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Highly selective silica-supported copper catalysts derived from copper phyllosilicates in the hydrogenation of adipic acid to 1,6-hexanediol

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Abstract

Hydrogenation of adipic acid (AA) is a potential way to prepare 1,6-hexanediol (HDOL). Herein, silica-supported copper catalysts derived from copper phyllosilicates were synthesized, characterized, and tested in the hydrogenation of AA to HDOL. In a full conversion of AA, a high yield of HDOL (approximately 90%) was obtained through the use of each Cu-based catalyst. The turnover frequency calculated according to the consumption rate of AA was discovered to be dependent on the $Cu^+/(Cu^0+Cu^+)$ ratio and the reduction condition. Moreover, recycling tests showed that a catalyst derived from a copper phyllosilicate had better stability compared with Cu/SiO_2 made through impregnation due to a stronger interaction between Cu and silica. The kinetic analyses based on the global rate expression and Langmuir–Hinshelwood–Hougen–Watson (LHHW) formalism of AA conversion were conducted. The possible competitive adsorption between AA and its derivatives, including hydroxycaproic acid and ε -caprolactone, was thereby revealed.

Keywords: adipic acid; copper; 1,6-hexandiol; hydrogenation; phyllosilicate

Introduction

Adipic acid (AA) is an important chemical used in polymer synthesis and food manufacturing.^[1] The production of AA through oxidation of ketone-alcohol (KA) oil with nitric acid is industrialized^[1] and with gaseous oxygen is under development.^[2] Lately, the method for AA to derive from renewable feedstocks such as 5-hydroxymethylfurfural and lignin fragments has been explored.^[3] The productivity of AA grows steadily due to the blooming coal-based industry.^[4]

The increasing productivity and decreasing market price of AA carves a niche for AA as a raw material to synthesize high-value chemicals. 1,6-Hexanediol (HDOL), a versatile chemical being used in polyurethanes and coatings, can be synthesized from AA. The global market of HDOL is expected to grow from USD 727.8 million in 2016 to USD 1,042.1 million by 2021.^[5] The conventional way to prepare HDOL from AA is through a two-step process: esterification of AA and methanol for preparing dimethyl adipate (DMA) and selective hydrogenation of DMA for producing HDOL.^[6] However, energy-intensive operations such as separation of DMA and water^[7] and distillation of crude products for purifying HDOL are required,^[8] making the two-step process economically unattractive.

Hydrogenation of AA to HDOL has the potential to replace the integrated esterificationhydrogenation process. The major obstacle of hydrogenation of AA is the rigid (low electrophilicity) carbonyl carbon, which hinders the polarization of carbonyl groups.^[9] Bifunctional catalysts, i.e., combinations of noble metals (such as Ru,^[7, 10] Rh,^[6, 11] Pd,^[12] or Pt^{[6, ^{12-13]}) and oxophilic oxides (such as SnO_x ,^[7, 10a, 12] MoO_x ,^[6, 10b, 11, 13] WO_x ,^[6, 11a] or ReO_x ,^[6, 11a]) are commonly used. The intimacy between a metal and an oxide promoter weakens the strength of the C=O bond and facilitates hydride attack on the adsorbed carboxylate.^[9, 14] Toba et al.^[10a] synthesized RuSn/Al₂O₃ catalysts with different methods including sol-gel and impregnation. They claimed that the Ru-enriched surface is favorable to enhance the HDOL yield (ca. 71%) in AA hydrogenation. Takeda et al.^[15] reported that the presence of AA affected the degree of reduction of PdRe/SiO₂ and thus resulted in different hydrogenation activities in HDOL production.} Precious-metal-based catalysts have not yet been commercialized in the fatty alcohol industry.^[16] Costly prices, unsatisfying HDOL yields (mostly lower than $80\%^{[6-7, 10a]}$), and possible corrosion for stainless reactors^[17] could be the hurdles. Copper chromite catalysts have been widely deployed in the production of alcohols from hydrogenation of esters.^[16] Copper-based catalysts such as CuZn,^[18] CuMn,^[19] and CuFe^[20] have also been developed, and some of them displayed better performances than copper chromite did. Surprisingly, limited efforts have been dedicated to utilize Cu-based catalysts in hydrogenation of carboxylic acids to alcohols. Formation of copper soap and sintering of copper could be the challenges.^[16, 21] On the premise of enhanced stability, Cu-based catalysts should be promising in direct hydrogenation of AA to HDOL. The advantage of using Cu-based catalysts is that the Cu⁺-Cu⁰ pair site is highly selective in hydrogenation of the C=O bond.^[22] Cu⁺ acts as an electrophilic site to polarize the C=O bond while Cu⁰ dissociates H₂ to form adsorbed hydrides for the subsequent hydride insertion.

