

# Thiol-assisted aerosol synthesis of mesoporous Cu-SiO<sub>2</sub> catalysts for effective and stable ethanol dehydrogenation

Giovanni Pampararo<sup>1\*</sup>, Marc Antoine Colinet<sup>1</sup>, Francois Devred<sup>1</sup>, Damien P. Debecker<sup>1\*</sup>

\* Giovanni.Pampararo@uclouvain.be, Damien.Debecker@uclouvain.be

1. Université catholique de Louvain (UCLouvain), Institute of Condensed Matter and Nanosciences (IMCN), Place Louis Pasteur 1, Louvain-la-Neuve, 1348, Belgium

ELECTRONIC SUPPLEMENTARY INFORMATION

## CHARACTERIZATION

### Nitrogen physisorption

The textural properties of the catalysts were thoroughly analyzed using N<sub>2</sub> physisorption at 77 K with a Micromeritics Tristar 3000 instrument. Before analysis, 60 mg of the calcined samples were degassed overnight at 423 K under vacuum in a Micromeritics Vacprep 061 degasser until the pressure fell below 80 mTorr, ensuring the removal of all previously adsorbed compounds. The specific surface area (m<sup>2</sup>/g) was determined using the Brunauer-Emmett-Teller (BET) model over a relative pressure range of 0.05-0.30. Total pore volume (V<sub>p</sub>) and mean pore diameter (D<sub>p</sub>) were calculated from the adsorption isotherm at p/p<sub>0</sub> = 0.98 using the Barrett, Joyner, and Halenda (BJH) method.

### X-ray diffraction (XRD)

X-ray diffraction analysis was carried out using a Bruker D8 Advance diffractometer set to Bragg-Brentano geometry. The system operates with a Cu K $\alpha$  radiation source ( $\lambda = 0.15418$  nm) at a power of 1200 W (30 mA, 40 kV) and uses a Bruker Lynxeye XE-T detector. Diffraction patterns were collected over a range of  $2\theta$  from 5° to 100°. The step size was set at 0.05°, with each step lasting 1.5 seconds. Phase identification was carried out using using DIFFRAC. EVA V4.2.1 software. CuO and Cu crystallite sizes were specifically assessed using the Scherrer formula on the strongest peaks identified at  $2\theta = 35.59^\circ$  for CuO and  $2\theta = 43.39^\circ$  for metallic Cu.

### Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

14 mg of catalyst is placed in a 50 ml tube with 2.5 ml of concentrated HBF<sub>4</sub> and 2.5 ml of concentrated HNO<sub>3</sub>. The solution was left overnight to ensure complete dissolution of the catalyst. Once dissolved, the volume was adjusted to 45 g by weighing. Before analysis, 1 g of this solution is diluted to 50 g with deionised water. This diluted solution is used for the ICP-AES measurements of Si and Cu. The analysis was carried out using an ICP-AES spectrometer with automatic reading times and five repetitions. The plasma is maintained at a flow rate of 10 L/min, with an auxiliary flow rate of 0.2 L/min and a nebulisation flow rate of 0.60 L/min. The power applied was 1500 Watts, with an axial view of 15 mm. The sample is introduced at a flow rate of 1.50 mL/min, with a 30-second rinse between each sample at a flow rate of 1.50 mL/min. The analytes measured were Cu at 327.398 nm and Si at 251.613 nm, with argon at 420.069 nm used as the internal standard. The method uses the peak area for integration, with

seven points per peak. Background correction is automatic, with no correction for spectral overlap.

