Electronic Supplementary Material (ESI) for ChemComm.
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Supporting information

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

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Experiment Section

Chemicals: Coconut oil was purchased from J&K Co. The analytical reagents of methyl laurate, methyl myristate, methyl palmitate, and methyl stearate were obtained from J&K Co. The analytical pure chemicals of lauric acid, copper (II) nitrate trihydrate, ammonium hydroxide solution, and ammonium chloride were provided by Sinopec Co., Ltd. Nano-silicon dioxide was purchased from J&K Co. Air, hydrogen and nitrogen gases (99.999 vol. %) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

Synthesis of Cu/SiO$_2$ by hydrothermal method (Cu/SiO$_2$-HT): Firstly, $Cu(NO_3)_2{\cdot}3H_2O$ was dissolved in deionized water, then adding a solution of NH_4Cl and $NH_3{\cdot}H_2O$ together with SiO_2 into the copper solution with stirring at ambient temperature for 0.5 h. Afterwards, the mixture was ultrasonic treated for another 0.5 h, and transferred into a Teflon autoclave for 3 h at 120 °C. After cooling down to room temperature, the solid in the autoclave was filtered and washed by deionized water until pH value attained 7. Finally, the precursor was dried at 60 °C overnight, and calcined in flowing air at 450 °C for 4 h (heating rate: 2 $°C{\cdot}min^{-1}$, flowing velocity: 100 $mL{\cdot}min^{-1}$) and reduced in flowing hydrogen at 450 °C for 4 h (heating rate: 2 $°C{\cdot}min^{-1}$, flowing velocity: 100 $mL{\cdot}min^{-1}$).

Synthesis of Cu/SiO$_2$ by impregnation method (Cu/SiO$_2$-IM): A typical Cu/SiO$_2$-IM was synthesized by impregnation method. Firstly, $Cu(NO_3)_2{\cdot}3H_2O$ (3.80 g) was dissolved in distilled water (10 mL). Then the copper precursor solutions was well-dropped onto SiO_2 (2 g), which kept magnetic stirring at ambient temperature to dry out the water. Finally, the solid was dried at 60 °C overnight, calcined in flowing air at 450 °C for 4 h (heating rate: 2 $°C{\cdot}min^{-1}$, flowing velocity:100 $mL{\cdot}min^{-1}$) and reduced in flowing hydrogen at 450 °C for 4 h (heating rate: 2 $°C{\cdot}min^{-1}$, flowing velocity: 100 $mL{\cdot}min^{-1}$).

Synthesis of Cu/SiO$_2$ by deposition-precipitation using urea as precipitant (Cu/SiO$_2$-DP): A typical catalyst Cu/SiO$_2$-DP was synthesized as follows. An aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.10 M, 350 mL) was prepared and divided into two parts. 200 mL was suspended with 2 g nano SiO_2 (solution A) and heated to 70 °C. The rest (50 mL) was dissolved with urea (6.3 g) (solution B), then drop-wise added into the former suspension. Next, the mixture was heated up to 90 °C and kept reflux condensation for 10 h. After cooling down to ambient temperature, the catalyst precursor was filtered and washed by distilled water several times. Finally, the solid was dried at 60 °C overnight, calcined in flowing air at 450 °C for 4 h (heating rate: 2 $°C{\cdot}min^{-1}$, flowing velocity:100 $mL{\cdot}min^{-1}$) and reduced in flowing hydrogen at 450 °C for 4 h (heating rate: 2 $°C{\cdot}min^{-1}$, flowing velocity: 100 $mL{\cdot}min^{-1}$).

Catalyst characterization

Cu contents were quantified by inductively coupled plasma atomic emission spectroscopy (ICP–AES) performed on a Thermo IRIS Intrepid II XSP emission spectrometer after dissolving the catalyst in the HF solution. N_2 adsorption measurements were carried out at 77 K on a BEL-MAX gas/vapor adsorption instrument. The surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. Powder X-ray diffraction (XRD) patterns were detected to confirm the structure and crystal size by Rigaku Ultima IV X-ray diffractometer utilizing Cu-K_α radiation (λ = 1.5405 Å) operated at 35 kV and 25 mA. The IR spectra (IR) were collected by Nicolet Nexus 670 FT-IR spectrometer in absorbance mode at a spectral resolution of 2 cm^{-1} using KBr technique. Hydrogen temperature programmed reduction (TPR) was conducted by TP-5080 multi-purpose automatic adsorption instrument by at the ramp rate of 10 K min^{-1}. Scanning electron microscopy images (SEM) were performed on the Hitachi S-4800 microscope. To illuminate crystal morphology and size, transmission electron microscopy (TEM) images were obtained by the FEI Tecnai G^2 F30 microscope working at 300 kV. X-ray photoelectron spectroscopy (XPS) were performed with Al K_α ($h\nu = 1486.6$ eV) radiation on a Thermo Scientific K-Alpha spectrometer. Charging effects were corrected by using the C 1s peak due to adventitious carbon with EB fixed at 284.6 eV.

Catalytic tests

A typical test was carried out as follows: methyl laurate (1.0 g), methanol (40 mL) and Cu/SiO_2-HT catalyst (0.1 g) were added into a batch autoclave (70 mL). The reactor was then flushed with N_2 (2 MPa) at ambient temperature for three times to remove the residual air. After evacuating nitrogen, it was heated up to 240 °C. The reaction was conducted for 4 h at a stirring speed of 450 rpm. After cooling down to ambient temperature, liquid products were analyzed on a gas chromatograph (GC) equipped with a mass spectrometer (GC-MS, Shimadzu QP-2010 Ultra) with a Rtx-5Sil MS capillary column (30 m × 0.25 mm × 0.25 μm). Analysis for gaseous products was performed on a GC (Techcomp 7900) equipped with thermal conductivity detector (TCD) and columns (TDX-01: 30 cm × 3 mm, TDX-01: 2 m × 3 mm), as well as flame ionization detector (FID) and a HP-PLOT Q capillary column (50 m × 0.53 mm × 25 μm).

