

Electronic Supporting Information

Achieving efficient and robust catalytic reforming on dual-sites of Cu species

Kui Ma, Ye Tian, Zhi-Jian Zhao, Qingpeng Cheng, Tong Ding, Jing Zhang, Lirong Zheng, Zheng Jiang, Takayuki Abe, Noritatsu Tsubaki, Jinlong Gong*, and Xingang Li*

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Experimental Section

1. Catalyst preparation

Synthesis of Cu-AE catalyst. Cu-AE catalysts were prepared by the vacuum-rotary ammonia evaporation (VR-AE) method described as follows. Firstly, a certain amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 150 mL deionized water with the adding of 28% ammonia aqueous solution (20 mL). Meanwhile, SBA-15 (2 g) was dissolved in 40 mL deionized water under ultrasonic treatment for 0.5 h. Thereafter, the suspension of SBA-15 was added to the copper ammonia complex solution and stirred for another 4 h (pH=11). Then the mixture was transferred to rotary evaporators preheated at 60 °C, allowing for filling of SBA-15 channels, the evaporation of ammonia and the deposition of copper species. Consequently, the evaporation process was terminated when pH value decreased to 7. After centrifugation and washing, the blue precipitate was dried at 80 °C overnight (denoted as as-prepared catalysts), and then calcined at 450 °C for 4 h. The final calcined catalysts were denoted as xCu-AE, where x ($x = 10, 20, 25, 30$ and 40) represents the content of Cu by weight.

Synthesis of 25Cu-IM catalyst. For comparison, the Cu-IM catalyst containing 25 wt.% of Cu was prepared by wet impregnation method using rotary evaporators with an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ on SBA-15. The conditions of drying and calcinations were the same as those of the Cu-AE catalysts, and finally denoted as 25Cu-IM.

Synthesis of Cu-SP and Cu-SP-N catalysts. Differently from the above wet chemical method, a facile physical-sputtering method¹ was introduced to synthesize the Cu-SP catalyst. The metallic copper NPs were sputtered onto the SBA-15 powder with a metallic Cu sputtering target (purity 99.9%, $5 \times 10 \text{ cm}^2$, Toshima Ltd.) in polygonal barrel-sputtering equipment. The vacuum chamber was carefully evacuated to $9.9 \times 10^{-4} \text{ Pa}$, followed by introducing pure Ar (purity: 99.995%) at a flow rate of 30 mL min^{-1} into the chamber until the pressure reached 2.0 Pa. Generated Ar plasma was used to attack the Cu target and to sputter Cu clusters onto the SBA-15 surface (input power 200 W, frequency $13.56 \text{ MHz} \pm 5 \text{ KHz}$, rotating rate 3.5 rpm). The whole experiment took 100 min, and around 5.0 wt.% of Cu (detected by the X-ray fluorescence spectrometry) was deposited onto the SBA-15 powder. Thereafter, a pure N_2 flow

(30 mL min⁻¹) was gradually introduced into the cavity barrel to reach the atmospheric pressure, and kept for 1 h to stabilize the metallic Cu-supported sample. The sample was calcined at 450 °C for 4 h in N₂ to obtain the Cu-SP catalyst. The Cu-SP-N catalyst was prepared by the subsequent treatment of Cu-SP. After pretreated with 10% H₂/N₂ (30 mL min⁻¹), the Cu-SP catalyst was exposed in 50% N₂O/N₂ flow (30 mL min⁻¹) to ensure the surface copper completely oxidized to Cu⁺.

Synthesis of 25Cu-SiO₂ catalyst. In addition, the 25Cu-SiO₂ catalyst was also prepared by VR-AE method. The silica sol JA-25 (Qingdao Grand Chemical Co., 25 wt.%) instead of SBA-15 was used as silicon source, and the amount of Cu(NO₃)₂·3H₂O was adjusted to yield 25 wt.% of Cu in the final calcined catalyst.

Synthesis of traditional Cu/ZnO/Al₂O₃ catalyst. The Cu/ZnO/Al₂O₃ catalyst was prepared by a conventional co-precipitation method according to the industrial catalysts.² Contents of CuO, ZnO and Al₂O₃ in the catalyst were 63 wt.%, 27 wt.% and 10 wt.%, respectively.

2. Materials characterizations

Transmission electron microscopy (TEM) images were taken using a JEOL JEM 2100F system at an accelerating voltage of 200 kV equipped with a field emission gun. Temperature-programmed reduction (TPR) was carried out on a Thermo-Finnigan TPDRO 1100, and 30 mg of catalysts was heated in 5% H₂/N₂ (30 mL min⁻¹) at a heating rate of 10 °C min⁻¹ up to 900 °C. X-ray photoelectron spectroscopy (XPS) analysis was carried out on the Perkin-Elmer PHI-1600 ESCA spectrometer using Al K α as radiation source and calibrated by C 1s peak. The metallic Cu surface areas and copper dispersion were performed by N₂O titration³ at Thermo-Finnigan TPDRO 1100 (50% N₂O/N₂, 30 mL min⁻¹). The Cu⁺ surface areas were quantified using irreversible CO adsorption isotherms, collected with a chemisorption module of the Micromeritics ASAP 2020 instrument. Textual properties of the catalysts were determined by a nitrogen adsorption-desorption method using a Quantachrome QuadraSorb SI instrument at -196 °C. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet Nexus spectrometer in the range of 4000 to 400 cm⁻¹, and the 4 cm⁻¹ resolution, 32 scans were recorded for each spectrum. UV-Raman spectra of the catalysts were

recorded on the Raman spectrometer (Thermo, DXR Model) using an excitation laser wavelength of 325 nm. X-ray diffraction (XRD) measurements were performed on a Bruker D8 diffractometer operating at 200 mA and 40 kV, employing the graphite filtered Cu K α as the radiation source. For low-angle analysis, the data were collected in reflection mode in the 2θ range from 0.5 to 5° with a step of 0.01°. For wide-angle analysis, the data were collected in the 2θ range from 10 to 80° with a step of 0.05°. For the XRD experiment upon reduction, the catalysts were pre-reduced in 10% H₂/N₂ at 400 °C for 1 h, and then protected with N₂ to prevent their contact with air before collection. The crystallite size (d) of copper was calculated by X-ray broadening technique using the Scherrer's equation:

$$d = \frac{0.89 \lambda}{B \cos \theta} \quad (\text{Eq.1})$$

Here, λ is the wavelength of the radiation source (0.15418 nm); B is the half width of the strongest diffraction peak in the radian unit; and θ is its diffraction angle.

3. X-ray absorption data collection, analysis, and modelling

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were performed at the XAFS station in the 1W1B beamline of Beijing Synchrotron Radiation Facility (BSRF) and BL14W1 of Shanghai Synchrotron Radiation Facility (SSRF). The *ex-situ* Cu K -edge absorption spectra of the catalysts were collected in transmission mode at room temperature (RT). For the *in-situ* reduction experiment, 5% H₂/N₂ was introduced and then the sample chamber was heated from RT to 650 °C. The spectra were collected at RT, 100, 150, 180, 200, 220, 240, 250, 300, 350, 400, 450, 500, 550, 600 and 650 °C by the mode of Quick-XAFS (QXAFS). Each spectrum was collected within 30 s. The *in-situ* steady-state XAFS spectra were collected after the reduction by 10% H₂/N₂ at 400 °C and subsequently switched to the reactive atmospheres. Each spectrum was collected under the normal mode and the sampling time was 0.5 h. During the *in-situ* experiments, a copper foil was employed for energy calibration. To compensate for the diminishing amplitude due to the decay of photoelectron wave, the back-subtracted EXAFS function was converted into k space and weighted by k^3 . The Fourier transforming of the k^3 -weighted EXAFS data was performed

in the range of $k = 3\text{--}11 \text{ \AA}^{-1}$ using a Hanning window function to get the radial structure function (RSF) of Cu *K*-edge. The XANES spectra of metallic Cu (Cu foil), Cu₂O, CuO and copper phyllosilicates were employed as the references. All of the data are analyzed by the software of Athena.

4. *In-situ* DRIFTS data collection and analysis

The *in-situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was conducted using the Harrick HVC high temperature transmission cell. This unit operates with a Thermo Nicolet Nexus FTIR spectrometer equipped with a mercury cadmium telluride (MCT) detector. For the *In-situ* DRIFTS of CO adsorption experiment, the loaded catalyst was firstly heated to 400 °C under a flow of 10% H₂/N₂ (30 mL min⁻¹) to reduce the catalyst for 1 h. Subsequently, pure He was introduced into the cell for 1 h to remove the residual H₂/N₂ in the cell and H₂ adsorbed on the catalyst, followed by cooling to RT. After a 0.5 h holding time, the background spectra were recorded under this condition. A pure CO flow (30 mL min⁻¹) was then introduced into the cell to achieve saturation adsorption. Finally, the steady-state CO adsorption at RT was taken after 1 h of sweeping with pure He. For the *in-situ* DRIFTS experiments under reaction conditions, both reactants were dosed via saturators in a N₂ stream and their concentrations in the combined stream were calculated based on the Antoine equation. Each catalyst was *in-situ* reduced by 10% H₂/N₂ at 400 °C for 1 h and then cooled to 230 °C in N₂ to take the background spectra. The samples were then exposed to 5% reactant ($n_{\text{CH}_3\text{OH}}/n_{\text{H}_2\text{O}} = 1/2$, 50 mL min⁻¹) to achieve steady-state conditions. For the time-dependent *in-situ* DRIFTS experiments, the methanol adsorption was performed in the atmosphere of 5 % methanol in N₂ at 230 °C. Thereafter, 5% reactant ($n_{\text{CH}_3\text{OH}}/n_{\text{H}_2\text{O}} = 1/2$) diluted by N₂ was introduced to the cell (50 mL min⁻¹). All of the DRIFTS spectra were collected at a resolution of 4 cm⁻¹ after 32 scans, and then transformed into the Kubelka-Munk function.

5. TPSR-MS experiments design

The experiments of temperature programmed surface reaction-mass spectroscopy (TPSR-MS) were performed on a home-made setup using Hiden HPR-20 mass spectrometer with a Quartz Inlet Capillary (QIC) system to monitor the reactor effluents. 5% reactant ($n_{\text{CH}_3\text{OH}}/n_{\text{H}_2\text{O}} = 1/2$)

in He was used as the feeding gas, and the flow rate and reaction temperature were 50 mL min⁻¹ and 230 °C, respectively. The effluent was collected into the ionization chamber of the MS using the QIC system. The working pressure of the ionization chamber was 5×10^{-6} Pa.

6. Catalytic activity tests and microkinetics calculations

Catalytic testing in steam reforming was performed in a continuous-flow fixed-bed reactor. Each granulated catalyst (500 mg, copper catalysts: γ -Al₂O₃=2:1) was placed into the reactor and reduced in 10% H₂/N₂ at 400 °C for 1 h. The reactant consisting of 50% H₂O (g) and 12.5% DME (S/C = 2/1) was at a constant gas hourly space velocity (GHSV) of 18,000 h⁻¹, with 37.5% N₂ as the equilibrium gas. Compositions of inlet and outlet gases were analyzed by an online gas chromatograph (GC) (Agilent 7890A).