#### Temperature programmed reduction (TPR)

BELCAT II Microtrac MRB instrument, manufactured by BEL Japan, is used to perform Temperature-Programmed Reduction (TPR) analysis. This instrument allows precise calibration of gases in the Thermal Conductivity Detector (TCD) to ensure accurate results. The main objective of this analysis is to determine the reducibility of copper-based catalysts. For instance, TPR profiles can reveal that small copper oxide particles on the surface reduce at lower temperatures (around 473K to 573K), while larger particles or embedded species may require higher temperatures (623K to 773K) for reduction<sup>1</sup>. The TCD is used to monitor the reduction process, and a trap is employed to capture any unwanted species during the analysis, which would not have been eliminated during the pre-treatment. For TPR analysis, 50 mg of catalyst is inserted into a quartz tube. In the pre-treatment phase, the catalyst is heated to 393K and maintained at this temperature for 30 minutes in argon (Ar) at a total flow rate of 75 ml/min. A stabilization period of 30 minutes is allowed for the detector to ensure that everything adsorbed is removed, the aim is to eliminate physisorbed water and volatile impurities that could interfere with the TPR analysis. The reducing agent used is a gaseous mixture of 2% hydrogen (H<sub>2</sub>) in argon (Ar) at a flow rate of 75 ml/min. During the measurement, the temperature is gradually increased from 393K to 1073K at a rate of 10K per minute, with a target temperature hold time of 20 minutes.

#### NH<sub>3</sub> Temperature Programmed Desorption (NH<sub>3</sub>-TPD)

NH<sub>3</sub>-TPD experiments were performed on a Belcat II instrument (Microtrac). Prior to ammonia adsorption (30ml/min of 2.5 % NH<sub>3</sub> in Ar at 333 K during 45 min), 20-25 mg of sample powders were reduced in 30 ml/min of 5%H<sub>2</sub> in Ar at 573 K during 60 min. Temperature programmed desorption was then carried out in 30ml/min of Argon from 333 K to 823 K at 10 K/min. All gases mixtures are provided by AirLiquid (gaz quality alphagaz 1). A quadrupole mass spectrometer Bellmass II was used for data collection.

#### Dispersion analysis

To quantify the dispersion of the active phase on the support, a sequential TPR-N<sub>2</sub>O-TPR analysis is carried out<sup>1,2</sup>. Nitrous oxide (N<sub>2</sub>O) is chosen for its ability to selectively oxidise the copper surface of the catalyst without affecting the bulk Cu nanoparticles at low temperatures

(308K). As a first step, a TPR analysis is carried out using the same pre-treatment and measurement conditions as described above in general TPR. However, the measurement is stopped at 593K to ensure that all the copper in the sample has been completely reduced without sintering. This first TPR will be referred to as “TPR1”. After this TPR1, the sample is first cooled to 308K for 30 minutes under argon flow (75 ml/min). Next, partial oxidation is carried out by exposing the sample to a 10% N<sub>2</sub>O/He mixture at 308K for 60 minutes. An argon purge is then carried out for 60 minutes at 308K to ensure complete removal of the N<sub>2</sub>O from the system (75 ml/min). In the end, a second TPR, called “TPR2”, was carried out using the same measurement method as the general TPR method (reducing agent: 2% H<sub>2</sub>/Ar, 75 ml/min, 293K to 1093K, 10K/min, hold time 20 min).

Copper dispersion can be calculated using the formula shown below, where the moles of copper on the surface ( $n_{Cu\ surface}$ ) are derived from TPR2, and the total moles of copper in the catalyst ( $n_{Cu\ total}$ ) are known from the initial loading. In this context, each mole of H<sub>2</sub> dissociates to form two moles of hydrogen atoms, each bonded to a copper atom on the surface. Consequently, the number of active copper sites interacting with hydrogen is multiplied by a factor of 2 [45].

$$D. (\%) = n_{Cu_{surface}} / n_{Cu_{total}} \times 100$$

#### UV-visible diffuse reflectance spectroscopy

DR-UV-vis-NIR spectra of the catalyst samples were collected using a UV3600i Plus, Shimadzu instrument. The powders were gently pressed into the sample holder to ensure a smooth surface for analysis. Blank was analysed to establish a baseline. Data analysis was carried out using Shimadzu's proprietary UVProbe 2.62 software.