Test of the coconut oil components

Coconut oil (5.0 g), methanol (100 mL), and CaO (0.8 g) were added into a batch autoclave (Parr, 300 mL). The reactor was then flushed with N_2 at ambient temperature for three times. After evacuating nitrogen, it was heated up to 80 °C. The reaction was conducted for 2 h at a stirring speed of 600 rpm. After cooling down to ambient temperature, liquid products were analyzed by GC coupled with GC-MS.

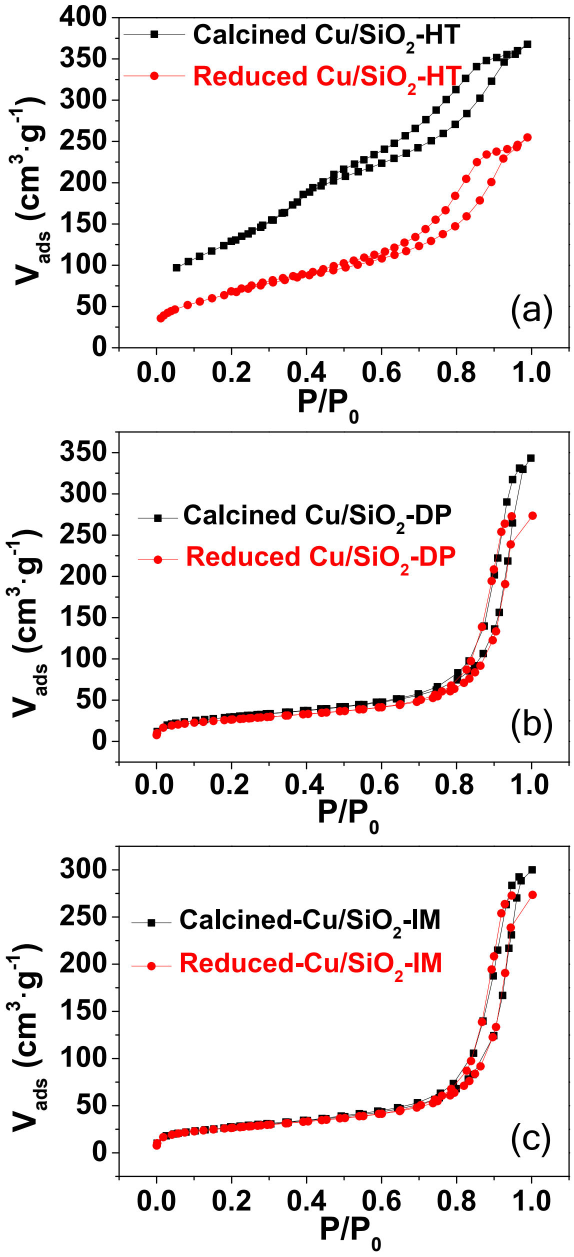

Fig. S1 N_2 adsorption and desorption isotherms of (a) Cu/SiO$_2$-HT, (b) Cu/SiO$_2$-DP and (c) Cu/SiO$_2$-IM.

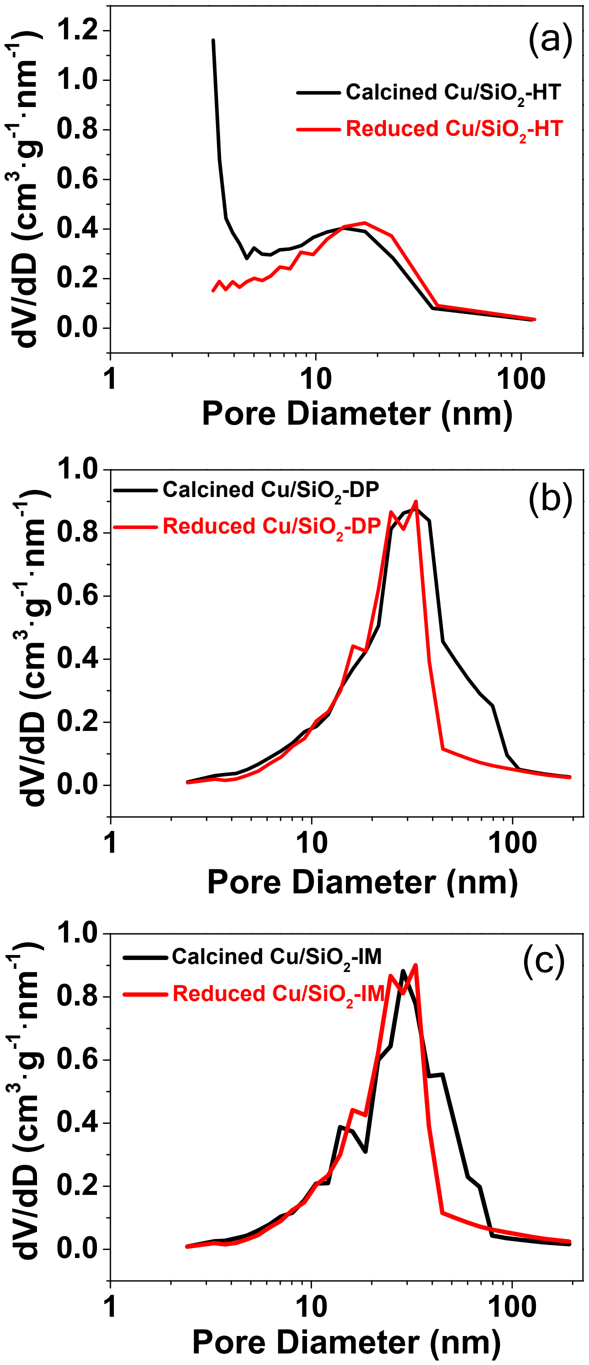

Fig. S2 BJH adsorption pore size distributions of (a) Cu/SiO_2-HT, (b) Cu/SiO_2-DP and (c) Cu/SiO_2-IM.