The kinetics studies were conducted in a recycle fixed-bed reactor (Fig. S17). The very thin layer of tiled catalysts and the recirculation of the outlet gas are in order to eliminate the gradient in the reactor. Before the experiments, the internal and external diffusion limitations were eliminated. The reactant ($n_{\text{CH}_3\text{OH}}/n_{\text{H}_2\text{O}} = 1/2$) was pumped at a constant gas hourly space velocity (GHSV) of 90,000 h⁻¹, with N₂ as the equilibrium gas. Compositions of inlet and outlet gases were analyzed by an online GC (Agilent 7890A). To ensure the study in the kinetics region, the tests were conducted at 230 °C, where the CH₃OH conversion was below 20%. The experimental reaction rates were measured by adjusting the partial pressure of CH₃OH. Three separate samples were taken and the results were averaged for each experimental point.

7. Stability evaluation and thermal treatment experiment

Stability tests for the catalysts were conducted at 400 °C, and the feed gas was the same as that for the activity tests. The thermal treatment experiments began with a stability test at 400 °C for 30 h with a GHSV of 18,000 h⁻¹. Then the temperature was raised to 450 °C with a doubling GHSV of 36,000 h⁻¹ for 12 h. Subsequently, the stability was re-evaluated over the above catalyst for another 30 h at 400 °C with a GHSV of 18,000 h⁻¹.

8. Methods for the catalytic performance, reaction rate (*r*) and turnover frequency (TOF).

The DME conversion and the yield of H₂ were calculated as follows:

$$X_{DME} = \frac{F_{DME,in} - F_{DME,out}}{F_{DME,in}} \times 100\% \quad (\text{Eq. 2})$$

$$Y_{H_2} = \frac{F_{H_2}}{F_{DME,in}} \times \frac{1}{6} \times 100\% \quad (\text{Eq. 3})$$

The selectivity to C1 species are defined as follows:

$$S_{Ci} = \frac{F_{Ci}}{\sum F_{Ci}} \times 100\% \quad (\text{Eq. 4})$$

The reaction rate (*r*) was calculated as follows:

$$r = \frac{F_{DME,in} \times X_{DME}}{W_{Cat} \times n_{Sites}} \quad (\text{Eq. 5})$$

Turnover frequency (TOF) was calculated as moles of DME reacted or H₂ formed per mole of surface active sites:

$$TOF_{DME} = \frac{F_{DME,in} \times X_{DME}}{W_{Cat} \times n_{Sites}} \quad (\text{Eq. 6})$$

$$TOF_{H_2} = \frac{6 \times F_{DME,in} \times Y_{H_2}}{W_{Cat} \times n_{Sites}} \quad (\text{Eq. 7})$$

Where $F_{DME,in}$ is the influent molar flow rate of DME; $F_{DME,out}$ represent the influent and effluent molar flow rates of DME; X_{DME} is the DME conversion; Y_{H_2} is the H₂ yield; F_{H_2} is the effluent molar flow rate of H₂, and F_{Ci} is the effluent molar flow rate of C1-containing products, including CH₃OH, CH₄, CO, and CO₂; W_{Cat} is the weight of the loaded catalyst; n_{Sites} is the number of surface active sites in mole.

9. Methods for microkinetic model

The entire catalysis cycle of our “dual-sites” reaction pathway for methanol SR is given schematically in Figure 4B. Adopting the Hougen-Watson (HW) formalism, based on the Langmuir-Hinshelwood (LH) adsorption isotherms, the kinetics of this “dual-sites” catalysis cycle can be established using the following assumptions:

- (1) The dehydrogenation of the methoxy group is the rate-determining step; all of the other elemental reactions are in thermodynamic equilibrium.
- (2) Oxygenates competitively and mostly adsorb in one monolayer on surface Cu⁺ sites, whereas the H₂ dissociatively adsorbs on surface Cu⁰ sites.

(3) Only adsorbates observed in the DRIFTS spectra are considered in the adsorption term; in addition, the adsorption of the carbon dioxide is taken into account.

(4) Measuring in the low-conversion regime, and the reverse reaction is negligible.

The microkinetic rate equation of methanol SR is then given by the following equation, in which the index MDH means methoxy dehydrogenation:

$$\begin{aligned}
 r_{\text{MDH}} &= -\frac{\partial p_{\text{MeOH}}}{\partial t} = k_{\text{MDH}} c_{\text{CH}_3\text{O}(\text{Cu}^+)} c_{\text{Cu}^0} \\
 &= \left(k_{\text{MDH}} C_{\text{S}_{\text{Cu}^+}}^T + C_{\text{S}_{\text{Cu}^0}}^T K_{\text{CH}_3\text{O}(\text{Cu}^+)}^* (p_{\text{CH}_3\text{OH}}/p_{\text{H}_2}^{1/2}) \right) / \\
 &\quad \left(\left(1 + K_{\text{CH}_3\text{O}(\text{Cu}^+)}^* (p_{\text{CH}_3\text{OH}}/p_{\text{H}_2}^{1/2}) + K_{\text{OH}(\text{Cu}^+)}^* (p_{\text{H}_2\text{O}}/p_{\text{H}_2}^{1/2}) + K_{\text{HCOO}(\text{Cu}^+)}^* p_{\text{CO}_2} p_{\text{H}_2}^{1/2} + \right. \right. \\
 &\quad \left. \left. K_{\text{CO}_2(\text{Cu}^+)}^* p_{\text{CO}_2} \right) \left(1 + K_{\text{H}(\text{Cu}^0)}^{1/2} p_{\text{H}_2}^{1/2} \right) \right) \quad (\text{Eq. 8})
 \end{aligned}$$

Where k_{MDH} is the rate constant and C_{S}^T represents the concentration of Cu^0 or Cu^+ adsorption sites. Because these values can not be individually determined by parameter fitting, their product k^* was taken for the following process:

$$k^* = k_{\text{MDH}} C_{\text{S}_{\text{Cu}^+}}^T + C_{\text{S}_{\text{Cu}^0}}^T \quad (\text{Eq. 9})$$

The combined adsorption constants K^* given in the adsorption term are defined as

$$K_{\text{CH}_3\text{O}(\text{Cu}^+)}^* = \frac{K_{\text{CH}_3\text{OH}(\text{Cu}^+, \text{Cu}^0)}}{K_{\text{H}_2(\text{Cu}^0)}^{1/2}} \quad (\text{Eq. 10})$$

$$K_{\text{HCOO}(\text{Cu}^+)}^* = \frac{K_{\text{CO}_2(\text{Cu}^+)} K_{\text{H}_2(\text{Cu}^0)}^{1/2}}{K_{\text{HCOO}(\text{Cu}^+, \text{Cu}^0)}^*} \quad (\text{Eq. 11})$$

$$K_{\text{OH}(\text{Cu}^+)}^* = \frac{K_{\text{H}_2\text{O}(\text{Cu}^+, \text{Cu}^0)}}{K_{\text{H}_2(\text{Cu}^0)}^{1/2}} \quad (\text{Eq. 12})$$

The kinetics parameters (rate constants and adsorption equilibrium constants) in Table S6 are obtained by fitting data under different reaction conditions using the Powell method⁴. They were determined through a nonlinear regression method using eq (7), in which $r_{i,\text{exp}}$ represents the experimental rate and $r_{i,\text{pred}}$ stands for the predicted result of rates.

$$RSS = \sum_{i=1}^2 (r_{i,\text{exp}} - r_{i,\text{pred}})^2 \quad (\text{Eq. 13})$$

To obtain appropriate kinetics model, the model was examined with the same criterion:

- (1) The reaction rate constant and the adsorption equilibrium constant must be positive numbers;
- (2) The reaction rate constant and adsorption equilibrium constant should follow the Arrhenius (eq (8)) and Van't Hoff (eq (9)) equations, respectively.
- (3) The model should have a sufficiently low residual sum of squares between the experimental and predicted rates.

$$k = k_0 e^{-E_A / (RT)} \quad (\text{Eq. 14})$$

$$K = K_0 e^{-\Delta H_{\text{ads}} / (RT)} \quad (\text{Eq. 15})$$

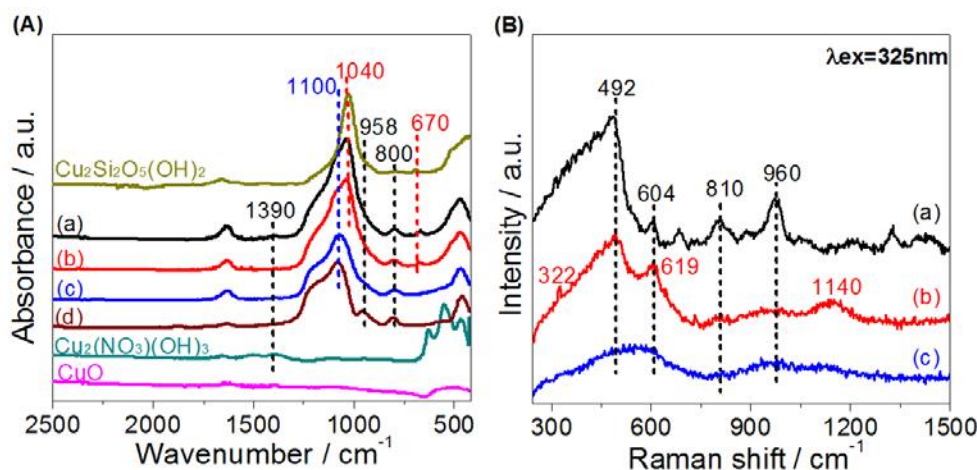


Figure S1. FTIR and UV-Raman Characterizations. (A) FTIR spectra of the (a) as-prepared, (b) calcined and (c) reduced 25Cu-AE, (d) SBA-15, and the reference compounds; (B) UV-Raman spectra of (a) the pristine SBA-15, (b) calcined and (c) reduced 25Cu-AE.

Figure S1A shows the FTIR spectra during the preparation procedures of 25Cu-AE. The presence of δ_{OH} and $\nu_{\text{Si-O-Si}}$ vibration at 670 and 1040 cm^{-1} suggests the existence of $\text{Cu}_2\text{Si}_2\text{O}_5(\text{OH})_2$. Obviously, the $\text{Cu}_2\text{Si}_2\text{O}_5(\text{OH})_2$ phase both existed in the as-prepared and calcined catalysts. After reduction, the unrecoverable $\equiv\text{Si-OH}$ peaks imply the transformation of $-\text{Si-O-Cu}^{2+}-\text{O-Si}-$ to $-\text{Si-O-Cu}^+$, simultaneously leaving abundant dangling bonds $-\text{O-Si}-$ (planar defects). In Figure S1B, the Raman spectrum of the pristine SBA-15 represents the main peaks at around 492, 604 and 810 cm^{-1} , which could be assigned to the vibrations of three and four silane rings and siloxane linkage. The spectrum of 25Cu-AE presents two weak peaks at 322 and 619 cm^{-1} , belonging to the CuO phase⁵. The peak at ca. 960 cm^{-1} is ascribed to the vibrations of the $\equiv\text{Si-OH}$ groups^{6,7}, the disappearance of which in 25Cu-AE also verifies the formation of $-\text{Si-O-Cu}^{2+}-\text{O-Si}-$ groups on the surface. Moreover, the peak at ca. 1140 cm^{-1} is related to the copper sites in SBA-15 framework ($-\text{Si-O-Cu}^{2+}-\text{O-Si}-$ groups in copper phyllosilicates), the disappearance of which after reduction implies the cleavage of Cu-O bond in the $-\text{Si-O-Cu}^{2+}-\text{O-Si}-$ groups in the reduced 25Cu-AE catalyst. No apparent Raman bands were observed in the reduced 25Cu-AE catalyst, which verifies the highly defective structure of the reduced catalysts⁸.