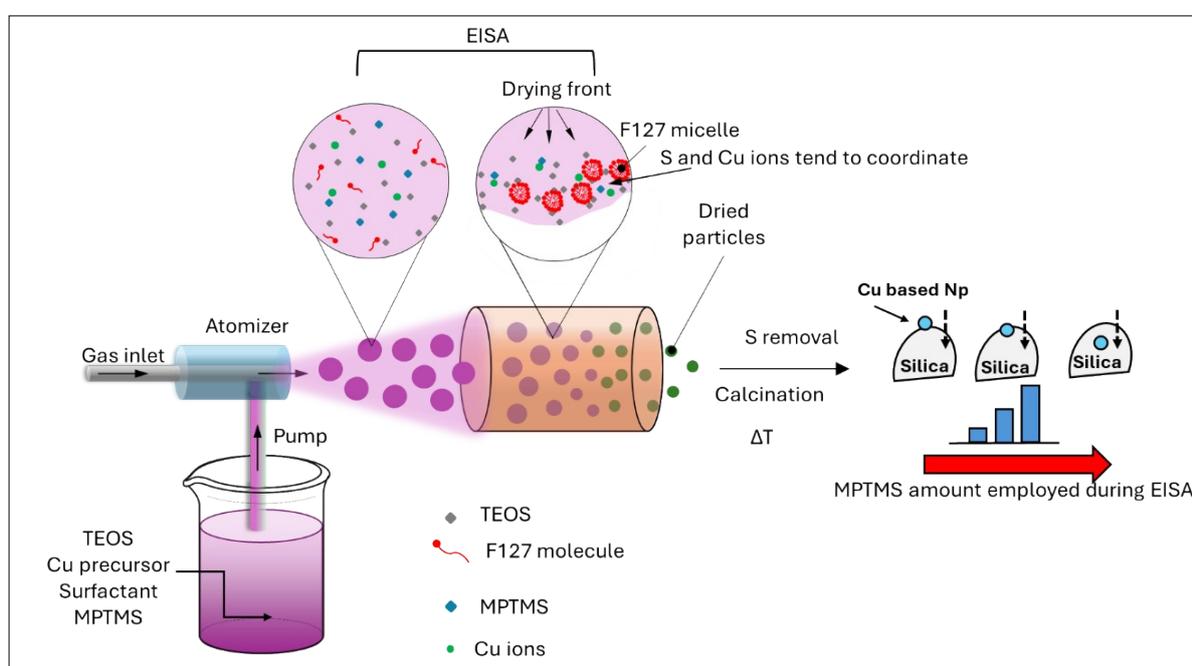
#### X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) analyses were carried out at room temperature using an SSI-X-probe photoelectron spectrometer (SSX 100/206) from Surface Science Instruments (USA). The instrument is equipped with a micro-focused monochromatic Al K $\alpha$  X-ray source (1486.6 eV). The samples were mounted on small sample holders using adhesive tape and placed on an insulating ceramic carousel (Macor®, Switzerland). To avoid charge effects, a nickel grid was placed over the samples, and an injection gun was set at 8 eV. The binding energy scale was calibrated by setting the Si 2p peak at 103.5 eV<sup>3</sup>. Data processing was carried out using the Casa XPS program (Casa Software Ltd., UK), where the spectra were

