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Selective Conversion of Coconut Oil to Fatty Alcohols in Methanol over Hydrothermally Prepared Cu/SiO_2 Catalyst without Extraneous Hydrogen †

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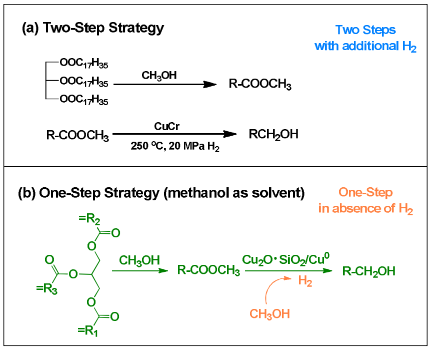
Liubi Wu, Lulu Li, Bolong Li and Chen Zhao*

A novel one-pot approach selects a hydrothermally synthesized Cu/SiO_2 catalyst (consisting of $Cu_2O·SiO_2$ and Cu^0 surface species) to catalyze the reduction of a series of fatty esters, fatty acids, and coconut oil to fatty alcohols at 240 °C in methanol without extraneous hydrogen, attaining around 85% conversion and 100% selectivity.

Fatty alcohols are important intermediates for the production of detergents, surfactants, food additives, pharmaceuticals, cosmetics, and for polyesters used for textiles, lubricants, and industrial solvents.[1, 2] The initial raw material can be obtained from petrochemical sources or biobased feedstock, such as seed and vegetable oils. To synthesize fatty alcohols from natural sources, the traditional two-step approach produces intermediate fatty acid methyl esters (FAMEs) after the transesterification of the triglycerides (Scheme 1a), followed by selective hydrogenation to fatty alcohols using heterogeneous catalysts. Adkins-type copper-based CuCr catalysts are traditionally used as fatty ester hydrogenation catalysts because of their resistance to free fatty acids and because of the low propensity of Cu for inducing decarboxylation or decarbonylation reactions.[3, 4] However, hydrogenation with Cu-based catalysts requires harsh reaction conditions, such as working temperatures above 250°C and hydrogen pressures greater than 20 MPa.

Due to toxicity problems associated with the disposal of Cr, more environmentally friendly bimetallic Cu-M catalysts[5, 6] using elements such as Zn, Fe, and Al have been developed. In addition, Ni catalysts are used for the hydrodeoxygenation of fatty esters to form natural substitutes for diesel fuel.[7, 8] Even with these alternative catalyst systems, harsh reaction conditions and large amounts of energy are still required. Noble metals,[9-12] such as Pt, Pd, Re, and Ru, have been used for the reduction of ester derivatives, but the high costs of these catalysts limit their usefulness. Supercritical fluids[13, 14] require lower hydrogen pressures. More recently, Ru-[15-18] and Fe-[19-21] based homogeneous catalysts have been developed, which allow reactions to be conducted at relatively mild conditions in the presence of hydrogen.



Scheme 1 The reaction sequences for conversion of coconut oil to fatty alcohols in methanol via (a) two steps with additional H_2 and (b) one step in the absence of H_2.

We developed a novel, highly efficient, and environmentally friendly hydrogenation catalyst for the reduction of various fatty esters (acids) to fatty alcohols using a highly active silica supported copper catalyst for one-pot hydrogenation of coconut oil to fatty alcohols. The process consisted of an initial methanol induced transesterification, followed by reduction to C_8-C_{12} fatty alcohols in the absence of extraneous H_2 (Scheme 1b). This Cu-based catalyst has the dual functionality of generating hydrogen from methanol in situ while simultaneously activating the molecular hydrogen for transfer into the substrates as hydrogen radicals.