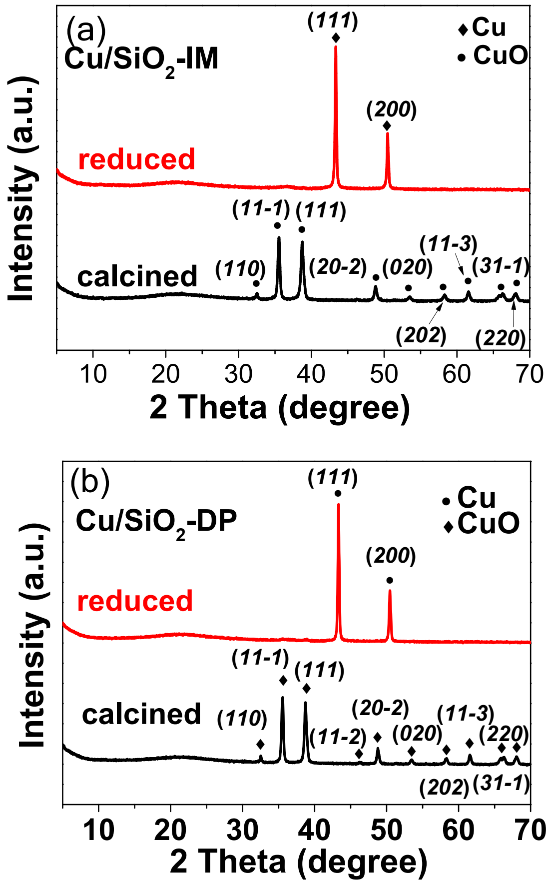

Fig. S3 XRD patterns of (a) Cu/SiO$_2$-IM and (b) Cu/SiO$_2$-DP after air-calcination and hydrogen-reduction.

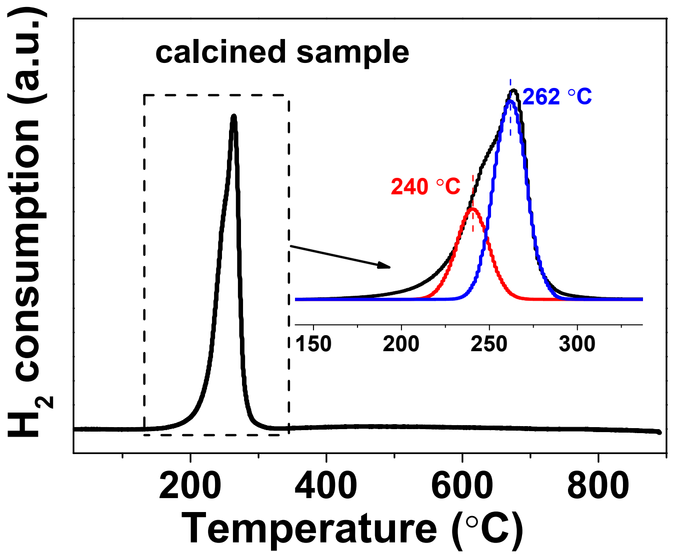

Fig. S4 H$_2$-TPR profile of calcined Cu/SiO$_2$-HT catalyst.

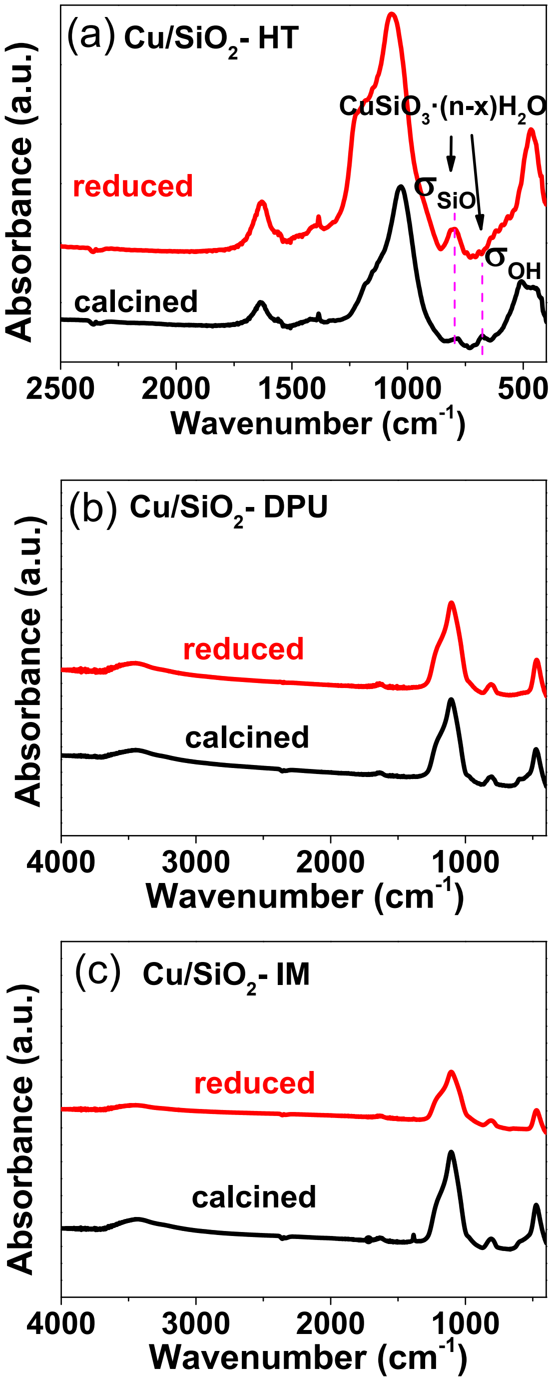

Fig. S5 IR spectra of different stateds of (a) Cu/SiO$_2$-HT, (b) Cu/SiO$_2$-IM and (c) Cu/SiO$_2$-DP.