This study investigated silica-supported Cu catalysts derived from copper phyllosilicates (CuPSs) in the hydrogenation of AA to HDOL, and then compared the CuPSs-derived catalysts with Cu/SiO₂ synthesized by impregnation. In a full conversion of AA, each Cu-based catalyst had a high yield of HDOL at approximately 90%. However, the use of catalyst derived from CuPS displayed a better stability (reusability) than the use of Cu/SiO₂ made through impregnation. The strong interaction between Cu and silica formed by CuPSs not only improves catalyst stability, but also increases the surface $Cu^+/(Cu^0+Cu^+)$ ratio, which is likely to enhance hydrogenation activity. In addition, a plausible reaction network of AA hydrogenation was established and a kinetic analysis was conducted. To our knowledge, this is the first-time report on deploying CuPS-derived catalysts in hydrogenation of AA to HDOL, and this report could pave the way for hydrogenation of carboxylic acids to their respective alcohols.

Experimental

Materials

CuPSs were prepared by the ammonia evaporation hydrothermal method.^[22b, 23] Briefly, 25 wt% of ammonia aqueous solution and appropriate amount of Cu(NO₃)₂•3H₂O were mixed in 70 mL of deionized water under vigorous stirring. 2.5 gram of colloid silica (LUDOX® HS30, Aldrich) was then added into the mixture with controlled pH value in the range of 11 to 12 and stirred for 24 h. The yielded suspension was heated in a water batch at 80 °C to allow ammonia evaporation gradually. The yielded mixture was transferred into a hydrothermal bomb and treated at 150 °C for 24 h. The precipitates were filtered, washed with deionized water three times, dried at 120 °C for 4 h, and calcined at 400 °C in air (50 mL/min) for 4 h. The yielded CuPSs, corresponding to 10 wt%, 20 wt%, and 30 wt% of Cu loadings, were denoted as 10CuPS, 20CuPs, and 30CuPS, respectively. For comparison, 20 wt% Cu/SiO₂ (denoted as Cu/SiO₂) was prepared by incipient wetness method. Prior to the activity evaluation, each catalyst was reduced in a fix-bed system at 350 °C in an 80% H₂/N₂ stream for 3 h. After cooling to ambient temperature in a He stream (100 mL/min), the reduced sample was passivated in a 2% O₂/He stream for 4 h. The passivated catalysts were suffixed with "-red" in the following text.

Characterizations

The compositions of Cu and Si were quantified by the inductively coupled plasma-atomic emission spectrometry (ICP-AES, Kontron S-35). The crystallographic structures were verified by X-ray diffraction (XRD) patterns obtained by a Rigaku D/Max-IIB diffractometer using Cu K α radiation. The porosities were determined by the N₂ adsorption-desorption isotherms acquired using an automated N₂ physisorption analyzer (Micromeritics ASAP 2010 Plus). Surface morphology was observed by a high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2010). X-ray photoelectron spectra (XPS) of Cu 2p level were obtained by using a Kratos Axis Ultra DLD equipped with a focused monochromatic Al-K α X-ray (1486.7 eV) source. Binding energy shift was corrected by using the C 1s signal at 285.0 eV. Temperature-programmed reduction of H₂ (H₂-TPR) was performed on a chemisorption analyzer (Micromeritics, AutoChem II), and the signals were recorded by a thermal conductivity detector (TCD). The amount of hydrogen consumption was calibrated by using the H₂-TPR profile of Ag₂O at the same condition of tested catalysts. Detailed pretreatments and operating conditions were reported in earlier studies.^[24] The infrared (IR) spectra of CO-adsorbed samples were recorded by using a Thermo Scientific Nicolet iS50 spectrometer equipped with a transmission mode *in situ* quartz cell at 30 °C. The cell was connected to a vacuum system which can be operated with a residual pressure at approximately 2.5*10⁻³ Pa. Each sample was pelletized into a 15-mm diameter disk of 0.2 mm thickness, weighting approximately 40 mg. The absorbance spectrum was recorded by collecting 64 scans at 4 cm⁻¹ resolution using a mercuric cadmium telluride (MCT) detector. Detailed procedures of IR study of CO adsorption can be found in Appendix A of the Supporting Information.

Reactivity Evaluation

A batch-type reactor (Parr model 4561) was used to evaluate the catalytic performance. The mixture containing 0.2 g of AA, 60 mL of 1,4-dioxane, and 0.1 g of passivated catalyst with a particle size ranged from 0.125 mm to 0.180 mm (120 to 80 mesh sizes) was charged and then sealed in the reactor. Residual air inside the reactor was expelled by a N₂ stream (100 mL/min) for 10 min for three times, followed by purging with a H₂ stream (100 mL/min) for 10 min for three times. The reactor was then pressurized to 58 bar by H₂ and heated to 240 °C, yielding an autogenous pressure at approximately 90 bar. Once the system attends 240 °C, this point was set as the outset (t = 0) and the stirring system was started with an agitating rate of 500 rpm. After attending the proper reaction time, the reactor was immediately quenched in ice water. For the recycling test, each run was performed for 16 h. The recycled catalyst was washed with 1,4-dioxane three times, dried at 100 °C overnight, and subjected to the above-mentioned reduction and passivation treatment prior to the next recycling test. The quantification of the reactant and products was conducted by an external standard method by using a gas chromatograph (GC, Shimadzu 2010 Plus) with a 0.5 μ m x 60 m SH-Rtx-Wax capillary column. The definitions of conversion of AA and product yield are as below:

Conversion of AA (%) =
$$\frac{\text{Moles of AA consumed}}{\text{Moles of AA fed in}} \times 100\%$$
 (Eq. 1)

Yield of product
$$i$$
 (%) = $\frac{\text{Moles of product } i \text{ formed}}{\text{Moles of AA fed in}} \times 100\%$ (Eq. 2)

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To reveal the intrinsic activity of AA hydrogenation, the TOF was calculated as:

 $TOF = \frac{Moles of AA consumed}{(Time, h) \times (Moles of the sum of Cu⁰ and Cu⁺)}$ (Eq. 3)

Internal and external mass transfer limitations were evaluated by varying the catalyst article size (0.425 mm to 0.075 mm) and the agitating rate (400 rpm to 600 rpm), and both were found to be trivial (Figures S1 and S2). Kinetic parameters were estimated by the nonlinear regression using Athena Visual Studio^[25] based on the criterion of the least residual sum of the squares (RSS).

Results and discussion

Physicochemical Properties

Table 1 lists the Cu contents and the ratios of bulk Cu/Si ($(Cu/Si)^{bulk}$) of CuPSs and Cu/SiO₂ measured by ICP-AES. The actual Cu loading is close to its nominal value.

Table 1. Compositions and textural properties of tested samples

Sample	Cu (wt%)	(Cu/Si) ^{bulk}	$S_{BET}(m^2/g)$	$V_p (cm^3/g)$
10CuPS / 10CuPS-red	10.6	0.16	316 / 197	0.98 / 0.83
20CuPS / 20CuPS-red	20.5	0.36	348 / 309	1.03 / 0.84
30CuPS / 30CuPS-red	29.5	0.56	470 / 408	1.29 / 0.81
Cu/SiO ₂ / Cu/SiO ₂ -red	19.8	0.23	218 / 197	1.14 / 0.98

Figure 1 (a) shows the XRD patterns of CuPSs and reduced CuPSs. Cu/SiO₂ and Cu/SiO₂-red were included for reference. For Cu/SiO₂, diffraction peaks of CuO at 35.6° and 38.7° can be speculated. The CuO crystallite size of Cu/SiO₂ estimated with the Scherrer

equation was approximately 19.2 nm. For CuPSs, weak signals at 30.8° , 35.0° , 57.5° , and 62.4° , corresponding to the diffraction pattern of Cu₂Si₂O₅(OH)₂, were identified. All samples had a broad signal in the 20 range from 20° to 30°, suggesting the presence of amorphous SiO₂.

Figure 1 (b) displays the XRD patterns of the passivated samples. The peaks of metallic Cu at 43.2° , 50.4° , and 74.2° can be seen. The estimated Cu sizes were approximately 5.8 nm for 20CuPS-red, 6.9 nm for 30CuPS-red, and 17.2 nm for Cu/SiO₂-red. The crystallite size of Cu of 10CuPS-red could not be estimated due to the limitation of XRD technique in characterizing Cu particles smaller than 4 nm.^[26] The diffraction of the (1 1 1) plane of Cu₂O can be observed at 20 = 36.3° for each reduced CuPS. The estimated crystallite size of Cu₂O of 20CuPS-red was approximately 5.4 nm; 30CuPS-red, 5.6 nm. The signals of CuO were undetectable, implying little amounts of CuO and/or small CuO clusters were existed in the reduced catalysts.

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Figure 1. XRD patterns of as-synthesized copper phyllosilicates and their respective passivated Cu-based catalysts derived from reduction of copper phyllosilicates. Cu/SiO₂ and passivated Cu/SiO₂-red were included for references.

Table 1 lists the textural properties, and Figure 2 shows the N₂ adsorption–desorption isotherms and pore size distributions (PSD) calculated by the Barrett-Joyner-Halenda (BJH) equation using the desorption branches. CuPSs possessed relatively higher surface areas than Cu/SiO₂ did, and the surface areas of CuPSs displayed an ascending trend with an increase of Cu loading from 316 m²/g (10CuPS) to 470 m²/g (30CuPS). Measured pore volumes were similar, ranging from 0.98 cm³/g to 1.29 cm³/g.

Each sample displayed a type IV isotherm.^[27] The bimodal pore structure showed the mesopore diameter centered at 3.2 nm and 8.9 nm for 10CuPS; at 3.1 nm and 14.6 nm for 20CuPS; at 3.1 nm and 9.1 nm for 30CuPS. The smaller mesopores at approximately 3 nm were related to the narrow parallel plates of CuPS, while the larger mesopores could be attributed to the void space of agglomerated particles.^[28] Apparently, 10CuPS contains more large mesopores (approximately 96% of the mesoporosity) than 20CuPS (approximately 80%) and 30CuPS (approximately 65%) do.