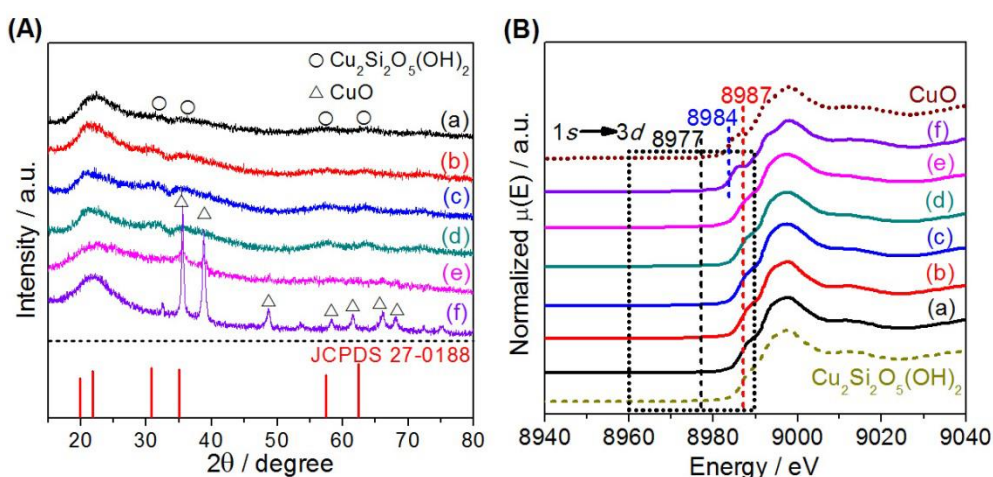


Figure S2. XRD and XAFS analysis. XRD patterns (A) and Cu K-edge XANES spectra (B) of the calcined catalysts: (a) 10Cu-AE, (b) 20Cu-AE, (c) 25Cu-AE, (d) 30Cu-AE, (e) 40Cu-AE, and (f) 25Cu-IM.

Figure S2B shows the normalized XANES spectra for the references and catalysts. The spectra of the Cu-AE catalysts and $\text{Cu}_2\text{Si}_2\text{O}_5(\text{OH})_2$ reference both show the higher edge position than those of CuO reference and the Cu-IM catalyst. The peak at ca. 8984 eV in CuO is attributed to $1s \rightarrow 4p$ transition with shakedown contributions⁹ and characteristic of tetragonal Cu^{2+} compounds. It shifted up in energy by 3 eV to ca. 8987 eV in $\text{Cu}_2\text{Si}_2\text{O}_5(\text{OH})_2$, suggesting a different ligand charge transfer. The shoulder at ca. 8994 eV in $\text{Cu}_2\text{Si}_2\text{O}_5(\text{OH})_2$, corresponding to the edge absorption due to multiple scattering effects, indicates an altered Cu local geometric structure compared with CuO .

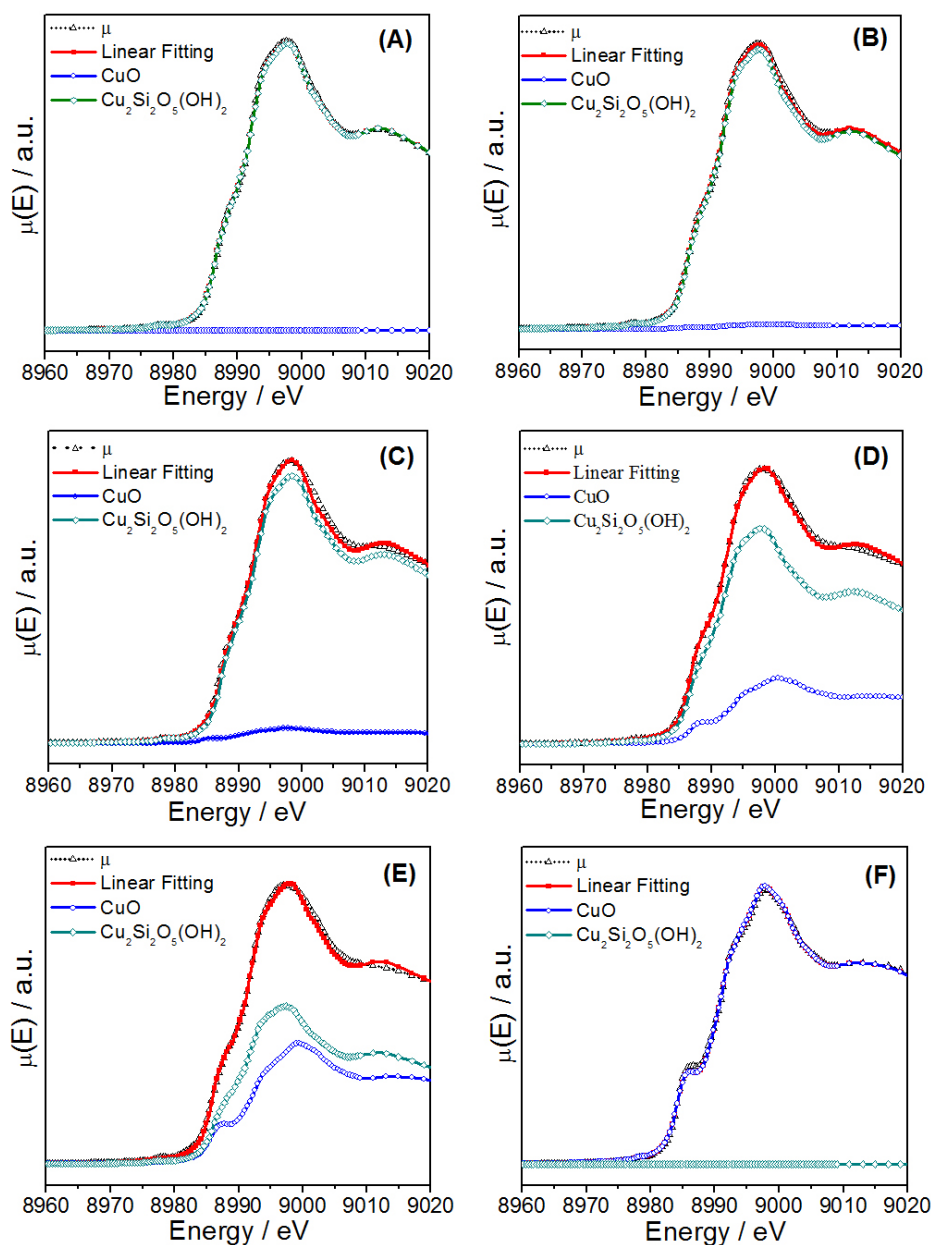


Figure S3. Linear combination fitting (LCF) results. XANES spectra and the corresponding fitting results of the (A) 10Cu-AE, (B) 20Cu-AE, (C) 25Cu-AE, (D) 30Cu-AE, (E) 40Cu-AE, and (F) 25Cu-IM catalysts.

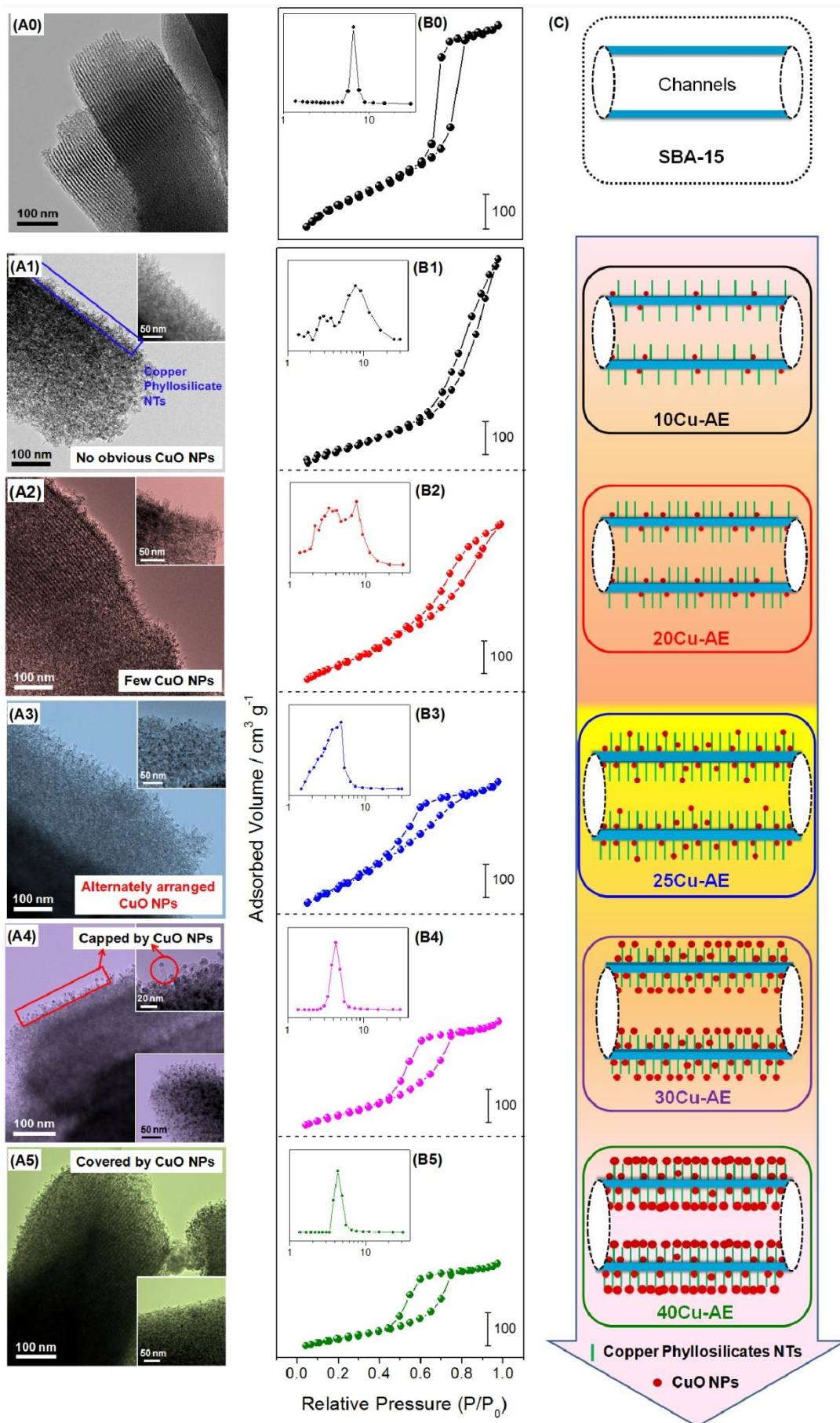


Figure S4. Formation of the “Cu surrounded by the Cu₂O” structure. (A0-A5) TEM images of the SBA-15 and xCu-AE catalysts (from top to bottom, x = 10, 20, 25, 30, and 40). The insets in (A1-A5) are the corresponding images with higher magnification to each catalyst; (B0-B5) N₂ adsorption-desorption isotherms and pore size distribution calculated by BJH equation from desorption branch (insets); and (C) Schematic illustration for the spatial arrangement of the copper phases.

