 16 L.g⁻¹.h⁻¹, and H₂:CO₂ feed ratio of 4:1.

4. Deactivation

4.1. Causes of Deactivation

Analogous to supported Cu catalysts, CuPS-cats suffered from deactivation caused by sintering of Cu particles, leaching of Cu and Si, and carbonaceous species deposition. These negative impacts hamper the industrial practice of CuPS-cat mainly because of the unacceptable deactivation rate and poor recyclability.

4.1.1. Copper Sintering

Although CuPS-cats had good thermal stability, Cu sintering is frequently reported [76,77,79,91,95,96,101,102,107,167]. About 50% of copper surface area loss during reduction at 350 °C for 4 h [79] or at calcination temperature higher than 450 °C [102], mainly caused by Cu agglomeration. Gong et al. [96] also found the growth of Cu and Cu₂O of post-reaction catalysts (Figure 26). In principle, sintering of Cu and Cu₂O sintering occurs at temperature higher than their Hüttig temperatures (T_Hüttig of Cu and Cu₂O are 137 and 179 °C, respectively) and lower than their Tamman temperatures (T_Tamman of Cu and Cu₂O are 405 and 481 °C, respectively) [77]. In this range of temperature, Cu atoms at edges and corners or defect positions become mobile. Driving force of the sintering was supposed to be caused by the Ostwald ripening [200]. Besides, the dynamic Cu state in the process of reaction was claimed to cause Cu sintering [95]. In DMO hydrogenation using CuPS-cat, He et al. [95] proposed that Cu⁰ was oxidized to Cu⁺ by DMO and Cu⁺ was reduced to Cu⁰ by H₂ concurrently. The transition of each state enhanced Cu mobility and weakened Cu-SiO₂ interaction, resulting in Cu agglomeration. The aggregation of Cu nanoparticles and the changes in distribution of surface Cu species were responsible for the deactivation of CuPS-cats [85,95,115,167].

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**Figure 25.** Reduction of FFAL to MF [104,106] and HMF to DHMF (adapted from [172]).
4.1.2. Leaching of Copper and SiO$_2$

In liquid medium, the deactivation caused not only by the sintering but also by the leaching. Wen et al. [201] and Popa et al. [79] indicated the dissolution of silica from the support evidenced by the formation of tetramethoxysilane (TMOS) in the resultant solution of DMO hydrogenation. ICP analysis indicated that more than 55% of Cu was leached out after three consecutive cycling runs of AA hydrogenation [111]. Deactivation of CuPS-cats was expected in hydrogenation of AA [119] and LA [175] accompanying the decline of Cu loading after each cycling run (Table 2).

Table 2. Residual and leached amount of Cu, Ni in Cu$_{41}$PS-cats and Cu$_{36}$Ni$_5$PS-cats after each round of activity test (reproduced from [119] with permission from American Chemical Society). The figures were determined by ICP-AES analysis.

|            | Cu$_{41}$PS-Red | Cu$_{36}$Ni$_5$PS-Red |
|------------|----------------|----------------------|
|            | Cu (wt%)       | Leached Cu (ppm)     | Leached Cu (ppm) | Ni (wt%) | Leached Ni (ppm) |
| Fresh      | 40.4           | 35.6                 | 3.9              |
| 1$^{st}$ cycle | 37.2  | 3.9                  | 33.1             | 3.1      | 3.8              |
| 2$^{nd}$ cycle | 34.8  | 3.5                  | 31.8             | 2.9      | 3.9              |
| 3$^{rd}$ cycle | 32.9  | 3.2                  | 31.1             | 2.9      | 3.8              |

ND = undetectable.

4.1.3. Coke Deposition

Coking is a continuous carbon deposition process accompanying the evolution of the extent of reaction. Carbonaceous deposition or coking may be induced by many different reactions on acidity catalysts. In case of CuPS-cats, Cu$^+$ incurred from the reduction in CuPS-cats was Lewis acidic, and can be a potential site of carbonization. Some studies indicated coke fouling on CuPS-cats in dry reforming of methane [136] and DME steam reforming [109]. Especially, a serious coking was reported after DEO hydrogenation reaction with approximately 20% of coke deposition on the used catalysts [92]. The decomposition of hydrocarbons into small active carbon species and accumulation of these carbonaceous species on the catalysts surface increases transfer limitations of reactants and products, and encapsulation of active sites by carbon causes CuPS-cats become less reactive. Fortunately, it is possible to rejuvenate catalyst activity by coke burning.

4.2. Remedial Actions

Sintering, Cu leaching, and coke deposition were responsible for CuPS-cats deactivation. Surpassing sintering and leaching are more complicated than coking because
accumulation of carbon can be removed and the catalytic performance of the used CuPS-cats can be regenerated when treated in a flow of 30 vol% O$_2$ at 500 °C for 30 min [202]. In order to inhibit the sintering of Cu, many strategies were proposed. Doping another metal such as Ag [159], La [167], Sn [110], Ce [85], or Zn [86] was supposed to stabilize the chemical state of Cu and alleviate Cu sintering. Binary oxides support such as SiO$_2$-TiO$_2$ [162], SiO$_2$-MgO [163], or SiO$_2$-CeO$_2$ [164] was developed to enhance the Cu-support interaction and to maintain Cu dispersion as its fresh state. Moreover, spatial confinement effect of mesoporous silica [91,113] and CuPSNTs [107] allowed hosted Cu to possess high thermal stability. Surface modification by dextrin [83] and by glucose [203] and silylation [204] were found to hurdle the growth of Cu particles as well.