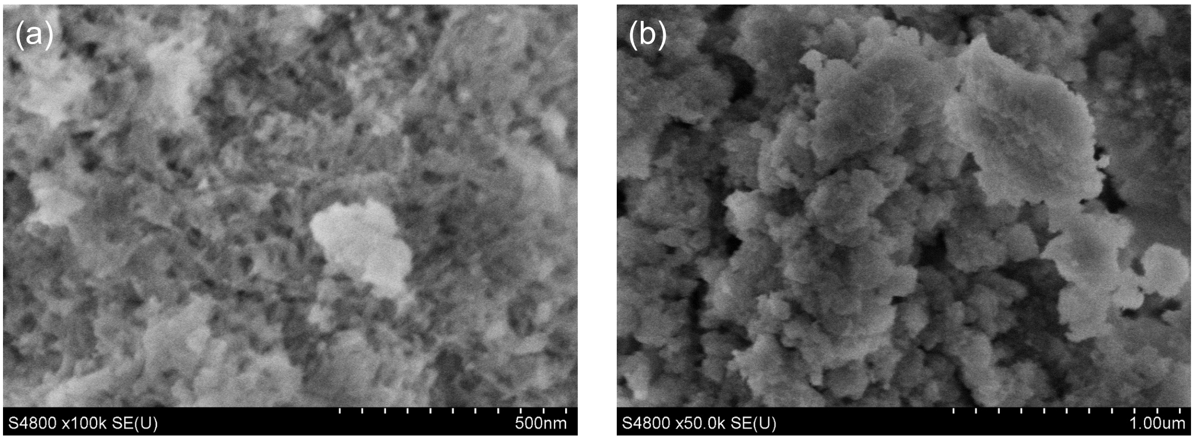

Fig. S6 SEM images of (a) calcined Cu/SiO_2-HT and (b) reduced Cu/SiO_2-HT catalysts.

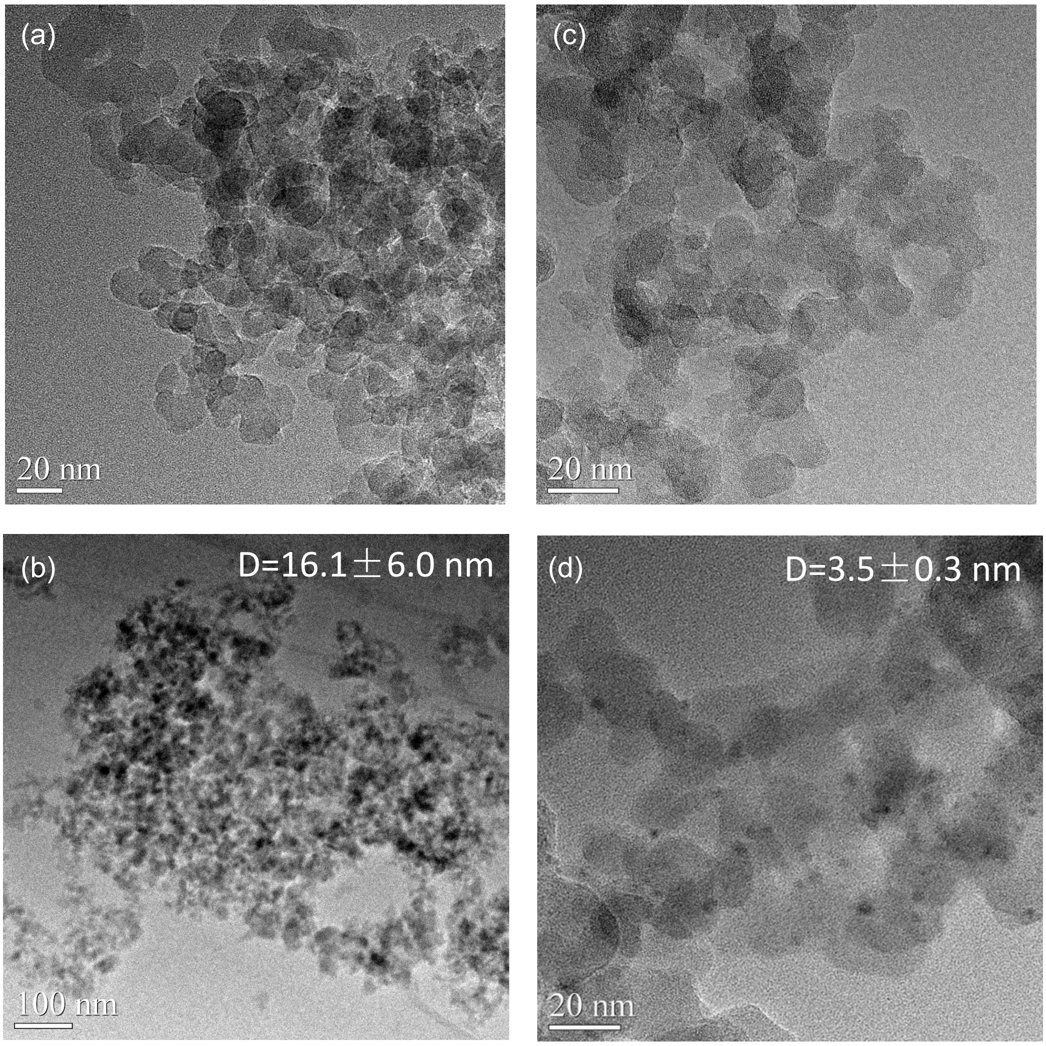

Fig. S7 TEM images of (a) calcined Cu/SiO$_2$-IM, (b) reduced Cu/SiO$_2$-IM, (c) calcined Cu/SiO$_2$-DP, and (d) reduced Cu/SiO$_2$-DP samples.