A typical TEM image of the 10Cu-AE in Figure S4A1 shows loosely arranged Cu₂Si₂O₅(OH)₂ NTs, and few CuO NPs were observed. Then, the Cu₂Si₂O₅(OH)₂ NTs grew tightly and dotted with some CuO NPs in the 20Cu-AE (Figure S4A2). The obtained 25Cu-AE shows a well-proportioned Cu₂Si₂O₅(OH)₂ NTs and CuO NPs (Figure S4A3). When the copper loading continued to increase, the amount of the CuO NPs continuously increased. And, the head of Cu₂Si₂O₅(OH)₂ NTs was gradually capped (Figure S4A4), and eventually covered (Figure S4A5) by CuO NPs.

The pore structure of the Cu-AE catalysts was characterized by nitrogen adsorption-desorption measurements (Figure S4B), and the insets are the pore size distributions. Obviously, the pores at ~7 nm represent the mesoporous channels of SBA-15. The pores at 2-3 nm are widely reported as the slit-shaped pores that are typical for copper phyllosilicates.¹⁰ Initially, the pores at ~7 nm derived from the well-ordered channels of SBA-15, increased slightly with a wider distribution, which is contributed by the corroded silica walls during the preparation process. Simultaneously, the pore size distribution at 2-3 nm appeared, indicating the formation of Cu₂Si₂O₅(OH)₂. Then, the new pore at ~ 4.3 nm in the Cu-AE catalysts with the higher Cu loadings (e.g., 25Cu-AE, 30Cu-AE and 40Cu-AE) are originated from the copper loading in the mesopore channels, which can be supported by the low-angle XRD results.

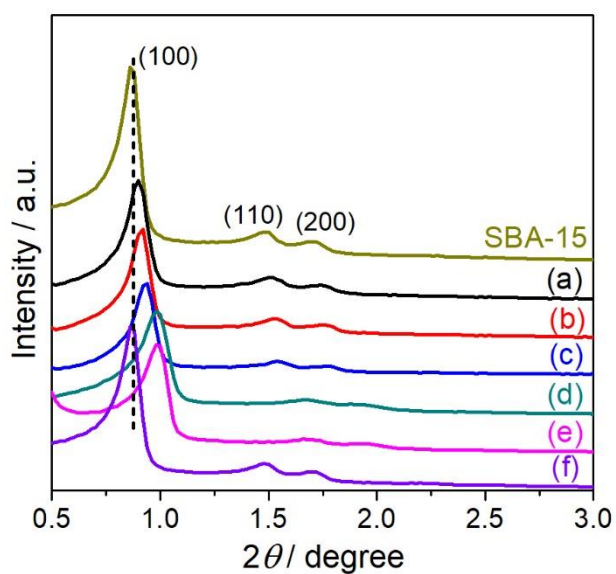


Figure S5. Low-angle XRD patterns of the calcined catalysts. Low-angle XRD patterns between 0.5 and 3° for SBA-15 and calcined catalysts: (a) 10Cu-AE, (b) 20Cu-AE, (c) 25Cu-AE, (d) 30Cu-AE, (e) 40Cu-AE, and (f) 25Cu-IM catalysts.

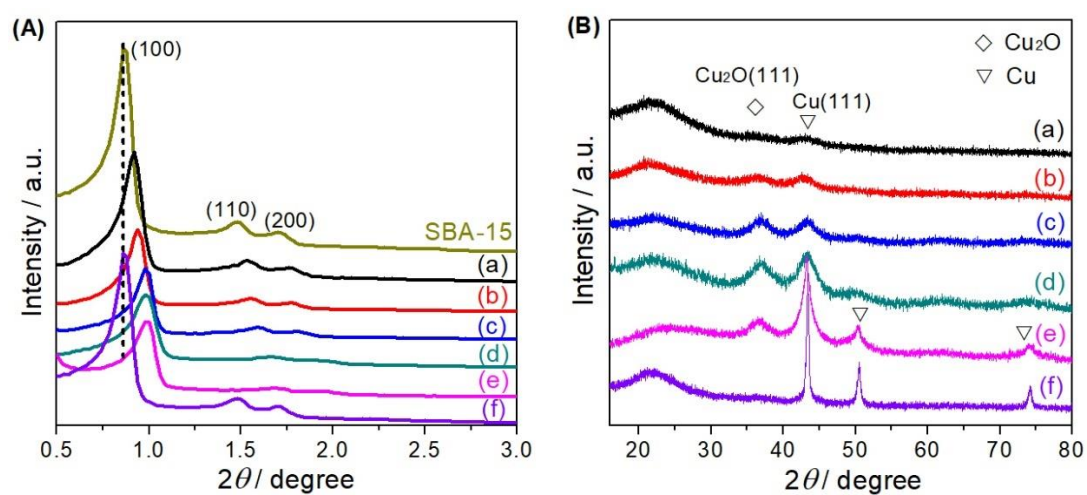


Figure S6. Crystalline phase of the catalysts after the reduction in 10% H_2/N_2 at 400 °C for 1 h. (A) Low-angle and (B) wide-angle XRD patterns for SBA-15 and (a) 10Cu-AE, (b) 20Cu-AE, (c) 25Cu-AE, (d) 30Cu-AE, (e) 40Cu-AE, and (f) 25Cu-IM catalysts.

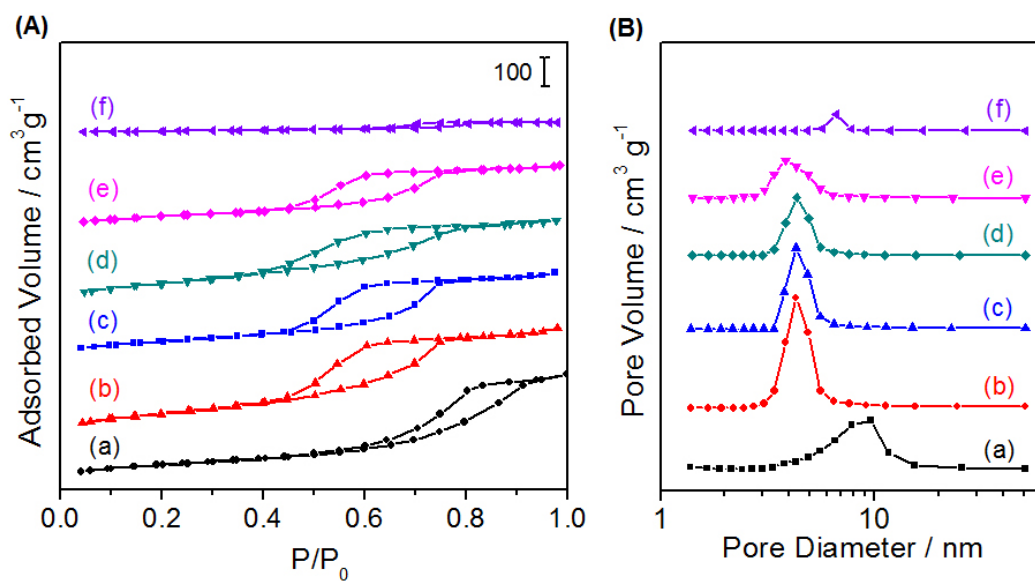


Figure S7. Porosity of the catalysts after the reduction in 10% H₂/N₂ at 400 °C for 1 h. (A) N₂ adsorption-desorption isotherms and (B) pore size distribution calculated by BJH equation in desorption branch of the (a) 10Cu-AE, (b) 20Cu-AE, (c) 25Cu-AE, (d) 30Cu-AE, (e) 40Cu-AE, and (f) 25Cu-IM catalysts.

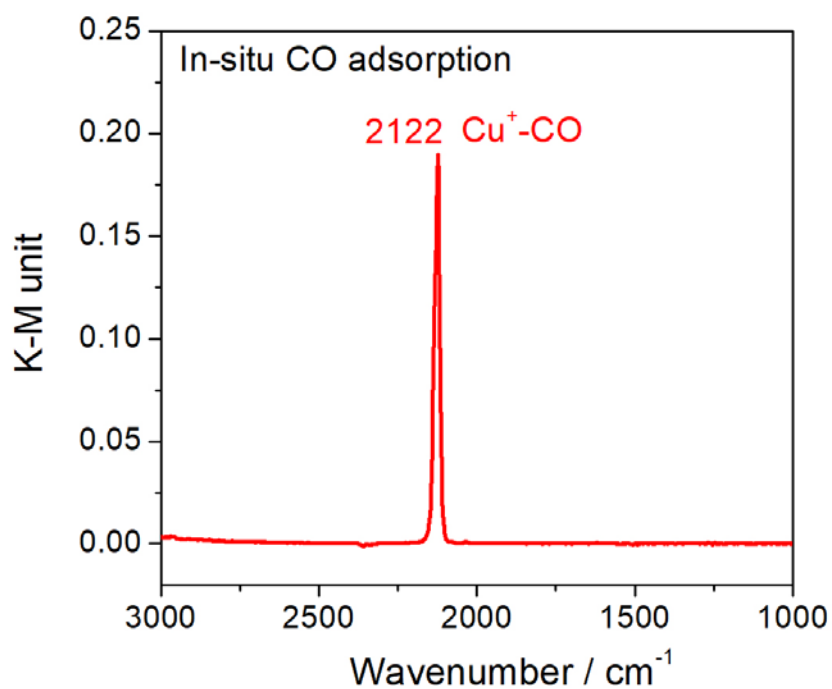


Figure S8. Steady-state *in-situ* DRIFTS spectra of CO adsorption at room temperature over the 25Cu-AE catalyst after the reduction in 10% H₂/N₂ at 400 °C for 1 h.

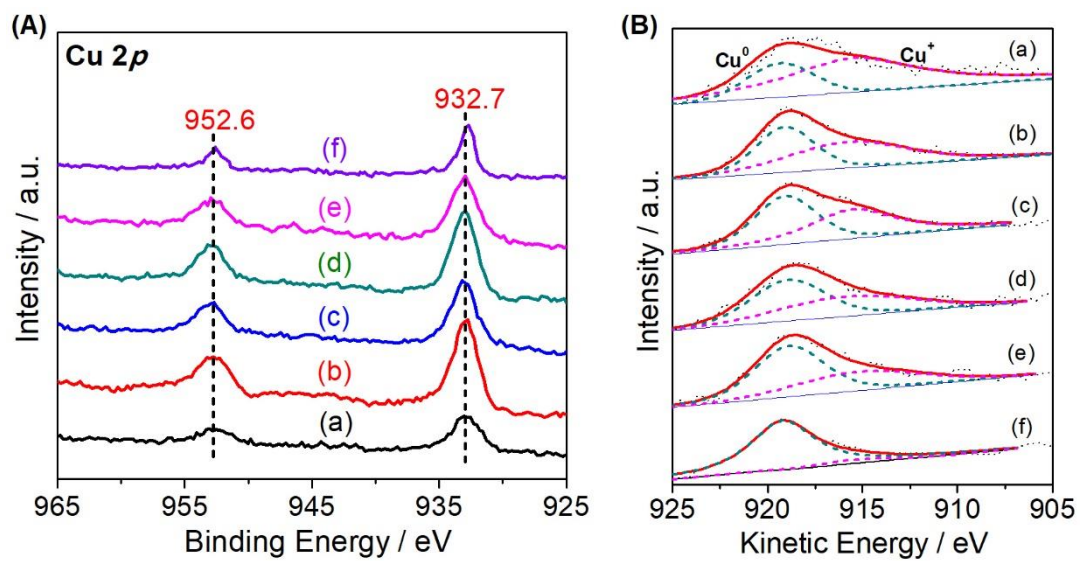


Figure S9. Surface chemical environment of the catalysts after the reduction in 10% H_2/N_2 at 400 °C for 1 h. (A) Cu 2p XPS and (B) Cu LMM Auger spectra of the (a) 10Cu-AE, (b) 20Cu-AE, (c) 25Cu-AE, (d) 30Cu-AE, (e) 40Cu-AE, and (f) 25Cu-IM catalysts.