Leaching of Cu and silica might be caused by polarity of solvents and reactants. By amending the polarity, leaching extent of Cu might be eased. Transforming hydrophilic to hydrophobic surface of alkaline-grafted CuPS-cats was supposed to protect the catalyst from acid and water attacks, and ease the amounts of leached Cu [175]. Moreover, the solvent effect in inhibition of dissolution of SiO$_2$ in DMO hydrogenation reaction was indicated [79,201]. When MeOH was substituted by EtOH as a solvent, the dissolution of SiO$_2$ was inhibited in DMO hydrogenation [79]. The dissolution of SiO$_2$ occurs sequentially by nucleophilic attack of methoxy or ethoxy, that are induced from hydrolysis of MeOH and EtOH, to form mono-, di-, tri-, and tetra-alkoxide silane. Although both methoxy and ethoxy are nucleophilic, stearic effect of ethyl group might hinder the attack of later ethoxy molecules while small molecules of MeOH are more accessible to silica surface. Therefore, to overcome the leaching of silica, EtOH is a more appropriate solvent than MeOH in DMO hydrogenation reaction.

5. Challenges and Prospective

The most challenges hindering CuPS-cats from practical application were the low stability and reusability. Despite high activity, Cu sinter and leaching during the reaction caused deactivation. Cu Sintering at high temperature limited application of CuPS-cats for reactions at moderate conditions. After reaction, CuPS-cats were deconstructed and cannot be regenerated. Our study indicated that CuPS-cats could not be regenerated after a reduction-oxidation cycle. So far, prolongation of the lifespan and stability of CuPS-cats has still challenged scientists.

Optimization of CuPS-cats from synthesis methods and promoters has been ploughed extensively. The next generation of CuPS-cats will mainly focus on the innovations of facile and environmentally friendly synthesis methods. For example, organic-inorganic hybrid [83] or surface modification [175,204]. Another possibility to improve CuPS-cat is the innovation of CuPS-cats with novel topologies such as CuPSNTs. Spatial confinement of CuPS-cat usually has a positive effect in hydrogenation reactions. Meanwhile, in-depth studies of CuPS-cats structure, reaction mechanisms, kinetics and their structure-activity correlation are limited. Only few studies were conducted, such as the observation of exsolution behavior of Cu species of CuPS by using TEM with an in situ manner under temperature-programmed reduction condition [173]. It seems the basic studies of Cu exsolution from the octahedral of CuPS is the key to clarify the unsolved questions of CuPS-cat catalysis. Advanced techniques, especially in situ methods used in Cu species characterization like TEM, XAS, and XAES, should be helpful.

Burgeoning research of CuPS-cats in the hydrogenation of other carbonyls such as carbonate [105,108,169,203,205], carboxylic acid [111,119,175], and aldehyde [104,106,160,172] have shown their potentials recently. Alternative applications of CuPS-cats, should be explored such steam reforming of DME [109,114,166], water-gas-shift reaction [206,207], dehydrogenation ethanol [98,202], dry reforming CH$_4$ [136], ethynylation of formaldehyde [117]. Moreover, process design for large scale, continuous processing by using CuPS-cat as the catalyst is needed.

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Abbreviations

AA Adipic acid
AC Ammonium carbonate deposition–precipitation method
AE Ammonia evaporation method
AEH Ammonia evaporation hydrothermal method
AH Ammonium chloride (NH₄Cl) assisted hydrothermal method
AM30 Sodium-stabilized silica
AS30 Ammonium-stabilized silica
CHDM 1,4-Cyclohexane dimethanol
CP Co-precipitation method
CuPS Copper phyllosilicate
CuPS-cats Copper phyllosilicate-derived catalysts
CuPSNTs Copper phyllosilicate nanotubes
DEM Diethyl malonate
DEO Diethyl oxalate
DHMF 2,5-dihydroxymethylfuran
DMCD Dimethyl 1,4-cyclohexanedicarboxylate
DMM Dimethyl maleate
DMO Dimethyl oxalate
EA Ethyl acetate
EC Ethylene carbonate
EG Ethylene glycol
EtOH Ethanol
FFAL Furfural
GVL γ-valerolactone
HDOL 1,6-Hexanediol
HMF 5-Hydroxymethylfurfural
IM Impregnation
IWI Incipient wetness impregnation
LA Levulinic acid
MA Methyl acetate
MeOH Methanol
MF 2-Methylfuran
MG Methyl glycolate
m-SiO₂ Mesoporous silica
OMS Ordered mesoporous silica
OTS Octyl triethoxysilane
PDO 1,3-propanediol
TEOS Tetraethyl orthosilicate or tetraethoxysilane
THF Tetrahydrofuran
UHDP Urea hydrolysis deposition-precipitation
UH Urea hydrolysis hydrothermal
USG Urea-assisted sol-gel
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