First, three silica supported copper catalysts (Cu/SiO_2) were prepared by impregnation (IM), by deposition-precipitation (DP) using urea as the precipitation agent, and by hydrothermal synthesis (HT) using mixed $NH_4Cl/NH_3·H_2O$ as the base agent. We selected a neutral SiO_2 support with a relatively large surface area to avoid dehydration (catalyzed by acidic sites) of the target fatty alcohols. In the control experiment without an added catalyst, methyl laurate (the

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main FAME obtained from coconut oil) and methanol were mixed at 240 °C in the presence of N_2 (2 MPa) for 4 hours, with no reaction taking place. When the Cu/SiO_2-HT prepared catalyst was used, we found that dodecanol formed with a selective conversion of 84.6% and 99.8%, while the Cu/SiO_2-IM and Cu/SiO_2-DP catalysts had negligible conversions of 0.44% and 0.53% under identical conditions (Fig. 1).

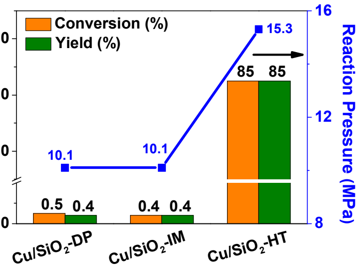

Fig. 1 The conversion and dodecanol yield for methyl laurate transformation in methanol using Cu/SiO_2 prepared by different methods in absence of H_2. Reaction conditions: methyl laurate (0.3 g), methanol (40 mL), catalysts (0.2 g), 240 °C, 4 h, N_2 (2 MPa), stirring at 400 rpm.

We used inductively coupled plasma-atomic emission spectroscopy (ICP-AES), N_2 sorption, powder X-ray diffraction (XRD), temperature programmed reduction by hydrogen (TRP-H_2), X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) characterization experiments to investigate the active species of the Cu/SiO_2-HT catalyst. The Cu contents of the three Cu/SiO_2 catalysts were similar at ca. 50 wt%, as analysed by ICP-AES. N_2 sorption results showed the BET surface area was 249 m^2/g, and the major pore size was centred at 13 nm (Fig. S1&S2). The XRD spectrum of the reduced Cu/SiO_2-HT catalyst exhibited peaks at 36 ° [PDF: 34-1354] and 43 ° [PDF: 04-0836] (Fig. 2a), which were assigned to Cu_2O or $Cu_2O{\cdot}SiO_2$ and Cu^0 species respectively, suggesting that hydrogen reduction resulted only in partial reduction of the catalyst. In contrast, calcined Cu/SiO_2-IM and Cu/SiO_2-DP samples were fully hydrogenated from copper oxide to metallic copper (Fig. S3). The Cu $2p_{1/2}$ and Cu $2p_{3/2}$ XPS spectrum of reduced Cu/SiO_2-HT demonstrated the presence of $Cu_2O{\cdot}SiO_2$ and Cu^0 sites, as well as some residual copper phyllosilicate (Fig. 2b), further confirming only partial reduction of the catalyst. The ratio of $Cu_2O{\cdot}SiO_2$ and Cu^0 on the reduced Cu/SiO_2-HT sample was 1.76:1, as calculated from the kinetic energy (KE) of the Cu LMM Auger electron spectrum (Fig. 2c). The H_2-TPR profile on the calcined Cu/SiO_2 sample showed two peaks at 252.8 °C and 263.4 °C (Fig. S4), which likely resulted from the reduction of the phyllosilicate to Cu^0 and Cu^+. The IR spectrum of the calcined Cu/SiO_2-HT catalyst further evidenced the presence of copper phyllosilicate, since the prominent peaks at 667 cm^{-1} and 802 cm^{-1} were from the copper phyllosilicate species[22] (Fig. S5a). However, these IR peaks were absent in the calcined Cu/SiO_2-IM and Cu/SiO_2-DP catalysts (Fig. S5b&S5c). The calcined and reduced Cu/SiO_2-HT catalyst exhibited substantial lamellar copper phyllosilicate structures, as shown from the SEM (Fig. S6) and TEM images (Fig. 2d and 2e). This lamellar structure was not observed in Cu/SiO_2-IM and the Cu/SiO_2-DP prepared samples (Fig. S7). The lattice fringes of Cu (111) and $Cu_2O{\cdot}SiO_2$ (111) indicated abundant copper species in the reduced Cu/SiO_2-HT, with highly uniform and well-dispersed Cu nanoparticles (6.1 ± 0.7 nm) present in the catalyst (Fig. 2e). Therefore, the characterization results consistently confirmed that the major Cu species on the reduced Cu/SiO_2-HT were $Cu_2O{\cdot}SiO_2$ and Cu^0, with some undecomposed copper phyllosilicate. In comparison, Cu^0 was the sole species on the reduced Cu/SiO_2-IM and Cu/SiO_2-DP samples.