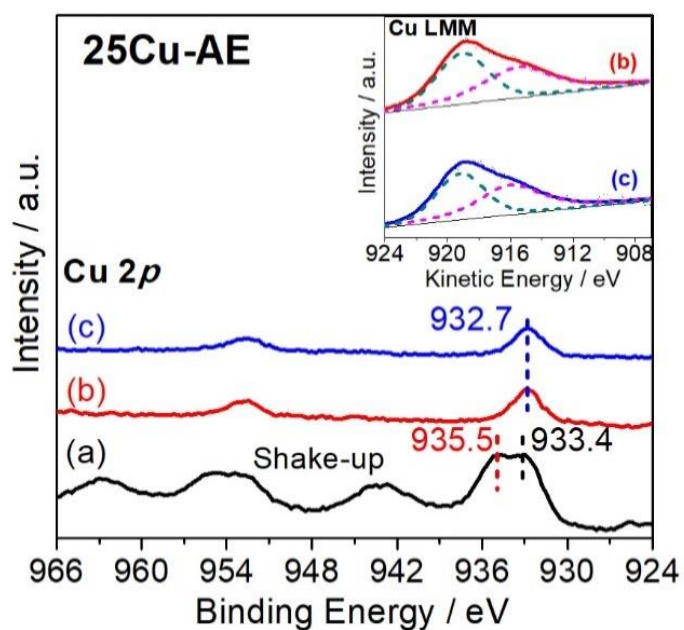


Figure S10. Surface chemical environment before and after single reaction cycle over the 25Cu-AE catalyst. Cu 2p XPS spectra and (inset) Cu LMM Auger spectra of (a) 25Cu-AE, (b) reduced 25Cu-AE, and (c) spent 25Cu-AE catalysts.

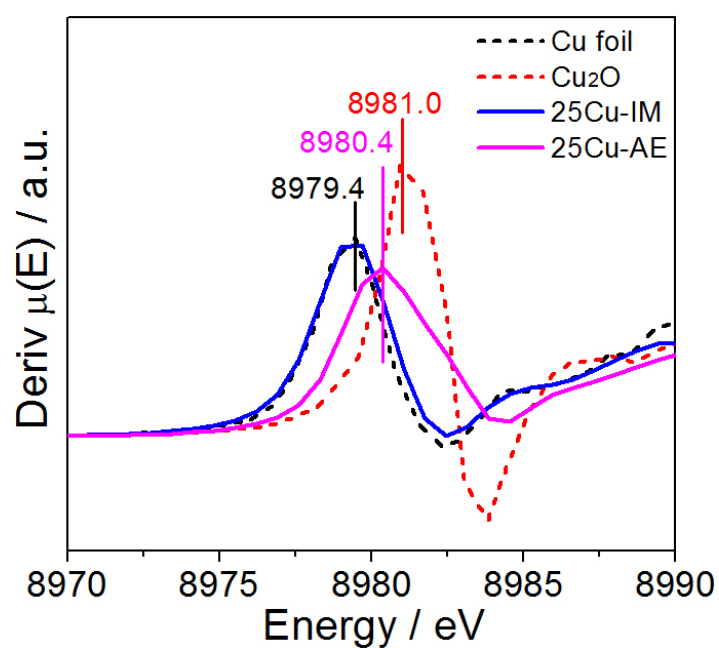


Figure S11. Discrimination of Cu species under DME SR operation. The first derivatives of the *K*-edge XANES spectra for 25Cu-AE, 25Cu-IM under DME SR operation, and the reference of Cu foil and Cu₂O.

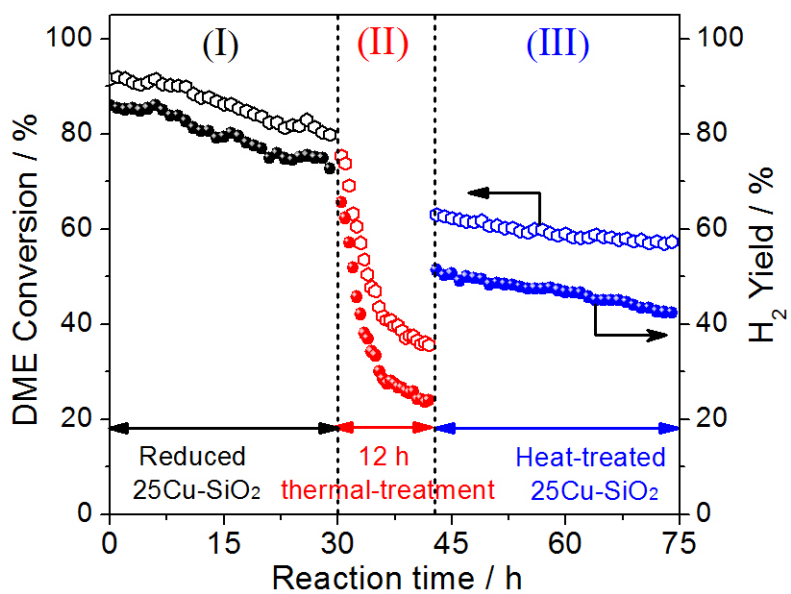


Figure S12. Stabilities of 25Cu-SiO₂ upon thermal treatment. Reaction conditions: (I) and (III): GHSV = 18,000 h⁻¹, S/C = 2/1 (mol/mol), N₂ balance, T = 400 °C; 12 h thermal treatment conditions (II): GHSV = 36,000 mL h⁻¹ g_{cat}⁻¹, S/C = 2/1 (mol/mol), N₂ balance, T = 450 °C.

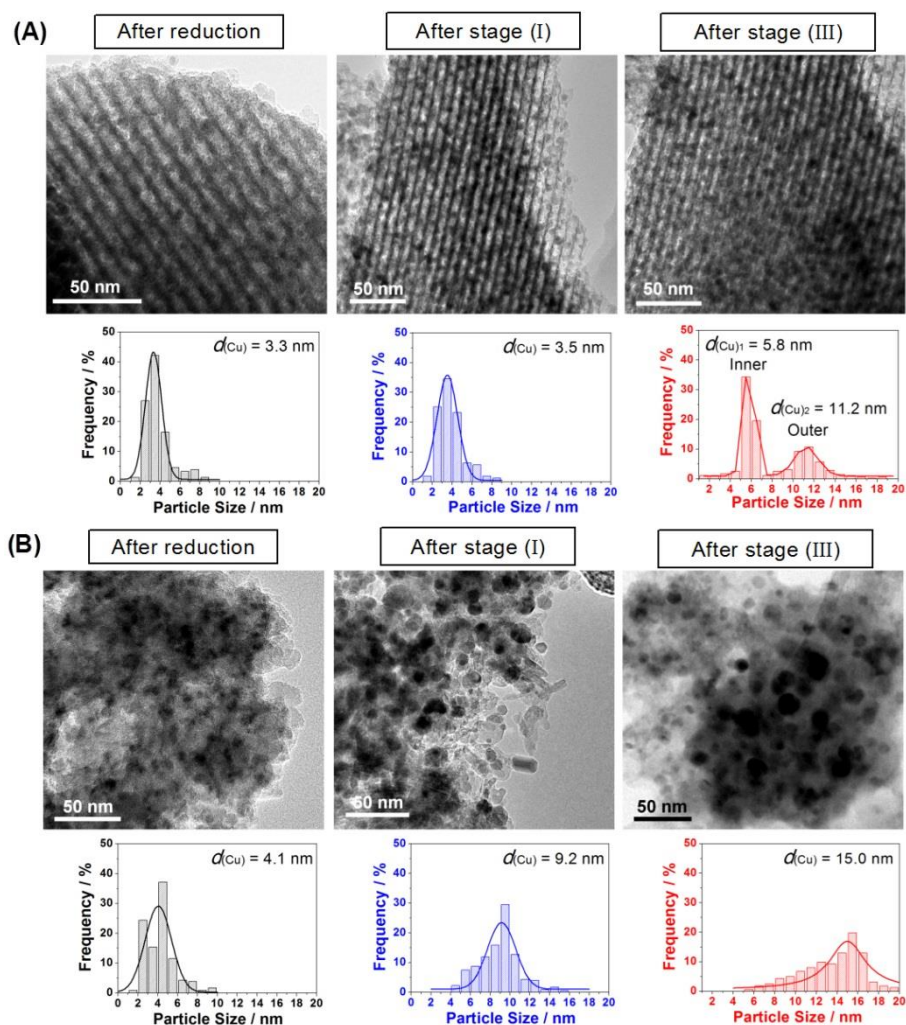


Figure S13. Confinement effects on copper NPs of Cu-AE and Cu-SiO₂. TEM images and particle size distribution of (A) 25Cu-AE and (B) 25Cu-SiO₂ during the stability tests.

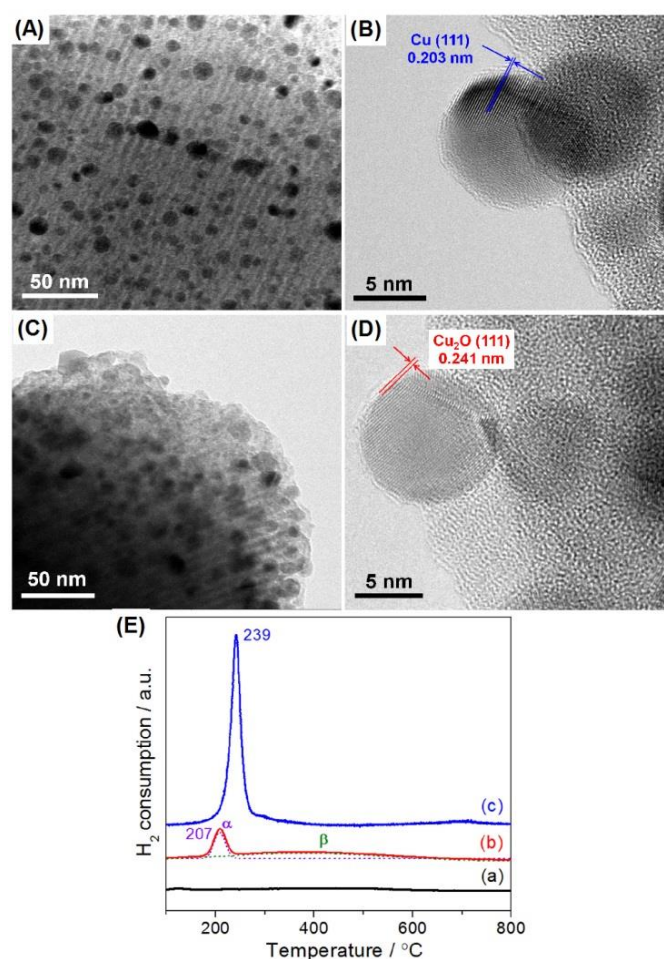


Figure S14. Morphology and reducibility of the sputtering catalysts. TEM images of (A, B) Cu-SP and (C, D) Cu-SP-N; (E) H₂-TPR profiles of (a) Cu-SP; (b) Cu-SP-N; and (c) 25Cu-AE. In most cases, the reduction of copper species occurs at 200-350 °C. In Figure S14E, no obvious peaks are observed on Cu-SP, suggesting that the copper NPs without reduction mainly exist in the form of metallic state. Estimated using the H₂-TPR peak area, the ratio of the metallic Cu to the total copper species is ~91.8%. As the Cu⁰ can be oxidized to Cu⁺ through N₂O treatment, the H₂ consumption peak at ~207 °C on Cu-SP-N demonstrate the reduction from surface Cu₂O to metallic Cu (labeled as α in b), whereas another broad and weak peak from ~250 to 650 °C (labeled as β in b) is most likely to be associated with the strong interaction between few Cu₂O clusters and the SBA-15 support. The single peak at ~239 °C of (c) could be attributed to the overlap of the stepwise reduction of the well-dispersed CuO to Cu⁰ and copper phyllosilicates to Cu⁺. Thus, after prereduction at 350 °C, the copper state exhibits complete Cu⁰ in Cu-SP, but the coexistence of Cu⁰ and Cu⁺ species in Cu-AE, as well as Cu-SP-N.