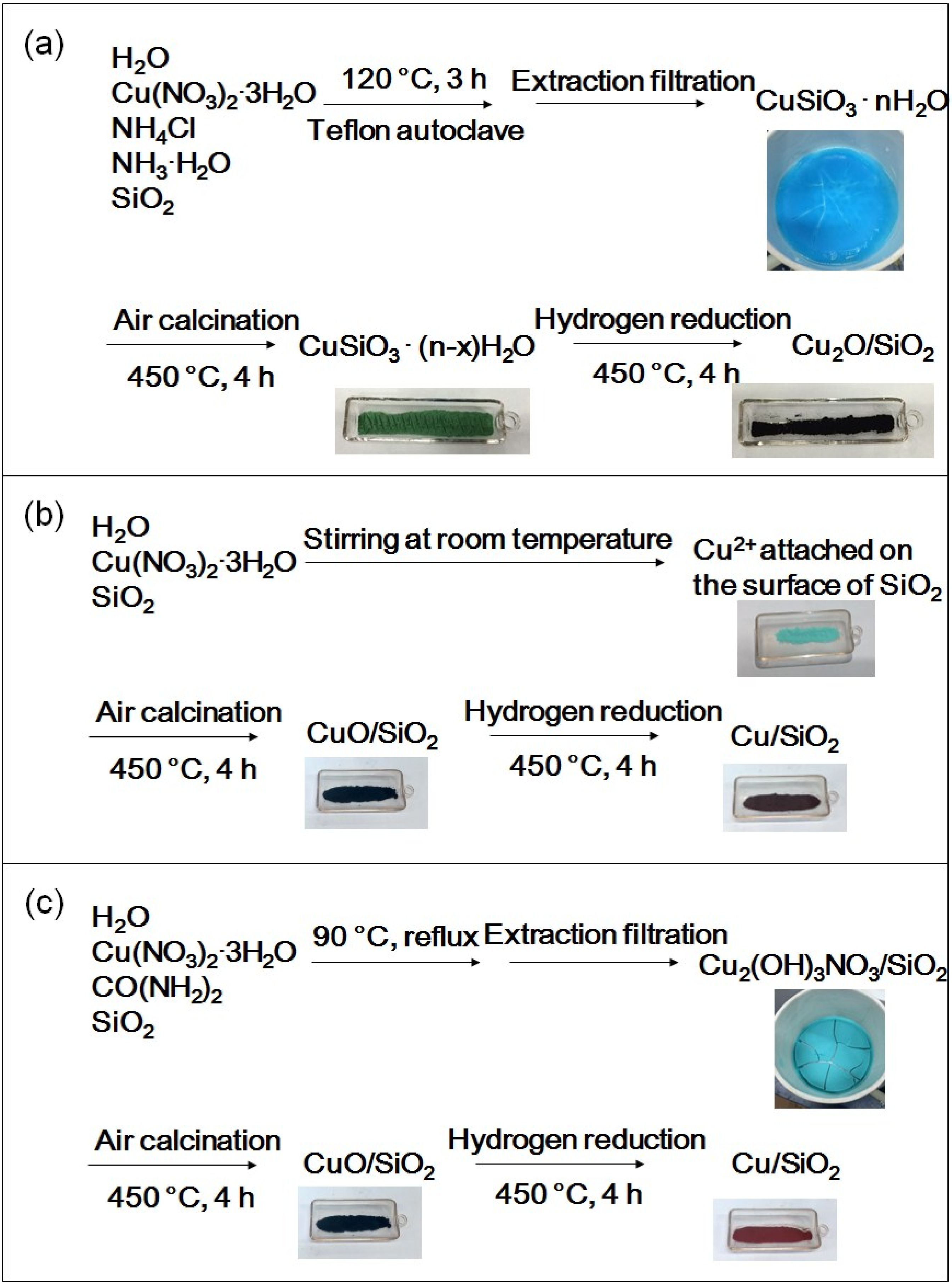

Fig. S8 The changes of Cu species on three Cu/SiO_2 catalysts during the preparation processes synthesized by (a) hydrothermal method, (b) impregnation method, and (c) deposition-precipitation method.

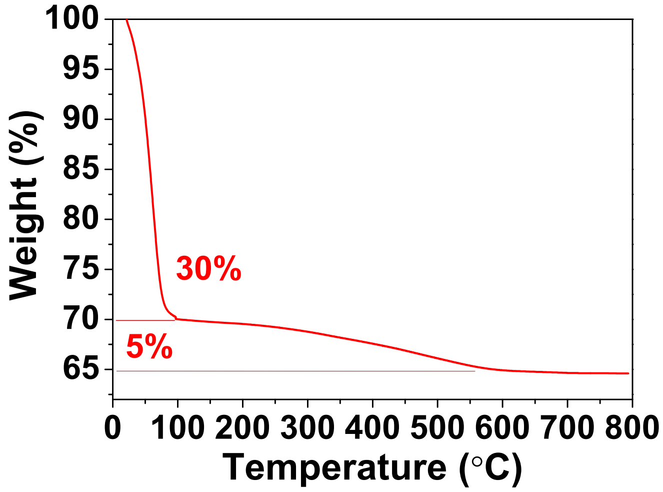

Fig. S9 The TGA profile of hydrothermally prepared Cu/SiO_2-HT (before calcination).

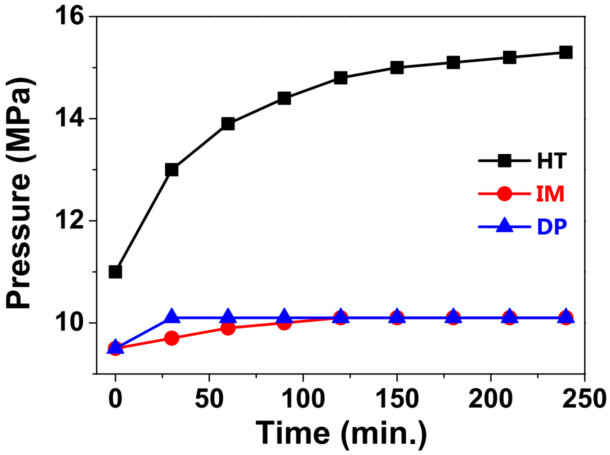

Fig. S10 Changed pressures were recorded in the autoclave with the varying time during the process of selective hydrogenation at 240 ˚C using three Cu/SiO$_2$ catalysts prepared by different methods. Reaction conditions: methyl laurate (0.3 g), methanol (40 mL), Cu/SiO$_2$ catalysts (0.2 g), 240 ˚C, 4 h, N$_2$ (2 MPa), stirring at 400 rpm.