The reduced samples displayed smaller surface areas and pore volumes compared with their calcined counterparts. A considerable loss of surface area (approximately 38%) was observed for 10CuPS-red compared with 10CuPS. 10CuPS-red also displayed a different type of hysteresis loop compared with 10CuPS; the difference was possibly due to the collapse of lamellar structures after the treatment of reduction. The PSD of Cu/SiO₂-red and 10CuPS-red displayed an average mesopore diameter of 35 nm and 25 nm, respectively. The average pore diameter of the smaller mesopores of 20CuPS-red and 30CuPs-red was approximately 2 nm, and the average pore sizes of the larger mesopores of these two catalysts were nearly unaltered. The decrease of the mean size of the smaller pores implied the shrinkage of interlayer distance; however, the lamellar structure could still hold. Similar porosities of 20CuPS and 30CuPS and the reduced forms of both CuPSs suggest that their phyllosilicate structures are more rigid than that of 10CuPS.





Figure 3 exhibits the TEM images and the histograms of Cu particle size distribution of reduced catalysts. The randomly oriented filamentous structure^[29] was observed for 20CuPS-red and 30CuPS-red. The dark, non-symmetrical Cu particles of Cu/SiO₂-red, 10CuPS-red, 20CuPS-red, and 30CuPS-red showed their average diameters of 8.3 nm, 3.3 nm, 4.0 nm, and 5.3 nm, respectively. The lattice spacing value of 0.2 nm, indexing the Cu (1 1 1) plane, evidences the presence of Cu particles. Figure S3 shows the patterns of energy dispersive spectroscopy (EDS) mapping of O, Si, and Cu of reduced catalysts. Homogeneously distributed O, Si, and Cu could be speculated. Among reduced CuPSs, well-dispersed Cu could be found on 10CuPS-red, whereas agglomerated Cu could be observed on 20CuPS-red and 30CuPS-red.

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Figure 3. TEM images and histograms of Cu particle size distribution of (a) Cu/SiO₂-red, (b) 10CuPS-red, (c) 20CuPS-red, and (d) 30CuPS-red.

The TEM images of CuPSs were also recorded (Figure S4); however, Cu particle could not be identified clearly. Formation of immobilized Cu during the reduction treatment of CuPSs (known as exsolution) is likely to cause the differences of resolutions of Cu particles between CuPSs and reduced CuPSs.^[30]

Figure 4 (a) exhibits the XPS spectra of Cu 2p level of calcined samples. The surface Cu/Si ratio ((Cu/Si)^{surf}) estimated by the intensity ratio of Cu 2p and Si 2p peaks showed an ascending order as follows: Cu/SiO₂ (0.02) < 10CuPS (0.15) < 20CuPS (0.40) < 30CuPS (0.49). The differences between (Cu/Si)^{surf} and (Cu/Si)^{bulk} of CuPSs were small, suggesting homogeneously dispersed Cu in phyllosilicate structures. In contrast, the value of (Cu/Si)^{surf} of Cu/SiO₂ is approximately ten times smaller than that of (Cu/Si)^{bulk}, indicating a low dispersion of Cu on the surface.^[31]

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Figure 4. Cu 2p XPS spectra of (a) Cu/SiO₂ and CuPSs and (b) reduced Cu/SiO₂ and CuPSs

The spectra of calcined samples showed the shakeup satellite peaks at approximately 943 eV together with the signals of Cu $2p_{2/3}$ core level in the range of 933 to 937 eV, indicating the presence of Cu^{2+.[32]} The peak of Cu $2p_{3/2}$ displayed an ascending order as follows: Cu/SiO₂

(933.1 eV) < 10CuPS (935.7 eV) < 20CuPS (936.0 eV) < 30CuPS (936.2 eV). The chemical shift of the Cu $2p_{3/2}$ level to higher binding energy implied a charge transfer from the metal ion toward the support oxide.^[33] That is, CuPSs, particularly 30CuPS, should have stronger Cu-SiO₂ interactions than that of Cu/SiO₂.^[22d]

Figure 4 (b) exhibited the XPS spectra of reduced catalysts. The binding energies of Cu^0 and Cu^+ are nearly identical, showing two peaks located at approximately 933 eV and 953 eV of Cu $2p_{2/3}$ and Cu $2p_{1/2}$ core levels.^[34] The absence of the satellite peak of Cu^{2+} suggests that the surface concentrations of Cu^{2+} of reduced catalysts should be negligible. The estimated $(Cu/Si)^{surf}$ ratios, listed in Table 2, displayed an ascending order as follows: Cu/SiO_2 -red (0.02) < 10CuPS-red (0.04) < 20CuPS-red (0.09) < 30CuPS-red (0.12). The (Cu/Si)^{surf} ratios of Cu/SiO_2 and Cu/SiO_2 -red were the same, implying the extents of sintering/agglomeration of Cu are trivial. Considerable decreases of (Cu/Si)^{surf} ratios were found for reduced CuPSs compared to those of CuPSs before reduction. The decreases of (Cu/Si)^{surf} ratios of reduced CuPSs indicated that exsolution of Cu from phyllosilicate structure could be promoted during reduction. Exsoluted Cu formed immobilized Cu particles on the surface,^[30] resulting in lower Cu-to-Si XPS intensity ratios of reduced CuPSs than those of CuPSs. The schematic diagram of the formation of exsoluted Cu particles through the reduction of CuPS was shown in Figure S5 of the Supporting Information.