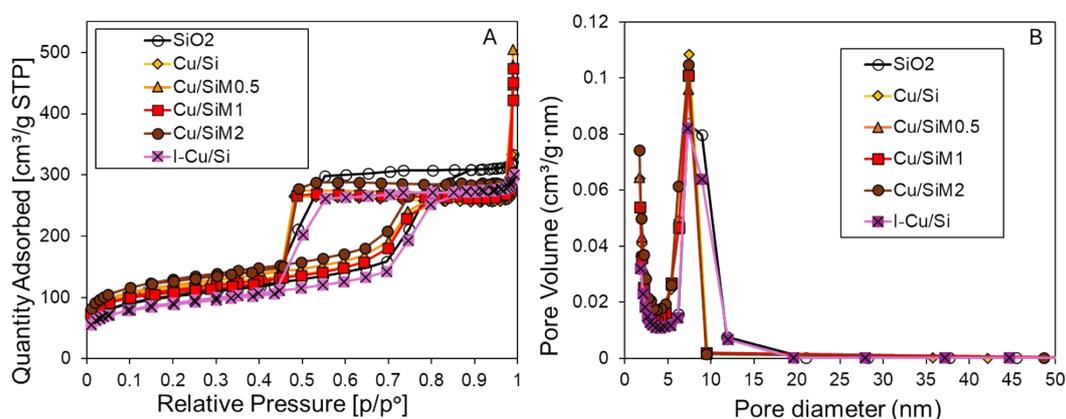
decomposed into sums of Gaussian/Lorentzian (85/15) peaks after subtracting a Shirley-type baseline.

Transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) combined with energy-dispersive X-ray spectroscopy (EDX) analysis was performed at 200kV on a Talos F200i Transmission Electron Microscope. The software used for the measurements was VELO.

Particle size distribution was evaluated on different TEM images (fresh and spent catalysts) using the software nanoDetect v2.2 (gaussian fitting) <sup>4</sup>.



**Scheme S1:** The aerosol-assisted process is based on the rapid evaporation of a volatile solvent from a liquid precursor mixture to generate dry particulate materials. Specifically, a homogeneous solution containing the inorganic precursors (in this case, Silicon, Copper and Sulfur sources) and the structure-directing agent (Pluronic F127) is atomized to form fine aerosol droplets, each possessing an identical composition. These droplets are subsequently transported through a heated zone, wherein the solvent rapidly evaporates. During this drying phase, the surfactant self-assembles into micellar structures, while the inorganic precursors undergo hydrolysis and polycondensation reactions, rapidly leading to the formation of an oxide-like network (EISA process). The resulting dry particles are collected on a filter and subjected to calcination, which removes sulfur (as confirmed by XPS on calcined catalysts, ESI Fig. S3), the organic template and induces the development of mesoporosity.



**Figure S1:** (A)  $N_2$  physisorption isotherms and (B) pore distributions (calculated from the adsorption branch of the isotherm, via the BJH model) of prepared catalyst.

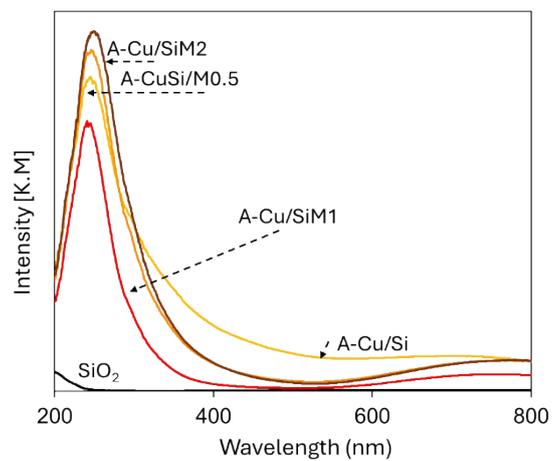
**Table S1.** Composition, reducibility, and texture of the catalysts

Sample	Cu wt.%- ICP-AES	mmol copper $g_{cat}^{-1}$ (ICP-AES)	TPR mmol copper $g_{cat}^{-1}$	Surf. area $[m^2 \cdot g^{-1}]$	$V_p$ [a] $[cm^3 \cdot g^{-1}]$	$V_{micro}$ [b] $[cm^3 \cdot g^{-1}]$	$D_p$ [c] [nm]
SiO <sub>2</sub>	/	/	/	350	0.49	0.045	7
Cu/Si	7.9	1.24	1.16	380	0.40	0.094	7
Cu/SiM0.5	7.5	1.27	1.15	400	0.43	0.080	10
Cu/SiM1	8.1	1.16	1.13	370	0.43	0.070	10
Cu/SiM2	7.3	1.13	1.15	430	0.45	0.115	7
I-Cu/Si	8.8	1.38	1.3	300	0.44	0.039	7