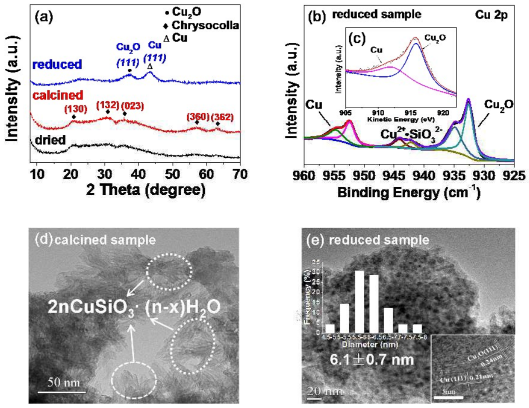

Fig. 2 (a) XRD patterns, (b) XPS spectra, (c) Cu LM2 Auger spectra and TEM images (d) and (e) of different states of Cu/SiO_2-HT.

The data from the characterization experiments helped identify the Cu species during the formation of the Cu/SiO_2-HT catalyst. After hydrothermal synthesis, which combined a homogeneously-dispersed copper (II) nitrate trihydrate suspension in the $NH_4Cl/NH_3{\cdot}H_2O$ buffer solution with SiO_2 at 120 °C for 180 minutes, the Cu/SiO_2-HT catalyst precursor (prior to calcination) was blue, indicating that the Cu^{2+} ions were coordinated to water. The XRD patterns demonstrated that the pre-calcined (dried) Cu/SiO_2-HT catalyst consisted of $CuO{\cdot}SiO_2{\cdot}nH_2O$ (Fig. 2a), known as chrysocolla. After air-calcination, the XRD peak pattern was unchanged, indicating that the major structure had little or no change (Fig. 2a). The nearly identical IR spectra of the dried and calcined Cu/SiO_2-HT samples further confirmed a negligible change in the structure of the catalyst upon calcination (Fig. S5a). However, the color

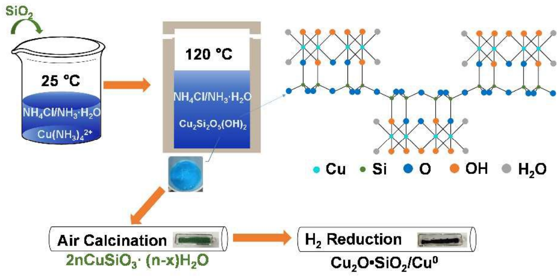

Fig. 3 Schematic illustration of the changes for Cu species supported on SiO_2 during the synthesis procedure.

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clearly changed from deep blue to green (Fig. S8) after calcination, as the water of crystallization was partially removed during the dehydration of the catalyst, forming $CuO\cdot SiO_2\cdot(n\text{-}x)H_2O$. The thermogravimetric analysis (TGA) experiment demonstrated that, during the calcination process, a weight loss of 5 wt% occurred as the temperature increased from 100 to 550 °C (Fig. S9). Upon reduction, Cu/SiO_2-HT turned into a black powder, and as expected, the IR peaks at 667 cm^{-1} and 802 cm^{-1} disappeared because copper phyllosilicate was converted to $Cu_2O\cdot SiO_2$ and Cu^0. Therefore, hydrothermal synthesis led to the formation of a blue Cu precursor ($CuO\cdot SiO_2\cdot nH_2O$) on the SiO_2 support, which partially dehydrated during the calcination process to form a green sample with the general formula $CuO\cdot SiO_2\cdot(n\text{-}x)H_2O$. After reduction, $Cu_2O\cdot SiO_2$ and Cu^0 were the main species loaded on the SiO_2 support, with a residual amount of copper phyllosilicate (Fig. 3).