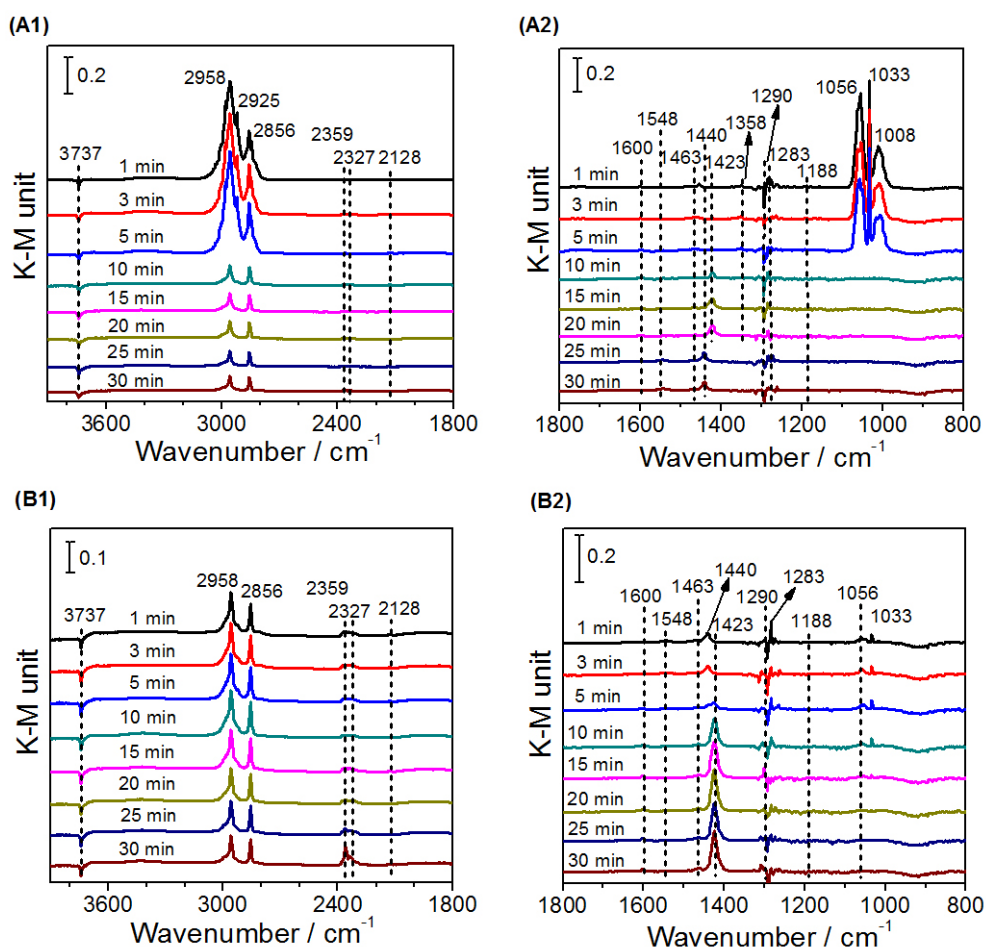


Figure S15. In-situ DRIFTS spectra of the reduced 25Cu-AE catalyst. Adsorption of CH₃OH alone (A1, A2) and subsequently adsorption of the CH₃OH/H₂O mixture at 1/2 (mol/mol) (B1, B2) over the reduced 25Cu-AE catalyst. All of the spectra collected at 230 °C. Figure S15 shows the time-resolved *in-situ* DRIFTS spectra of 25Cu-AE, which describes the transformation of the intermediates clearly during the reaction. During the CH₃OH adsorption (Figure S15A1, A2), the bands at ~1033 and 1008 cm⁻¹ are ascribed to the adsorbed methanol. Simultaneously, the emergence of peaks attributed to methoxy at ~2958, 2856 cm⁻¹ ($\nu_{\text{as(C-H)}}$ vibration) and 1440, 1423 cm⁻¹ ($\delta_{\text{a(C-H)}}$ vibration) indicates that the methanol is dissociatively adsorbed on the surface. Furthermore, the weak formate signals at ~2925 cm⁻¹ ($\nu_{\text{as(C-H)}}$ vibration) and 1548, 1358 cm⁻¹ ($\nu_{\text{(OCO)}}$ vibration) appear with the introduction of methanol and then disappear after about 10 min. After switching to the reaction feed of CH₃OH/H₂O mixture, the bands attributed to carbonate (1463 cm⁻¹) and gaseous CO₂ (2359 and 2327 cm⁻¹) appear (Figure S15B1, B2). Combined with the negative peaks of hydroxy at 3737 and 1290 cm⁻¹, we

propose that the methoxy reacts with hydroxy to form carbonate and finally desorbs as CO₂. Notably, the band of methoxy at 1423 cm⁻¹ is still detectable even after He flushing for 30 min, whereas formate signals at 1548, 1358 and 1600 cm⁻¹ almost disappear after 10 min. These findings indicate that methoxy is relatively stable than other intermediates over 25Cu-AE during the SR reaction.

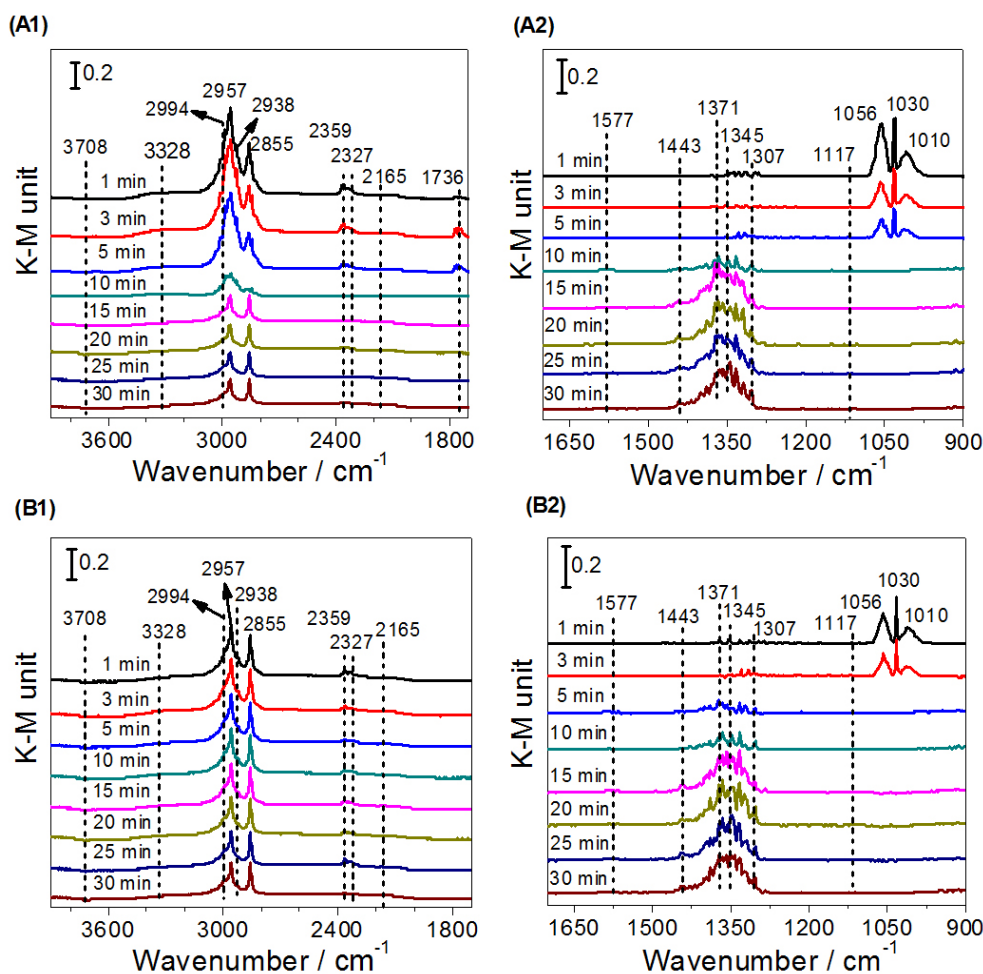


Figure S16. *In-situ* DRIFTS spectra of the Cu-SP catalyst. Adsorption of CH₃OH alone (A1, A2) and subsequently adsorption of the CH₃OH/H₂O mixture at 1/2 (mol/mol) (B1, B2) over Cu-SP. All of the spectra collected at 230 °C.

Figure S16 shows the time-resolved *in-situ* DRIFTS spectra of Cu-SP under the same conditions with that of 25Cu-AE. Similarly, the bands of methoxy at ~ 2957 and 2855 cm^{-1} ($\nu_{\text{as(C-H)}}$ vibration) indicate the dissociative adsorption of methanol over the surface initially (Figure S16A1, A2). The obvious bands at 2994 cm^{-1} ($\nu_{\text{(C-H)}}$ vibration) and 1345 cm^{-1} ($\nu_{\text{(OCO)}}$ vibration) attributed to formate are observed after 10 min, which remain visible even after 30 min. Additionally, we observed formaldehyde and gaseous CO at 1736 cm^{-1} ($\nu_{\text{(C-O)}}$ vibration) and 2165 cm^{-1} , respectively, suggesting that methanol is readily to decompose and form CO over Cu-SP. When the reaction feed is introduced, the formate signals rapidly disappear and re-appear to reach steady state after 10 min (Figure S16B1, B2), implying that the formate is the most stable intermediates over Cu-SP during the SR reaction.