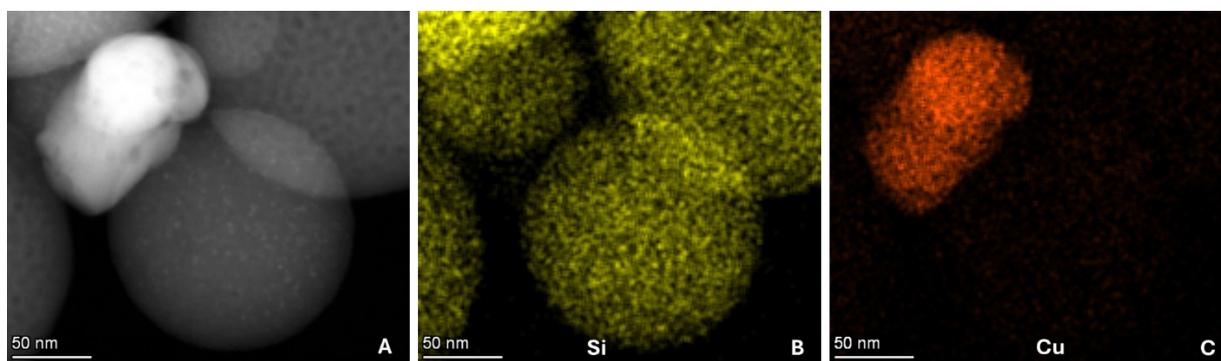
[a] Total pore volume, estimated from the adsorption branch of the isotherm at  $p/p_0 = 0.98$ .

[b] Microporous volume, estimated from the t-plot.

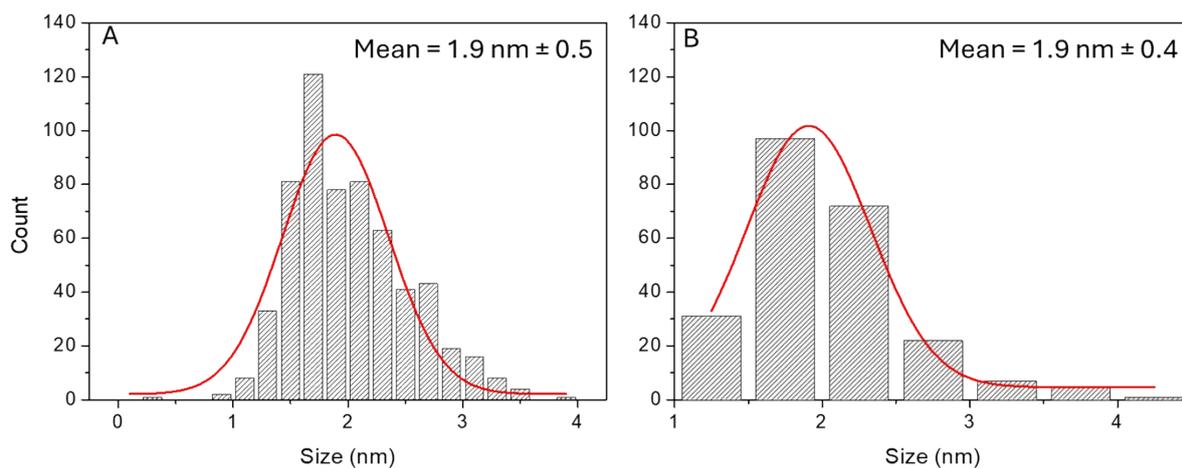
[c] Average pore diameter, estimated from the BJH model applied on the adsorption isotherms.