Figure 5 displays the H₂-TPR profile of each calcined sample and the peak area is denoted as A1. The sample that went through the H₂-TPR was then exposed to N₂O to oxidize the surface of metallic Cu.^[35] The sample with the Cu-oxidized surface then went through the second H₂-TPR test, and the area of the resulting profile was denoted as A2. The H₂-TPR profile of calcined Cu/SiO₂ displayed three responses at 231 °C, 256 °C, and 300 °C. The multi-response of Cu/SiO₂ is due to different Cu particle sizes.^[36] In comparison, CuPSs had major responses at approximately 250 °C and shoulders in the range of 275-350 °C. The single TPR peak indicates a relatively narrow distribution of Cu particle sizes in CuPSs.^[29]



Figure 5. The first H_2 -TPR profiles (solid line) and the second H_2 -TPR profiles (dash line) after N_2O oxidation of calcined catalysts.

The second H₂-TPR profile showed a broad peak at approximately 170 °C for each sample.^[37] The H₂ uptake of A2 can be used to calculate the concentration and surface area of accessible Cu⁰ with the assumption that the specific surface area of Cu is 1.46 * 10¹⁹ atoms/m²,^[22b] listed in Table 2. Table 2 also presents the dispersion (D_{Cu}) of accessible Cu calculated by 2*A2/A1*100%.^[37] The values of D_{Cu} showed a descending trend as the following order: 10CuPS-red (55.3%) > 30CuPS-red (27.4%) > 20CuPS-red (25.3%) > Cu/SiO₂-red (11.1%). Apparently, CuPSs derived catalysts had better dispersions of Cu⁰ than that of Cu/SiO₂-red. Among reduced CuPSs, an outstanding high D_{Cu} was achieved by 10CuPS-red, while those of 20CuPS-red and 30CuPS-red were similar.

Sample	(Cu/Si) ^{surf}	C_{Cu0}	S_{Cu0}	D _{Cu}	C_{Cu^+}	$Cu^+/(Cu^0+Cu^+)$
		(mmol/g)	(m^2/g)	(%)	(mmol/g)	
10CuPS-red	0.04	0.87	37.7	55.3	0.15	0.15
20CuPS-red	0.09	1.15	49.6	25.3	0.27	0.19
30CuPS-red	0.12	1.33	57.4	27.4	0.61	0.31
Cu/SiO ₂ -red	0.02	0.42	18.2	11.1	-	-

Table 2. Chemical properties of Cu species of tested catalysts^a

^a $(Cu/Si)^{surf}$ was estimated from the intensities of XPS spectra of Cu 2p and Si 2p levels; surface C_{Cu0} and S_{Cu0} were estimated from the second H₂-TPR profile after N₂O oxidation; D_{Cu} was estimated by 2* A2 (the second H₂-TPR peak area) / A1 (the first H₂-TPR peak area) * 100%; surface concentration of Cu⁺ was estimated from the IR spectrum of adsorbed CO of each reduced and N₂O-oxidized catalyst.

Figure 6 shows the IR spectra of CO adsorption of reduced catalysts and their N₂Ooxidized forms at an equilibrium pressure of approximately 2.5*10⁻³ Pa. According to the literature, the IR signals of CO adsorption at approximately 2110 cm⁻¹ can be attributed to CO adsorbed linearly on metallic Cu (forming CO-Cu⁰ carbonyls), while the signal at approximately 2130 cm⁻¹ can be assigned to CO adsorbed linearly on Cu⁺ (forming CO-Cu⁺ carbonyls).^[38] The unstable CO-Cu²⁺ species in the interval of 2150-2240 cm⁻¹ can hardly been seen at room temperature.^[39]

After evacuation, the unstable CO-Cu⁰ species were removed and CO-Cu⁺ carbonyls were preserved on reduced and N₂O-oxidized CuPSs.^[28, 39a] Noted that the CO-Cu⁺ band was absent on Cu/SiO₂-red, suggesting negligible amounts of Cu⁺-O-Si units. The Cu⁺ cations of Cu/SiO₂-red should be mainly in Cu₂O clusters bounded weakly with silica support.^[40] The integrated absorbance band of CO-Cu⁺ was used to estimate the surface concentration of Cu⁺. The area of CO-Cu⁺ band of each reduced sample (A_{IR}1) was smaller than the area (A_{IR}2) of its subsequent N₂O-treated form due to N₂O-induced oxidation of Cu⁰ to Cu⁺.^[28, 41] Hence, the difference (ΔA_{IR}) by subtracting A_{IR}1 from A_{IR}2 can be correlated to the concentration of N₂O-

oxidized Cu⁰. The concentration of Cu⁺ (C_{Cu⁺}, see Table 2) of each catalyst was then calculated from the equation: $(C_{Cu^+}) = (A_{IR}1/\Delta A_{IR}) (C_{Cu0})$.