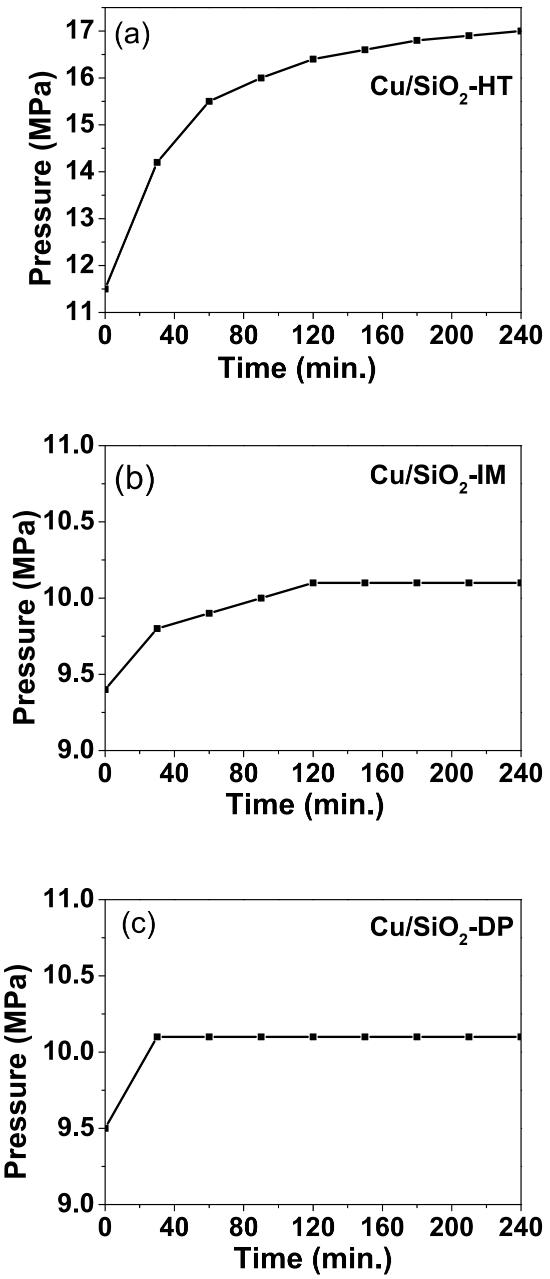

Fig. S11 Comparison of the recorded pressure changes for methanol decomposition over (a) Cu/SiO$_2$-HT, (b) Cu/SiO$_2$-IM and (c) Cu/SiO$_2$-DP. Reaction conditions: methanol (40 mL), catalysts (0.2 g), 240 °C, N$_2$ (2.0 MPa), stirring at 400 rpm.

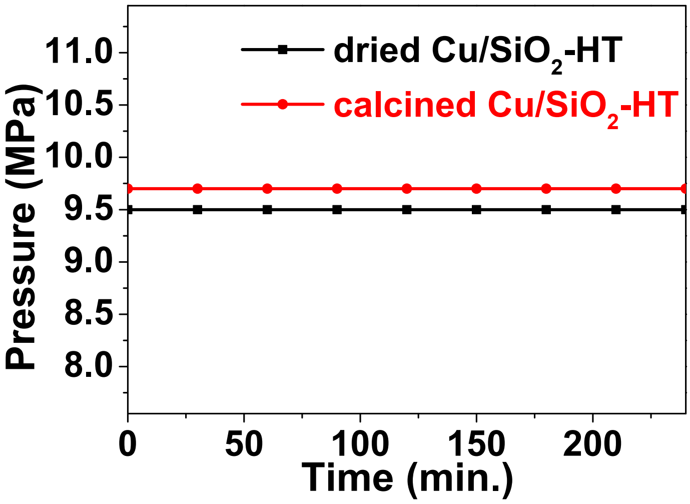

Fig. S12 The recorded pressure changes for methanol decomposition over Cu/SiO$_2$ after (a) drying and (b) calcination. Reaction conditions: methanol (40 mL), catalysts (0.2 g), 240 °C, N$_2$ (2.0 MPa), stirring at 400 rpm.