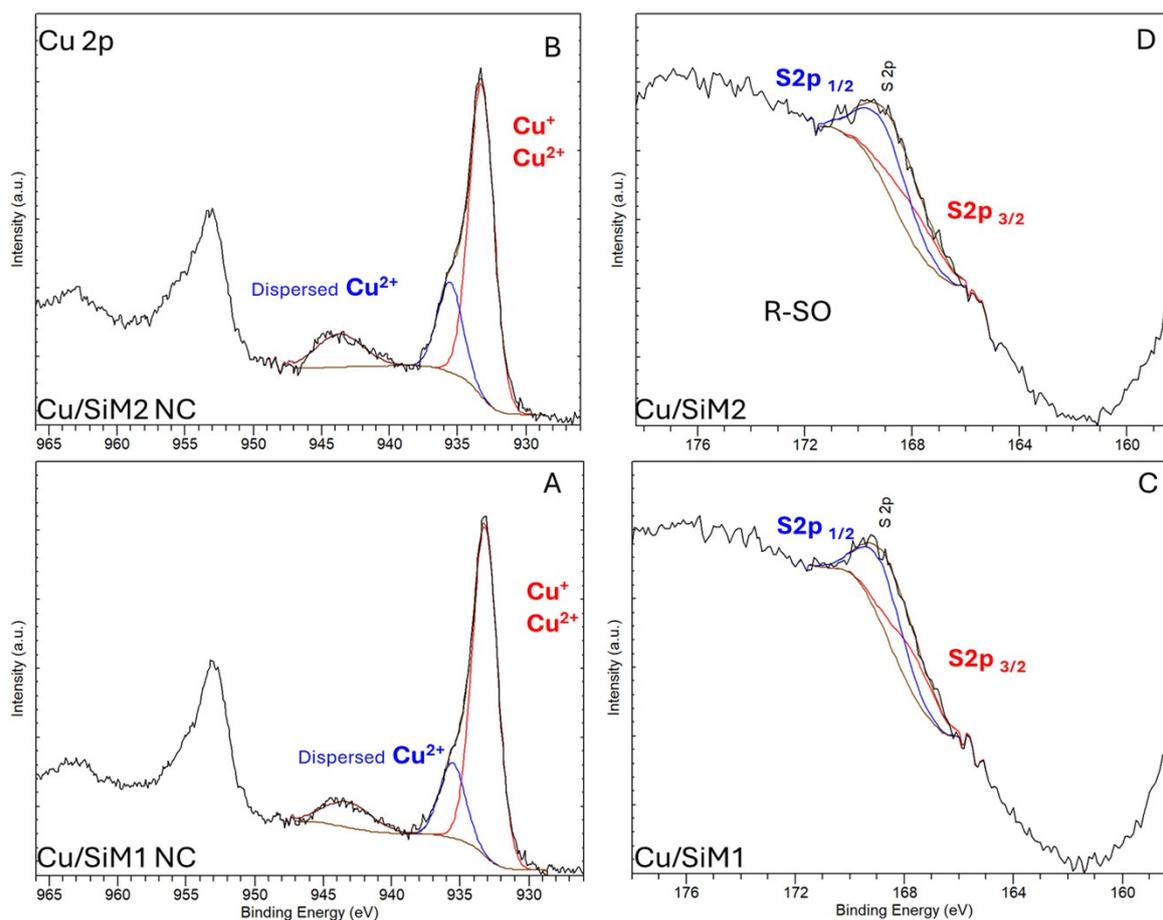
**Figure S2:** UV-Vis spectra of prepared catalysts.



**Figure S3:** HAADF-EDX (A-C) images of fresh Cu/Si catalyst with spot on a large Cu rich aggregate.



**Figure S4:** Figure S5: Particle size distribution of fresh Cu/Si (A) and fresh Cu/SiM1 (B)



**Figure S5:** High resolution spectra of Cu 2p region over not calcined catalysts (panels A and B) and S 2p region of calcined catalysts (panels C and D).