Figure 6. IR spectra of CO adsorbed on reduced (solid) and on N₂O-oxidized (dash) samples at 30 $^{\circ}$ C with a residual pressure of 2.5*10⁻³ Pa.

Table 2 also presents the ratios of $Cu^+/(Cu^0+Cu^+)$. The $Cu^+/(Cu^0+Cu^+)$ ratio exhibited an ascending order as follows: 10CuPS-red (0.15) < 20CuPS-red (0.19) < 30CuPS-red (0.31). Presumably, the surface concentration of Cu^+ can be enhanced by improving the strength of the Cu-O-Si bond, and the catalysts derived from CuPSs (particularly 30CuPS-red) have stronger interaction between Cu and silica.

Activity Evaluation

Table 3 presents conversions of AA and the yields of detected products, including hydroxycaproic acid (HCA), ε-caprolactone (ε-CPL), HDOL, and 1-hexanol (HNOL) by using

reduced catalysts at different reaction times. Most trials of tested catalysts had mass balance of carbon greater than 90%. Conversions of AA increased with time, but different catalysts showed different rates. At low conversions of AA (< 30%), HCA, ε -CPL and trace HDOL were detected. With increased reaction time, the yields of HCA and ε -CPL increased. When AA was totally consumed, HDOL was the major product for each catalyst. A sudden increase of HDOL together with abrupt declines in HCA and ε -CPL in a full conversion of AA occurred was observed for each catalyst, and will be discussed later in the section of Kinetic Analysis. The highest HDOL yield (96.6%) was obtained by using 20CuPS-red for 6 h reaction time. Scheme 1 exhibits the proposed reaction network

Catalyst	Time	CB	Х	Y (%)			TOF	
	(h)	(%)	(%)	HCA	ε-CPL	HDOL	HNOL	(h ⁻¹)
Cu/SiO ₂ -red	1	99.1	12.3	8.1	3.1	0.2	0	0.36
	3	99.3	34.2	24.6	8.4	0.5	0	-
	6	77.8	78.4	25.2	28.2	2.8	0	-
	16	92.2	100	0	0	91.8	0.4	-
10CuPS-red	1	98.8	9.7	5.9	2.5	0.1	0	0.12
	3	97.2	27.2	15.7	8.5	0.2	0	-
	12	90.5	79.5	31.0	35.5	3.5	0	-
	20	94.8	100	0	0	94.5	0.3	-
20CuPS-red	0.5	94.2	27.1	18.2	3.0	0.1	0	0.47
	1	93.5	39.7	26.2	6.5	0.5	0	
	2	88.0	71.8	34.6	23.0	2.2	0	-
	6	97.4	100	0	0.1	96.6	0.7	-
30CuPS-red	0.1	93.3	27.8	15.1	4.8	1.2	0	1.05
	0.5	98.8	54.9	41.0	11.2	1.5	0	-
	1	91.4	81.0	49.6	20.3	2.5	0	-
	3	88.2	100	0	0.1	87.2	0.9	-

Table 3. Catalytic performances of tested catalysts in AA hydrogenation

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30CuPS-red-300	0.1	98.3	11.3	8.5	1.1	0	0	0.37
30CuPS-red-400	0.1	91.2	17.3	7.5	1.0	0	0	0.73



Scheme 1. Proposed reaction network of hydrogenation of AA by using Cu-based catalysts (adapted from Toba et al. ^[10a]).

Table 3 also presents the TOF values at initial conditions. The TOF showed a descending trend as the following order: 30CuPS-red $(1.05 \text{ h}^{-1}) > 20$ CuPS-red $(0.47 \text{ h}^{-1}) >$ Cu/SiO₂-red $(0.36 \text{ h}^{-1}) >$ Cu/ h^{-1}) > 10CuPS-red (0.12 h^{-1}). 30CuPS-red had the highest TOF, even though it had a D_{Cu} close to that of 20CuPS-red. A possible explanation is that 30CuPS-red had a higher $Cu^+/(Cu^0+Cu^+)$ ratio (0.31) than that of 20CuPS-red (0.19), yielding a higher concentration of Cu^+-Cu^0 pairs for the contact synergy of C=O bond hydrogenation. Contrastively, 10CuPS-red had a significantly low TOF value (0.12 h⁻¹), even though the $Cu^+/(Cu^0+Cu^+)$ ratio of 10CuPS-red (0.15) was comparable to that of 20CuPS-red (0.19). Presumably, the outstandingly high D_{Cu} (55.3%) of 10CuPS-red leads to a finely dispersed but isolated Cu⁺ and Cu⁰ sites, resulting in a low proximity of Cu⁺ and Cu⁰ on the surface. A similar catalytic behavior was observed using a low Cu-loading (8 wt%) catalyst derived from CuPS in furfural hydrogenation to 2-methylfuran. The low Cu-loading catalyst derived from CuPS displayed an activity lower than that of the catalyst containing a moderate Cu loading (24 wt%).^[34b] It should be noted that Cu/SiO₂-red showed considerable TOF value, even though it contained negligible amounts of Cu⁺ species. The noticeable TOF value of Cu/SiO₂-red implied that the C=O bond of AA can be activated not only by Cu⁺-Cu⁰ pairs, but also by interfaces of adjacent Cu⁰ and Cu₂O.^[42]