The pressure increase was highly fast in the presence of Cu/SiO_2-HT with a rate of 2.0 $MPa\cdot g^{-1}\cdot h^{-1}$ in the reduction of methyl laurate in methanol, under the reaction conditions of 240 °C, N_2 at 2 MPa (Fig. S10). The rates attained for the same reaction but with Cu/SiO_2-IM and Cu/SiO_2-DP in a sealed autoclave were 0.2 and 0.6 $MPa\cdot g^{-1}\cdot h^{-1}$, respectively (Fig. S10). When the experiment used only methanol, a rate exceeding 5.4 $MPa_{H2}\cdot h^{-1}$ was observed with Cu/SiO_2-HT due to H_2 release during dehydrogenation (Fig. S11a). The rates for methanol dehydrogenation were 0.15 and 0.13 $MPa_{H2}\cdot h^{-1}$ using Cu/SiO_2–IM and Cu/SiO_2–DP as the catalysts (Fig. S11b, S11c). The higher rate observed with Cu/SiO_2 HT suggested that the combined $Cu_2O\cdot SiO_2$ and Cu^0 species formed a more active catalyst than those solely comprised of the Cu^0 species, such as the Cu/SiO_2–IM and Cu/SiO_2–DP catalysts, for H_2 generation via methanol dehydrogenation.

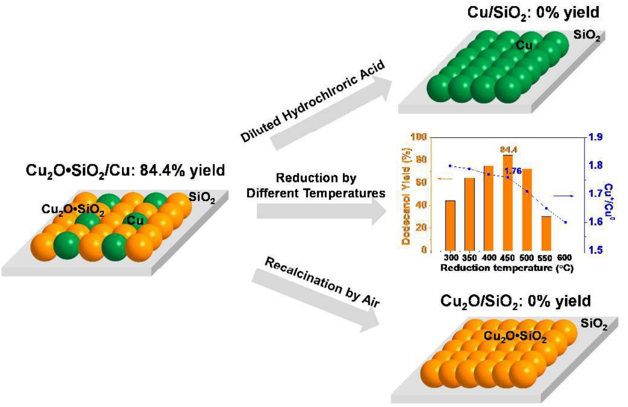

Fig. 4 Determination of the active Cu species for methyl laurate reduction reaction. Reaction conditions: methyl laurate (0.3 g), methanol (40 mL), catalysts (0.2 g), 240 ˚C, 4 h, N_2 (2 MPa), stirring at 400 rpm.

A series of experiments were conducted to investigate the role of each Cu species ($Cu_2O\cdot SiO_2$, Cu^0, and copper phyllosilicate) in H_2 generation and ester reduction (Fig. 4). We tested the activity of dried and calcined copper phyllosilicate for methanol dehydrogenation in the presence of N_2, but no reaction occurred (Fig. S12). Therefore, the copper phyllosilicate residue was excluded as an active species on the reduced Cu/SiO_2. Next, we washed the reduced Cu/SiO_2-HT catalyst with dilute hydrochloric acid (2 wt%) to remove $Cu_2O\cdot SiO_2$, and the remaining Cu^0 nanoparticles, as confirmed by the XRD pattern shown in Fig. S13b, were inactive for H_2 generation and ester reduction. Exposing a reduced Cu/SiO_2-HT sample to air re-calcination generated a Cu_2O species almost exclusively, as determined by the XRD pattern shown in Fig. S13c. This modified catalyst was also inactive for methanol dehydrogenation and ester reduction. The reduced Cu^0 species on the Cu/SiO_2 (IM) and Cu/SiO_2 (DP) catalysts were also considerably less active, demonstrating the necessity of combining Cu^0 and Cu_2O centers for obtaining maximum catalyst efficiency. The Cu^+/Cu^0 ratio was further adjusted by varying the hydrogen reduction temperatures of the catalyst from 300 to 600 °C. Based on the XPS spectral results (Fig. S13d), the Cu^+/Cu^0 ratios varied from 1.60 to 1.80. The yield from the methyl laurate hydrogenation increased from 44% to a maximum of 83% at a reduction temperature of 450 °C (with the optimal Cu^+/Cu^0 ratio of 1.76), and no hydrogenation occurred at 600 °C. The combined results suggested a synergistic role for the combined $Cu_2O\cdot SiO_2$ and Cu^0 species for the initial *in situ* catalytic methanol dehydrogenation. Thus, the formed H_2 is activated for reduction by the Cu^0 centers, where it undergoes homolysis and transfer to methyl laurate for reduction to lauryl alcohol.