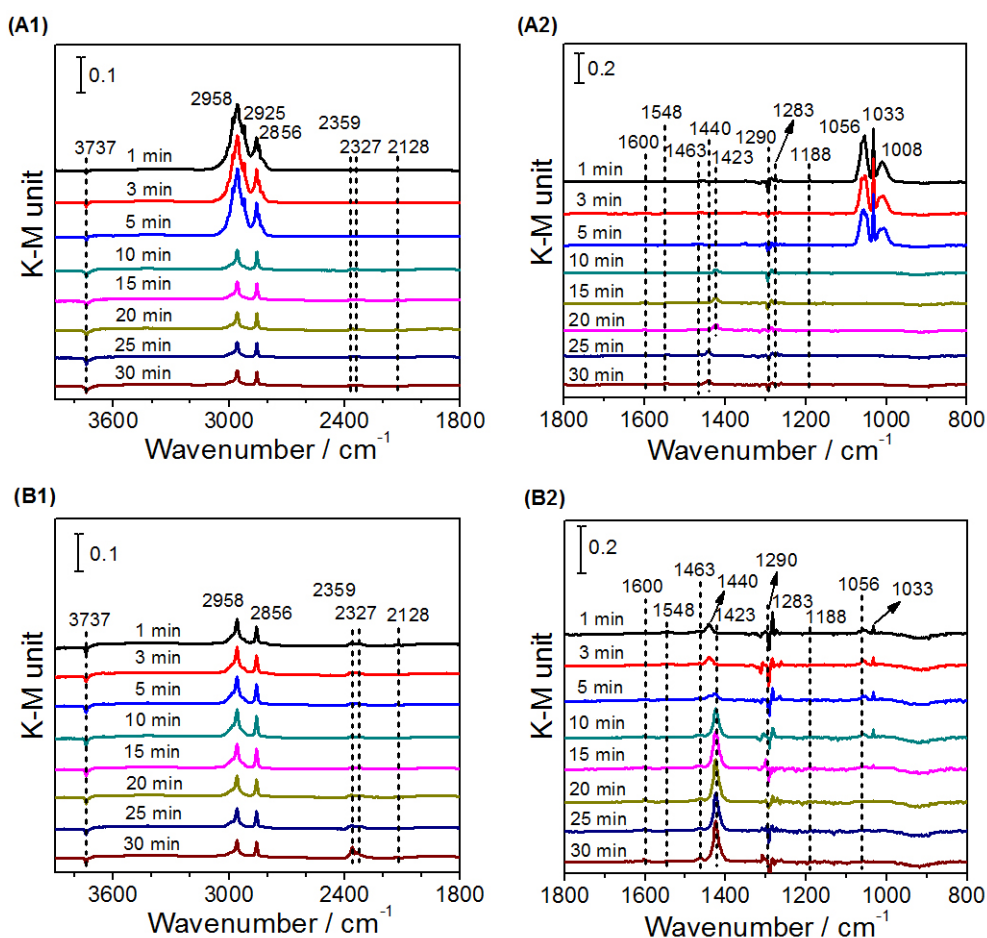


Figure S17. *In-situ* DRIFTS spectra of the Cu-SP-N catalyst. Adsorption of CH₃OH alone (A1, A2) and subsequently adsorption of the CH₃OH/H₂O mixture at 1/2 (mol/mol) (B1, B2) over Cu-SP-N. All of the spectra collected at 230 °C.

As shown in Figure S17, the time-resolved *in-situ* DRIFTS spectra of Cu-SP-N were also collected. The bands and their transformation process are similar with that of 25Cu-AE (Figure S15). Thus, over the Cu-SP-N catalyst, the methoxy but not the formate is the most stable intermediate during the SR reaction. The species assignment for all the observed bands in Figures S15-S17 are summarized and listed in Table S6.

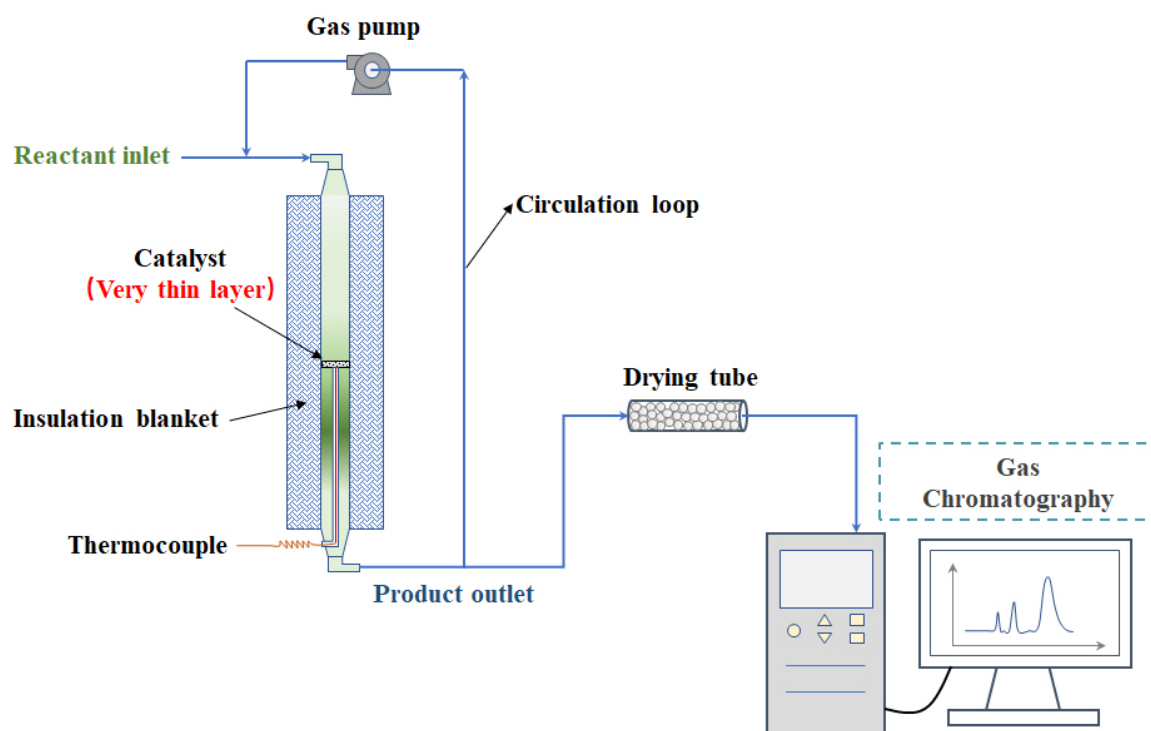


Figure S18. Schematic diagram of kinetics testing system.

Table S1. Relative contents of Cu species in the catalysts determined by LCF method.

Catalysts	P[CuO] (%) ^a	P[Cu ₂ Si ₂ O ₅ (OH) ₂] (%) ^b	C[Cu ₂ Si ₂ O ₅ (OH) ₂] (%) ^c
10Cu-AE	5.4	94.6	8.8
20Cu-AE	11.7	88.3	16.2
25Cu-AE	15.6	84.4	19.2
30Cu-AE	31.9	68.1	17.8
40Cu-AE	48.5	51.5	18.0
25Cu-IM	100.0	0.0	0.0

^{a,b} The atom ratio of the Cu species contributed from the CuO or Cu₂Si₂O₅(OH)₂ calculated by the LCF method; ^c The contents of the Cu₂Si₂O₅(OH)₂ in the catalysts.

Table S2. Physicochemical properties of the reduced catalysts.

Samples	Cu loading ^a (%)	Cu dispersion ^b (%)	S(Cu ⁰) ^b (m ² g ⁻¹)	S(Cu ⁺) ^c (m ² g ⁻¹)	A _{Cu⁺} ^d (%)	d _{Cu₂O} ^e (nm)	d _{Cu} ^e (nm)
10Cu-AE	9.3	37.0	22.2	67.6	75.3	1.9	2.9
20Cu-AE	18.3	30.6	36.1	43.9	54.9	2.3	3.2
25Cu-AE	22.8	28.2	41.4	41.7	50.2	3.1	3.3
30Cu-AE	26.1	28.0	47.1	37.9	44.6	2.9	4.5
40Cu-AE	35.1	19.1	43.1	25.0	20.7	3.1	6.7
25Cu-IM	24.2	7.9	12.3	-	-	-	29.0
Cu/ZnO/Al ₂ O ₃	23.2	13.3	20.6	-	-	-	15.5
CuZnAlCe _{0.1} O ¹¹	22.9	24.0	36.3	-	-	-	9.2
CuFe ₂ O ₄ Spinel ¹²	26.7 ^f	-	-	-	-	-	-

^a Determined by ICP-OES analysis. ^b Copper dispersion and surface area of Cu⁰ (S(Cu⁰)) were determined by N₂O titration and calculated on the basis of ICP-OES data. ^c Surface area of Cu⁺ (S(Cu⁺)) was determined from irreversible CO adsorption isotherms. ^d A_{Cu⁺} (Ratio of S(Cu⁰)/(S(Cu⁺) + S(Cu⁰))) was calculated on the basis of chemical adsorption results. ^e The grain size were calculated from the XRD data of the peak broadening of Cu₂O(111) or Cu(111) by Scherrer equation. ^f The theoretical content.

Table S3. Surface Cu species on the reduced catalysts based on Cu LMM Auger spectra deconvolution.

Catalyst	K.E. (eV) ^a		A.P. (eV) ^b		X _{Cu⁺} ^c (%)	R _{Cu/Si} ^d
	Cu ⁺	Cu ⁰	Cu ⁺	Cu ⁰		
10Cu-AE	915.5	919.3	1848.2	1852.0	80.1	0.07
20Cu-AE	915.6	919.1	1848.3	1851.8	62.7	0.14
25Cu-AE	916.0	919.2	1848.7	1851.9	53.2	0.19
30Cu-AE	915.9	919.0	1848.6	1851.7	40.5	0.24
40Cu-AE	915.2	918.9	1847.9	1851.6	23.3	0.37
25Cu-IM	915.6	919.2	1848.3	1851.9	3.5	0.08
Cu-SP	915.5	919.0	1848.2	1851.7	0.7	0.05
25Cu-AE (spent)	915.9	919.0	1848.6	1851.7	49.4	0.17

^a Kinetic energy. ^b Auger parameter. ^c Intensity ratio between Cu⁺ and (Cu⁺ + Cu⁰) by deconvolution of Cu LMM Auger spectra. ^d Atom ratio of Cu to Si of the catalysts determined by XPS.

Table S4. Representative catalysts for DME SR and methanol SR.