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To investigate the influence of reduction condition, 30CuPS subjected to different reduction treatments (300 °C and 400 °C for 3 h, denoted as 30CuPS-red-300 and 30CuPS-red-400, respectively) were tested in the hydrogenation of AA at an initial condition. The estimated concentrations of Cu⁰ (Figure S6) and Cu⁺ (Figure S7) are 1.18 mmol/g and 1.08 mmol/g of 30CuPS-red-300 and are 1.43 mmol/g and 0.32 mmol/g of 30CuPS-red-400. The conversion of AA and TOF of 30CuPS-red-300 were 11.3% and 0.37 h⁻¹, and were 17.3% and 0.74 h⁻¹ of 30CuPS-red-400. These values are much lower than those (27.8% and 1.05 h⁻¹) of 30CuPS-red. Moreover, 30CuPS-red produced higher yields of products, particularly HDOL, than those generated by using 30CuPS-red-300 and 30CuPS-red-400. The different activities underlined the importance of reduction treatment, which influences the nature and the contents of exsoluted Cu. It should be noted that 30CuPS-red-300 had the highest $Cu^{+}/(Cu^{0}+Cu^{+})$ ratio at 0.48 but displayed the lowest TOF value, in contradict to the aforementioned claim that a high TOF lies in a high surface $Cu^{+}/(Cu^{0}+Cu^{+})$ ratio. This mismatch may be attributed to different chemical states of copper species: various copper species such as Cu₂O, Cu⁺-O-Si units, Cu⁺-metal alloy, and Cu⁰ particles could be generated under different reduction conditions.^[43] Nevertheless, the interplay of these copper species and their catalytic performances is still unclear.

Catalyst Recycling

Table 4 presents the three sequential reactions of tested catalysts. The conversion of AA using Cu/SiO₂-red decreased significantly from 64.0% (the 1st cycle) to 26.6% (the 2nd cycle) and then to 8.3% (the 3rd cycle). The yields of products also varied significantly from the 1st cycle to the 3rd cycle: HCA decreased from 24.8% to 1.0%; ε -CPL decreased from 22.6% to 1.9%; HDOL decreased from 1.1% to undetectable level. Comparing to the fresh Cu/SiO₂-red, the XRD pattern (Figure S8) of used Cu/SiO₂-red showed increased crystallite sizes of metallic Cu and Cu₂O from 17.2 nm to 41.5 nm and from < 4 nm to 14.1 nm, respectively. The TPR profiles (Figure S9) displayed an approximately 50% decrease of reducible copper species. Moreover, the ICP analysis showed that the Cu loading is approximately 8.9 wt%, which indicated an approximately 55% loss of Cu content compared with its pristine form. This indicates sintering and Cu leaching of recycled Cu/SiO₂-red.

Catalyst	Run	Time	CB	Х		Y (%)	
		(h)	(%)	(%)	HCA	ε-CPL	HDOL
Cu/SiO ₂ -red	1	5	84.5	64.0	24.8	22.6	1.1
	2	5	90.1	26.6	9.8	6.9	0
	3	5	93.6	8.3	1.0	1.9	0
10CuPS-red	1	12	85.6	77.6	28.5	32.3	2.9
	2	12	86.8	67.6	31.7	22.6	0.1
	3	12	82.0	55.1	22.0	15.1	0.1
20CuPS-red	1	2	90.0	74.5	34.4	25.8	4.3
	2	2	88.6	69.2	30.4	24.4	3.0
	3	2	87.5	60.1	28.1	18.2	1.3
30CuPS-red	1	1	92.5	80.5	47.9	21.9	3.2
	2	1	89.2	77.5	43.3	20.5	2.8
	3	1	87.8	70.6	38.4	17.6	2.4

Table 4. Recycling tests of Cu/SiO₂-red and 20CuPS-red at 240 °C with a H₂ pressure of 90 bar