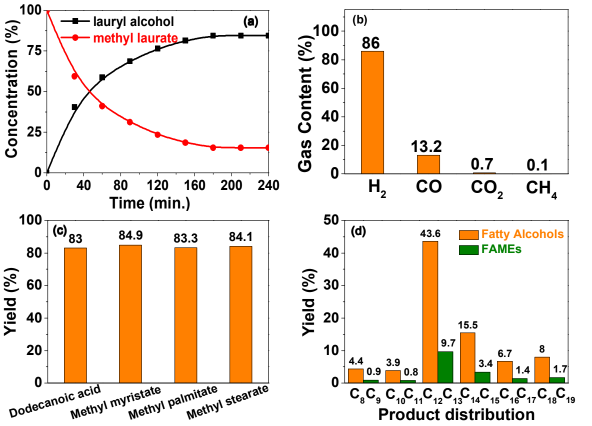

Fig. 5 (a) Kinetics of methyl laurate conversion with Cu/SiO_2-HT in methanol, (b) The gas compositions of conversion of methyl laurate in methanol as detected by GC, (c) Yield of corresponding alcohols from various fatty acid methyl esters with carbon chains ranging from C_{12} to C_{16} and a C_{12} fatty acid, (d) Products distribution of coconut oil hydrogenation by using Cu/SiO_2-HT (reduced at 450 ˚C). Reaction conditions: reactants (0.3 g), methanol (40 mL), Cu/SiO_2-HT (0.1 g), 240 ˚C, N_2 (2 MPa), stirring at 400 rpm.

Methyl laurate was converted to fatty alcohol with Cu/SiO_2-HT in methanol under a N_2 atmosphere within 4 hours, with close to 80% conversion and a selectivity of 100% for lauryl alcohol, and an initial reaction rate of 13.7 $mmol\cdot g^{-1}\cdot h^{-1}$ (Fig. 5a). The gas compositions after methyl ester hydrogenation were similar with H_2 (86%), CO (13%), CO_2 (0.7%), and CH_4 (0.1%) (Fig. 5b). In the liquid phase, highly selective dimethoxy methane (DMM, close to 100% selectivity) and trace amounts of formaldehyde were detected (Fig. S14). The presence of HCHO indicated that CH_3OH was majorly dehydrogenated to H_2 and HCHO over $Cu_2O\cdot SiO_2$ and Cu^0, and then the formed

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HCHO condensed with substantial CH_3OH to form DMM. Such a catalytic system can be used for the reduction of different FAMEs, with carbon chains ranging from C_{12} to C_{16} and a C_{12} fatty acid, producing 83-85% yields in fatty alcohols and 100% selectivity (Fig. 5c). The conversion of coconut oil containing a mixture of fatty acid derivatives, mainly lauric acid, with Cu/SiO_2-HT, under the optimized reactions conditions using MeOH as the solvent, 240 °C, 2.0 MPa N_2, and 4 hours, yielded C_8-C_{18} fatty alcohols in a one-pot reaction, with an 83 wt% yield, at an initial rate of 1.0 $g_{oil}\cdot g^{-1}\cdot h^{-1}$, without extraneous H_2. The most abundant product was C_{12} lauryl alcohol, with a 43.6% yield (Fig. 5d). In addition, incomplete hydrogenation of FAMEs (formed from transesterification between fatty esters in coconut oil and methanol) led to these partially reduced products with a 17% yield. The product distribution (analyzed by GC-MS, Fig. S15) perfectly mirrored the fatty acid derivative composition in the raw coconut oil (Fig. S16).