Reaction	Catalyst	T (K)	S/C ratio	GHSV ^a (h ⁻¹)	X (%)	H ₂	S _{H2} /Y _{H2} ^b (%)	S _{CO} (%)	S _{CO2} (%)	S _{CH4} (%)
						production rate (mol kg _{cat} ⁻¹ h ⁻¹)				
DME SR	25Cu-AE (This work)	673	2	18000	100	1145	95	10.4	89.3	0.3
	Cu/SiO ₂ +HPA/Al ₂ O ₃ ¹³	523	3.2	1200	36.6		2.9 ^c	9.5	90.5	
	1La-Cu/SiO ₂ +γ-Al ₂ O ₃ ¹⁴	653	2.5	(12000)	98.6	308	95.9	8.0	92.0	
	CuZnAl ¹⁵	673	1.5				87 ^b	12		1
	CuZnAl+ZSM-5-90(Si/Al=90) ¹⁶	573			90	144				
	CuZnAl+desilicated HZSM-5 ¹⁷	573	3	0.3 ^d	75		70 ^b	5		
	CuZnAl+HZSM-5 ¹⁸	573	2	0.6 ^d	85	180	81 ^b			
	CuZnAl+MgO-HZSM-5 ¹⁹	563	2	4000	95		93 ^b	8	90	2
	Cu/ZnO/carbon+Al ₂ O ₃ ²⁰	573	2.5	2000	87					
	CuZnAl _{0.8} Zr _{0.2} O ²¹	673	2	(15000)	95		92 ^b	17	83	
	CuZnAlCe _{0.1} ¹¹	673	2.5	(12000)			85 ^b	13	80	
	CuZn/ZrO ₂ -monolith ²²	753	1.5	(11300)	56		70.4	3.7	25.4	0.4
	Cu-CeO ₂ /γ-Al ₂ O ₃ ²³	623	1.5	10000	100	610				
	Cu-Ce-Co-O ²⁴	673	1.5	30000	85		70	20	7	
	Cu-Ce-Mn-O ²⁴	673	1.5	30000	68		70	10	12	
	Cu/CeO ₂ +H-mordenite ²⁵	523	1.7	4500	86	71				
	Cu/CeO ₂ +WO ₃ /ZrO ₂ ²⁶	548	1.8	4500		~50				
	CuFe ₂ O ₄ +Al ₂ O ₃ ²⁷	623	2.5	2000	93	35 ^e		8	89	3
	CuMn ₂ O ₄ +Al ₂ O ₃ ²⁷				70	24 ^e		13	83	4
	CuCr ₂ O ₄ +Al ₂ O ₃ ²⁷	623	2.5	2000	79	27 ^e		5	93	2
	CuGa ₂ O ₄ +Al ₂ O ₃ ²⁷	623	2.5	2000	88	30 ^e		10	86	4
	CuAl ₂ O ₄ +Al ₂ O ₃ ²⁷	623	2.5	2000	90	32 ^e		4	94	2
	CuFe _{0.75} Mn _{0.25} O ₄ +Al ₂ O ₃ ²⁷	623	2.5	2000	90	31 ^e		7	90	3
	CuZnAl+γ-Al ₂ O ₃ ²⁸	623	2.5	2000	~30	~20		88	2	10
	CuFe ₂ O ₄ +γ-Al ₂ O ₃ ²⁸	623	2.5	2000	~90	~70		86	10	4
	CuCr ₂ O ₄ +γ-Al ₂ O ₃ ²⁸	623	2.5	2000	~65	~45		91	4	5
	CuMn ₂ O ₄ +γ-Al ₂ O ₃ ²⁸	623	2.5	2000	~75	~50		80	15	5
	CuNiFe ₂ O ₄ +Al ₂ O ₃ ²⁹	648	2.5	9100	76	186		19.3	79.6	1.1
	CuFe ₂ O ₄ +Al ₂ O ₃ ³⁰ (heat	648	2.5	9100	86.6					
	CuFe ₂ O ₄ +Al ₂ O ₃ ³⁰ (heat	648	2.5	9100	84.3					
	Rh/Al ₂ O ₃ ³¹	923	3.0	100000	~100		42	5.9	10.6	1.7
	Pd/CeO ₂ +H-mordenite ²⁵	523	1.7	4500	75	53				
	Pd/ZrO ₂ ³²	753	1.5	1500	~80		70			
	Ru/Al ₂ O ₃ ³³	673	2.5	5400	~100		18		22	60
	Pt/Al ₂ O ₃ ³³	673	2.5	5400	~95		60	3	20	17
	Au/CeO ₂ -Al ₂ O ₃ ³⁴	773	0.5	8000			73 ^b			
	K-promoted Au/CeO ₂ -Al ₂ O ₃ ³⁴	773	0.5	8000	~100		87 ^b	~30	~4	
	Ga ₂ O ₃ /Al ₂ O ₃ ³⁵	673	1.5	(20000)	100		67 ^b	30	65	
	Ga ₂ O ₃ /TiO ₂ ³⁵	673	1.5	(20000)	98		55 ^b	59	38	
	ZnO-Al ₂ O ₃ ³⁶	733	2.4	7900	~100	315		59	38	
	ZnCr-TiAl ³⁷	703	2.4	7900	~90	345		~6		

	ZnAlCe _{0.2} + γ -Al ₂ O ₃ ³⁸	693	2.5	(12000)	~100		~100 ^b	~7	95
	Zn ₉ Ga ₁ O+ γ -Al ₂ O ₃ ³⁹	723	2.5	(12000)	95.4		95 ^b	~5	95
	Mo ₂ C/norit+Al ₂ O ₃ ⁴⁰	673	1.5	(8000)	~80		65 ^b		
Methanol	Commercial CZA ⁴¹	523	1.25	8900	88.7	566.6		1.9	98.1
SR	Cu/ZnO ⁴²	523	1		60				
	Cu/ZrO ₂ ⁴³	533	3	5.4 ^f	80	~200.2			
	Cu/SiO ₂ ⁴⁴	573	1.5	(21200)	80			1.25	
	CuO/CeO ₂ ⁴⁵	523	1.5	(16380)	80	270			
	CuO/CeO ₂ /ZrO ₂ ⁴⁵	523	1.5	(16380)		349.2			
	Cu/Al ⁴⁶	523	1.4		31	291.6		3	
	Cu/Zn/Al ⁴⁶	523	1.4		76	730.8		1.1	
	Cu/Zn/Ce/Al ⁴⁶	523	1.4		90	878.4		0.06	
	Cu/La ₂ O ₃ /ZrO ₂ ⁴⁷	573	1.3	(46320)	60	622.8			
	Cu/Y ₂ O ₃ /ZrO ₂ ⁴⁷	573	1.3	(46320)	70	896.4			
	Cu/CeO ₂ /ZrO ₂ ⁴⁷	573	1.3	(46320)	40	378			
	Cu/Al ₂ O ₃ /ZrO ₂ ⁴⁷	573	1.3	(46320)	50	522			
	Pd/ZnO ⁴⁸	493	1			39.2	99.5		
	Pd/AC ⁴⁸	493	1			1.4	100		
	Pd/CeO ₂ ⁴⁸	493	1			33.1	22		
	Zn-Pd/AC ⁴⁸	493	1			40.3	98		
	Zn-Pd/CeO ₂ ⁴⁸	493	1			45.4	95		
	Pd-ZnO/ Al ₂ O ₃ ⁴⁹	493	1.78	14400	46.5	182.9		0.6	99.4
	Pd-Zn/SBA-15 ⁵⁰	573	1.12		68		85		
	PdZnAl ⁵¹	523	1	(12480)	14	58	87		61.1
	PdMgGa ⁵¹	523	1	(12480)	15.3	52.6	72		16.4
	PdMgAl ⁵¹	523	1	(12480)	12.6	41	69		6.1
	NiAl ⁵²	653	1.2		35	342	73.6	4.6	21.8
	NiAl-Au ⁵²	653	1.2		99.4	204.8	36.2	1.6	26 36.2
	NiAl-Rh ⁵²	653	1.2		82.6	144.7	32.2	0.3	26.1 41.4
	NiAl-Ir ⁵²	653	1.2		92.9	220.7	40.1	0.3	25.7 33.9
	NiAl-LDH ⁵³	663	1.1		87.6	645.1			
	Pt/CeO ₂ ⁵⁴	623		(99375)	79.2			21.3	77.5 1.2
	Pt/Al ₂ O ₃ ⁵⁵	503	1					1	99
	Au-CeO ₂ (rod) ⁵⁶	523	1.3	42000		44.3			
	Au-CeO ₂ (cube) ⁵⁶	523	1.3	42000		0.7			
	Au-ZnO (polyhedral) ⁵⁷	673	1.3	34000		37.1			
	Au-ZnO (rod) ⁵⁷	673	1.3	34000		20.5			
	Au-Cu/CeO ₂ -ZrO ₂ ⁵⁸	573	2	(21000)	100		70.5	1	

^a In parentheses, space velocity (mL g_{cat}⁻¹ h⁻¹), when GHSV is unavailable. ^b H₂ yield (%). ^c H₂/(CO+CO₂) molar ratio. ^d Unit: g_{cat} h g_{DME}⁻¹. ^e Unit: mL min⁻¹. ^f WHSV (h⁻¹).

Table S5. Comparison of physicochemical properties and catalytic performance of 25Cu-AE and the sputtered catalysts.

Catalysts	Cu loading ^a (%)	Cu dispersion ^b (%)	S(Cu ⁰) ^c (m ² g ⁻¹)	S(Cu ⁺) ^d (m ² g ⁻¹)	d _{Cu2O} ^e (nm)	d _{Cu} ^f (nm)	TOF _{H2} ^g (s ⁻¹ × 10 ⁻²)	TOF _{DME} ^h (s ⁻¹ × 10 ⁻³)
25Cu-AE	22.8	28.2	41.4	41.7	3.1	3.3	14.7 ± 0.9	12.2 ± 0.3
Cu-SP	5.2	36.3	28.6	-	-	4.5	4.2 ± 0.2	4.0 ± 0.2
Cu-SP-N	5.2	36.3	ND	28.6 ⁱ	4.7	ND	11.1 ± 1.3 ^j	10.2 ± 0.5

^a Determined by ICP-OES analysis. ^{b, c} Copper dispersion and S(Cu⁰) were determined by N₂O titration and calculated based on ICP-OES data. ^d S(Cu⁺) was determined from irreversible CO adsorption isotherms. ^{e, f} The grain size were calculated from the XRD data of the (111) peak broadening of Cu₂O or Cu by Scherrer equation. ^g TOF_{H2} based on the Cu⁰ surface area and yield of H₂. ^h TOF_{DME} based on the total Cu surface areas and conversion of DME. ⁱ Assuming Cu⁺ ion occupying the same area as that of Cu⁰ atom and the metallic Cu in Cu-SP completely oxidized to Cu⁺ by N₂O. ^j TOF_{H2} of Cu-SP-N catalyst was specifically calculated based on the total Cu surface area with the unquantified Cu⁰ during the reaction.

Table S6. Observed frequencies from the DRIFTS spectra and their assignment to the vibrational modes.

Species	Mode ^a	Frequencies (cm ⁻¹)		Ref.
		Cu-AE/Cu-SP-N	Cu-SP	
Methoxy	$\nu_{\text{as}}(\text{CH}_3)$	2958	2957	59, 60
	$\nu_{\text{s}}(\text{CH}_3)$	2856	2855	59, 60
	$\delta_{\text{a}}(\text{CH}_3)$	1440	1443	60, 61
	$\delta_{\text{a}}(\text{CH}_3)$	1423	-	60, 61
	$\rho(\text{CH}_3)$	1188	1117	61, 62
	$\nu(\text{CO})$	1056	1056	61-63
Hydroxy	$\nu(\text{OH})$	3737	3708	61, 62, 64
	$\nu(\text{OH}\cdots\text{O})$	3432	3328	65, 66
	$\delta_{\text{a}}(\text{OH})$	1290	-	65, 66
Adsorbed CH ₃ OH	$\nu(\text{CO})$	1008, 1033	1010, 1030	39, 67
Formaldehyde	$\nu(\text{CO})$	-	1736	68
Formate	$\nu(\text{CH})$	2925	2994, 2938	63, 69
	$\nu_{\text{as}}(\text{OCO})$	1548 (bidentate),	1577	61, 69, 70
		1600 (monodentate)	(monodentate)	
	$\nu_{\text{s}}(\text{OCO})$	1358 (bidentate)	1345 (bidentate)	
	$\delta_{\text{ip}}(\text{CH})$	1283	1307	
	$\delta_{\text{op}}(\text{CH})$	-	-	
	$\delta(\text{OCO})$	-	-	
Gas phase or weakly adsorbed carbon dioxide	$\nu_{\text{as}}(\text{OCO})$	2359, 2327	2359, 2327	61, 64
Gas phase carbon monoxide		-	2165	64
Carbonyls		2128	-	63, 64, 71
Carbonate		1463	1371	61, 62, 64
		(monodentate)	(monodentate)	

^a Notations used: ν , stretching; δ , bending; ρ , rocking; a, asymmetric; s, symmetric; ip, in-plane; op, out-of-plane.

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