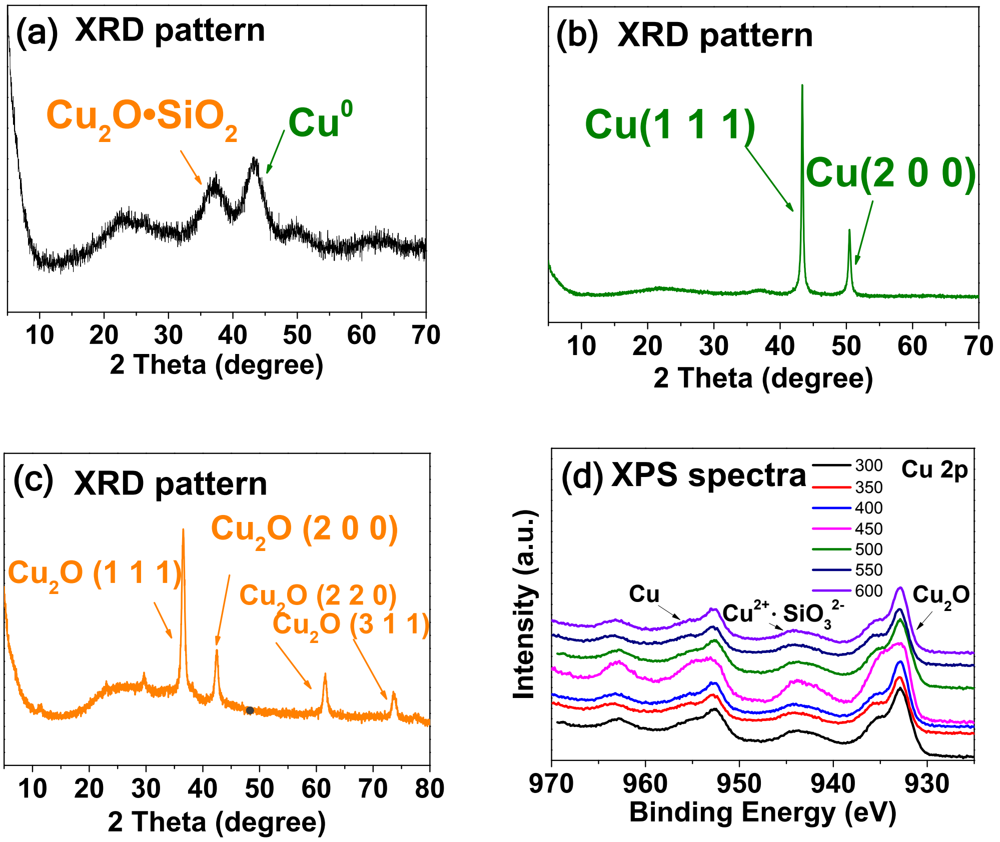

Fig. S13 The XRD patterns of (a) Cu/SiO$_2$-HT, (b) washed Cu/SiO$_2$-HT sample by 2 wt% HCl solution, (c) re-calcinated Cu/SiO$_2$-HT sample, and (d) the XPS spectra of Cu/SiO$_2$-HT samples by different reduction temperatures.

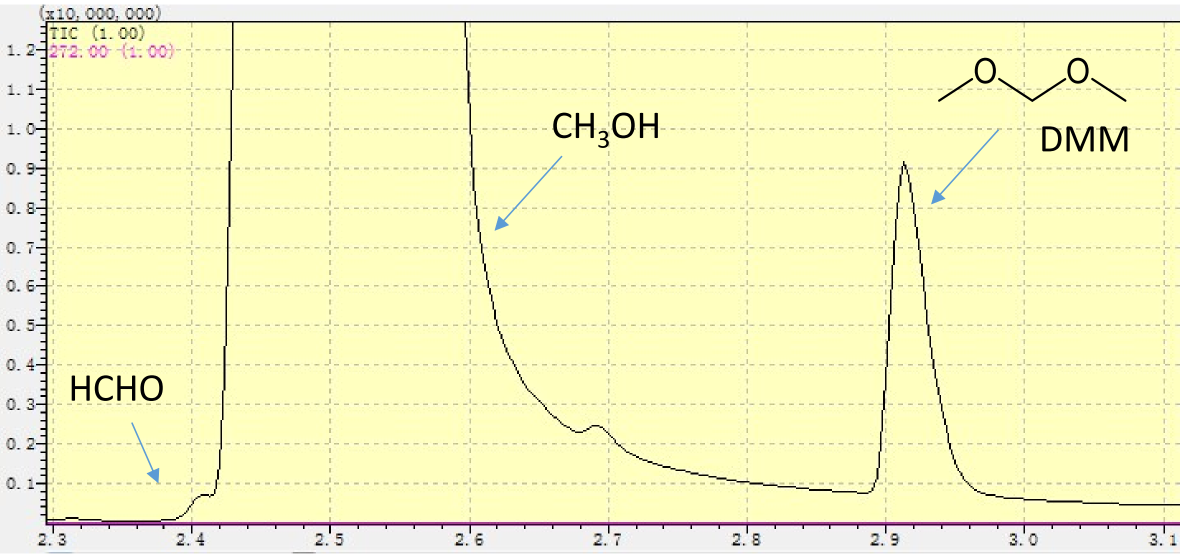

Fig. S14 The formed dimethoxy methane and formaldehyde products from methanol decomposition detected by GC-MS. Reaction conditions: methanol (40 mL), Cu/SiO_2-HT (0.2 g), 240 ˚C, 4 h, N_2 (2.0 MPa), stirring at 400 rpm.

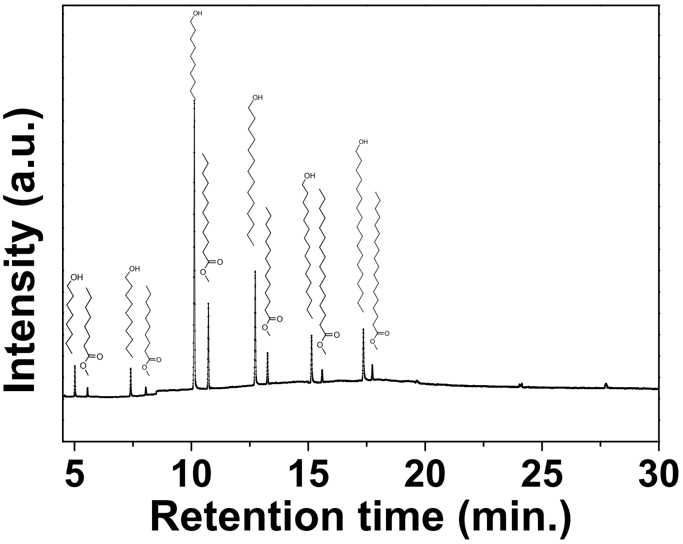

Fig. S15 The product distributions for coconut oil conversion detected by GC-MS. Reaction conditions: coconut oil (1.0 g), Cu/SiO_2-HT (0.2 g), methanol (40 mL), 240 ˚C, 4 h, N_2 (2.0 MPa), stirring at 400 rpm.