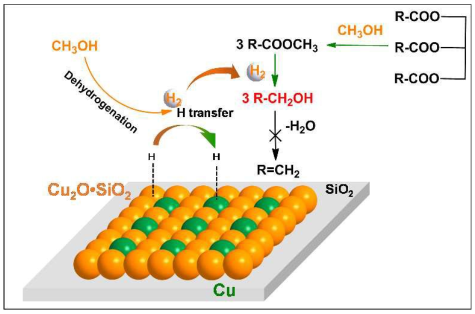

Fig. 6 The designed reaction pathway for Cu/SiO_2-HT catalyzed selective conversion of coconut oil to fatty alcohols in methanol. Reaction conditions: coconut oil (0.3 g), Cu/SiO_2-HT (0.2 g), methanol (40 mL), 240 ˚C, 4 h, stirring at 400 rpm.

The mechanism for the Cu/SiO_2-HT catalyzed reduction of fatty esters in coconut oil is described in Fig. 6. First, larger sized fatty esters (triglycerides) were converted into smaller FAMEs via transesterification with methanol. Simultaneously, methanol quickly dehydrogenated to produce H_2 on the $Cu_2O{\cdot}SiO_2/Cu^0$ sites, which then internally transferred to an adjacent Cu^0 site and underwent homolysis on the catalyst surface, forming H· radicals. The H· radicals reduced the FAMEs to fatty alcohols via an aldehyde intermediate. The recycling ability of Cu/SiO_2-HT was tested by re-using the catalyst (treated by sequential air-calcination and hydrogen-reduction) in four additional runs . A steady conversion of nearly 80% and a selectivity of approximately 100% were obtained when reusing the catalyst for the reduction of coconut oil in the absence of H_2 (Fig. S17), demonstrating that the developed catalyst was quite durable even after multiple runs. The incomplete conversion (80%) resulted from the reaction equilibrium between the *in-situ* produced H_2 and the ester reactant. Moreover, XRD and TEM analysis on the reused Cu/SiO_2-HT catalyst showed that the $Cu_2O{\cdot}SiO_2$ and Cu^0 active centers were still present and dispersed on the SiO_2 support (Fig. S18a & S18b), and TGA measurement evidenced no coke formation on the reused sample (Fig. S18c), demonstrating the robust nature of the catalyst for fatty ester reduction after consecutive tests.

In conclusion, we developed a simple and efficient one-pot process for the selective conversion of coconut oil and various fatty esters (acids) to fatty alcohols with nearly 100% selectivity using a highly active and inexpensive Cu/SiO_2 catalyst in methanol at 240 °C without extraneous H_2. The $Cu_2O{\cdot}SiO_2$ and Cu^0 sites acted synergistically on the surface of the Cu/SiO_2 catalyst prepared by the hydrothermal method and catalysed the generation of H_2 via methanol dehydrogenation. Homolysis of the generated H_2 occurred on the neighboring Cu^0 sites, resulting in the formation of H· species, which reduced the FAMEs to fatty alcohols. The developed catalyst combining $Cu_2O{\cdot}SiO_2/Cu^0$ centers had an optimal Cu^+/Cu^0 ratio of 1.76 for the tandem methanol dehydrogenation/reduction reaction of fatty esters. Additionally, single Cu^+ or Cu^0 catalysts had no activity for both the methanol dehydrogenation and the ester reduction. Hence, this new method resulted in the efficient and selective reduction of a series of inert fatty acids and esters *via* a simple and hydrogen-free process under mild conditions.

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