Comparatively, a little decrease of conversion of AA from 77.6% (the 1st cycle) to 55.1% (the 3rd cycle), 74.5% (the 1st cycle) to 60.1% (the 3rd cycle), 80.5% (the 1st cycle) to 70.6% (the 3rd cycle) were observed by using 10CuPS-red, 20CuPS-red, and 30CuPS-red, respectively. Moreover, the yields of products were similar for each run by using a CuPS-red. The small variation of yields of products implied that most of the active phases were unaltered after three sequential reactions. Comparing to the results of Figure 1(b), the XRD patterns (Figure S8) of recycled 10CuPS-red showed little increases in the crystallite diameters of metallic Cu and Cu₂O

from < 4 nm to 8.5 nm and from < 4 nm to 5.2 nm; recycled 20CuPS-red, from 5.8 to 8.6 nm and from 5.4 nm to 5.5 nm; recycled 30CuPS-red, from 6.9 nm to 7.3 nm and from 5.6 nm to 7.9 nm. Figure S9 shows the TPR profiles of used CuPSs-red. Compared to the profiles of their freshly prepared counterparts, the peaks of used CuPS-red shifted downward from approximately 250 °C to 200 °C. The low-temperature shifted peaks indicated destruction of some Cu-O-Si units. However, the peak areas of fresh and recycled catalysts were similar. The Cu loadings of used CuPSs-red determined by ICP analyses showed less than 15% losses compared to that of fresh CuPSs. This highlighted that CuPSs-red had better stability than Cu/SiO₂-red. To sum up, the Cu-O-Si bonding of CuPS-red stronger than that of Cu/SiO₂ is responsible for improving the stability.

Kinetic Analysis

A global kinetic analysis of AA hydrogenation was conducted by using 20CuPS-red. Detailed derivations (Appendix B), experimental data (Tables S1 and S2), and the comparisons of observed and model-calculated results (Figure S10) can be found in the Supporting Information. The differences between experimental and predicted concentrations are considerable, indicating that a more comprehensive analysis is needed.

Table S3 lists the possible steps of conversion of AA to HDOL and the derived rate expressions according to the Langmuir–Hinshelwood–Hougen–Watson (LHHW) formalism. Detailed derivations, assumptions,^[14b, 44] and simplifications^[45] we made can be found in the Appendix C of the Supporting Information. The resultant rate expressions were then fitted with experimental data (Table S4) via nonlinear regression. Table 5 presents obtained kinetic parameters, Figure S11 shows the experimental and the predicted concentration profiles of reactant and products, and Figure S12 exhibits the parity plot. The experimental and the estimated values are in a good agreement, suggesting that the proposed steps and the assumptions are rational.

Obtained kinetic parameters	20CuPS-red
$k_1 (dm^6/mol^2 \cdot h)$	0.12 ± 0.02
K_{AA} (dm ³ /mol)	16.3 ± 1.8
K_{HCA} (dm ³ /mol)	14.1 ± 1.2
$k_2(h^{-1})$	0.04 ± 0.003
$k_3 (dm^6/mol^2 \cdot h)$	0.01 ± 0.004
$K_{\epsilon-CPL}$ (dm ³ /mol)	10.0 ± 3.2
K _{HDOL} (dm ³ /mol)	0

Table 5. Estimated kinetic parameters obtained from the LHHW formalism

Through a close inspection of these parameters (see Table 5), we can find that k_1 is three times higher than k_2 and two orders of magnitude higher than k_3 , implying a faster reaction rate of AA conversion to HCA. Moreover, the equilibrium constant of the adsorption and desorption of AA (K_{AA} , 16.3) is larger than that of HCA (K_{HCA} , 14.1) and that of ϵ -CPL ($K_{\epsilon-CPL}$, 10.0), while K_{HDOL} is negligible. The similar equilibrium constants of AA, HCA, and ϵ -CPL indicate that these species are competing for active sites (competitive adsorption) when a reaction proceeds. In a pressurized liquid phase system, a full coverage of active sites is common.^[46] Since AA is the reactant, it should occupy most of the available sites initially. Once a high conversion of AA is achieved, some active sites are then available to adsorb HCA and ϵ -CPL for further transformation. The global kinetic analysis does not consider the influence of competitive adsorption, resulting in a substantial disagreement between the experimental and simulated results. Furthermore, the negligible K_{HDOL} indicates that HDOL is weakly adsorbed and is desorbed immediately once it is formed, thereby leading to a high HDOL productivity.

Conclusions

Cu-based catalysts derived from CuPSs were effective in direct hydrogenation of AA to HDOL. In a full conversion of AA, merely a trace of byproducts and remarkable high HDOL yields were generated by using CuPS-red catalysts. In addition, better reusabilities were discovered through the tests of CuPSs-red rather than Cu/SiO₂-red, and the differences are related to the stronger strengths of the Cu-O-Si bonds of CuPSs-red. The stronger Cu-silica interaction can also elevate the Cu⁺/(Cu⁰+Cu⁺) ratio. The Cu⁺/(Cu⁰+Cu⁺) ratio, the amounts of Cu⁰ and Cu⁺ sites, and the reduction condition could affect the intrinsic activity of hydrogenation of AA. The outcomes of kinetic analysis based on the LHHW formalism revealed that the competitive adsorption of AA and its derivatives, i.e., HCA and ϵ -CPL, could influence the catalytic behaviors of hydrogenation of AA to HDOL.

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Silica-supported copper catalysts derived from copper phyllosilicates are selective and stable in the hydrogenation of adipic acid to 1,6-hexandiol