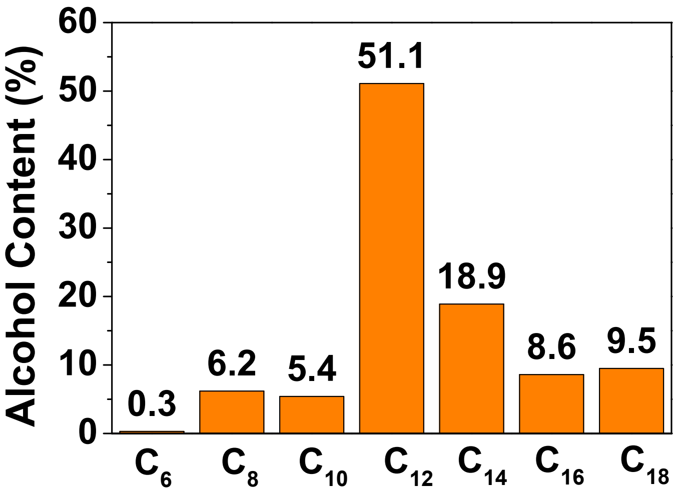

Fig. S16 The fatty acid compositions in coconut oil raw material detected by transesterification with methanol. Reaction conditions: coconut oil (1.0 g), CaO (1 g), methanol (100 mL), 80 °C, 2 h.

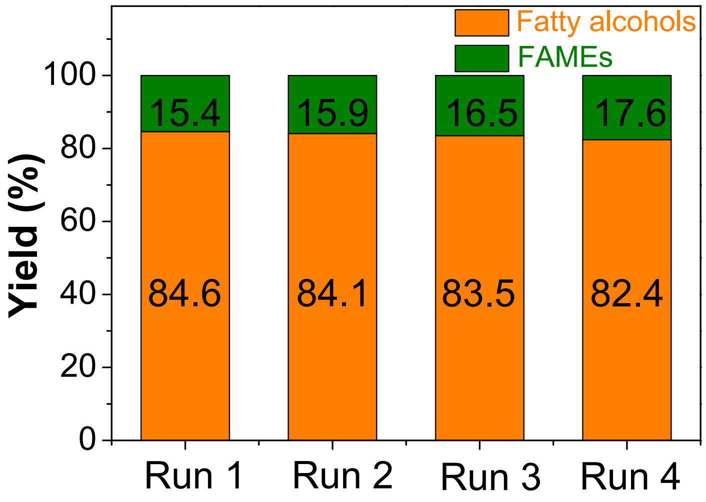

Fig. S17 Recycling test of the hydrogenation of coconut oil over Cu/SiO_2-HT (treated by sequential air-calcination and hydrogen-reduction). Reaction conditions: coconut oil (1.0 g), Cu/SiO_2-HT (0.2 g), methanol (40 mL), 240 ˚C, 4 h, N_2 (2.0 MPa), stirring at 400 rpm.

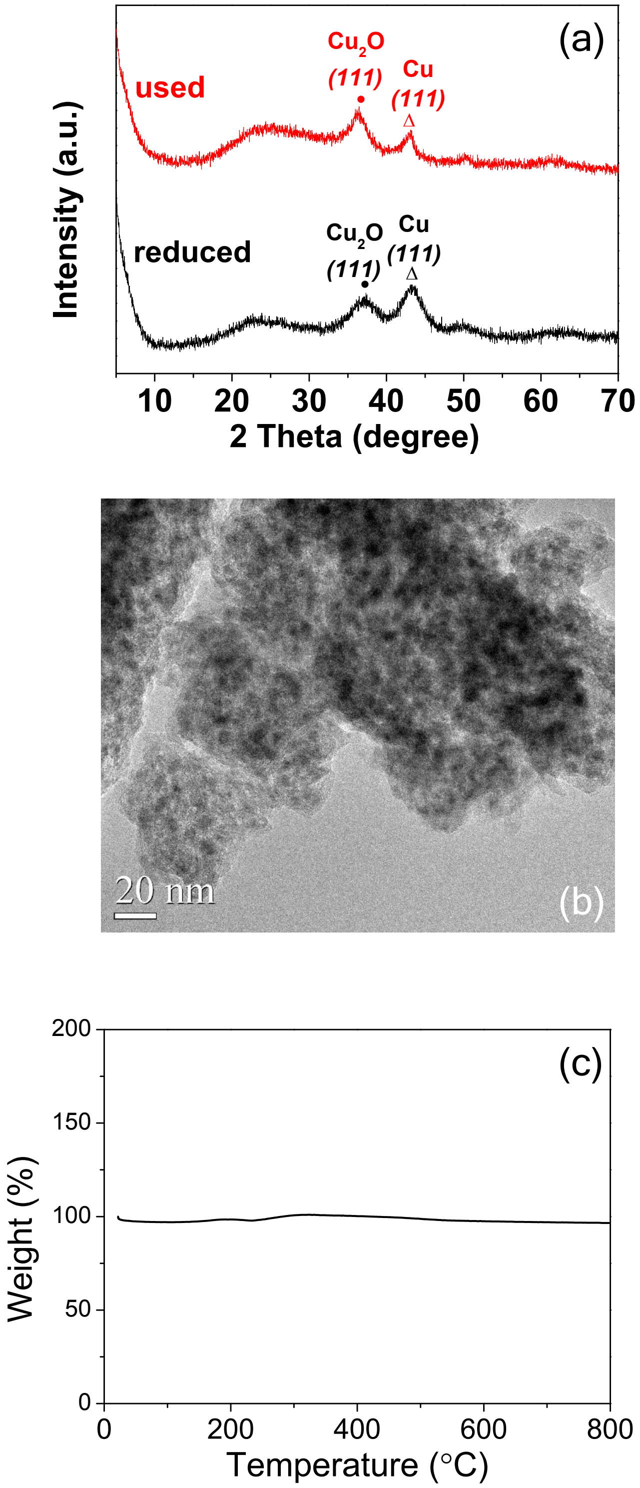

Fig. S18 (a) XRD patterns, (b) TEM image and (c) TGA measurement of used Cu/SiO_2-HT after reaction.