**Table S2:** selectivity during catalytic tests between 423 K and 673 K.

<b>Cu/Si</b>							
<b>T K</b>	<b>S CH<sub>3</sub>CHO</b>	<b>S C<sub>2</sub>H<sub>4</sub></b>	<b>S C<sub>4</sub>H<sub>10</sub>O</b>	<b>S CH<sub>4</sub></b>	<b>S CH<sub>3</sub>COOH</b>	<b>S CH<sub>3</sub>COOCH<sub>2</sub>CH<sub>3</sub></b>	<b>S C<sub>4</sub>H<sub>8</sub>O</b>
<b>423</b>	100%	0%	0%	0%	0%	0%	0%
<b>473</b>	100%	0%	0%	0%	0%	0%	0%
<b>523</b>	94%	0%	0%	2%	0%	1%	0%
<b>573</b>	97%	0%	0%	1%	0%	0%	0%
<b>623</b>	94%	3%	0%	2%	0%	0%	0%
<b>673</b>	87%	11%	0%	8%	0%	0%	0%
<b>Cu/SiM0.5</b>							
<b>423</b>	100%	0%	0%	0%	0%	0%	0%
<b>473</b>	100%	0%	0%	0%	0%	0%	0%
<b>523</b>	100%	0%	0%	0%	0%	0%	0%
<b>573</b>	100%	0%	0%	0%	0%	0%	0%
<b>623</b>	95%	4%	0%	0%	0%	0%	0%
<b>673</b>	88%	7%	0%	1%	0%	0%	0%
<b>Cu/SiM1</b>							
<b>423</b>	100%	0%	0%	0%	0%	0%	0%
<b>473</b>	100%	0%	0%	0%	0%	0%	0%
<b>523</b>	100%	0%	0%	0%	0%	0%	0%
<b>573</b>	100%	0%	0%	0%	0%	0%	0%
<b>623</b>	97%	4%	0%	0%	0%	0%	0%
<b>673</b>	96%	7%	0%	2%	0%	0%	0%
<b>Cu/SiM2</b>							
<b>423</b>	100%	0%	0%	0%	0%	0%	0%
<b>473</b>	100%	0%	0%	0%	0%	0%	0%
<b>523</b>	100%	0%	0%	0%	0%	0%	0%
<b>573</b>	100%	0%	0%	0%	0%	0%	0%
<b>623</b>	90%	5%	0%	0%	0%	0%	0%
<b>673</b>	88%	8%	0%	0%	0%	0%	0%
<b>I-Cu/Si</b>							
<b>423</b>	100%	0%	0%	0%	0%	0%	0%
<b>473</b>	100%	0%	0%	0%	0%	0%	0%
<b>523</b>	100%	0%	0%	0%	0%	0%	0%
<b>573</b>	100%	0%	0%	0%	0%	0%	0%
<b>623</b>	96%	7%	0%	0%	0%	0%	0%
<b>673</b>	75%	19%	0%	2%	0%	0%	0%

**Table S3:** selectivity during stability test at 573 K.

Cu/Si	Selectivity							Cu/SiM 1	Selectivity						
	S CH <sub>3</sub> CHO	S C <sub>2</sub> H <sub>4</sub>	S C <sub>4</sub> H <sub>10</sub> O	S CH <sub>4</sub>	S CH <sub>3</sub> COOH	S CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>	S C <sub>4</sub> H <sub>8</sub> O		Time (h)	S CH <sub>3</sub> CHO	S C <sub>2</sub> H <sub>4</sub>	S C <sub>4</sub> H <sub>10</sub> O	S CH <sub>4</sub>	S CH <sub>3</sub> COOH	S CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>
<b>1</b>	100.0 %	0.0 %	0.4%	0.3 %	0.8%	0.0%	0.0%	<b>1</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>2</b>	100.0 %	0.0 %	0.1%	0.0 %	0.0%	0.0%	0.0%	<b>2</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>3</b>	100.0 %	0.0 %	0.1%	0.0 %	0.0%	0.0%	0.0%	<b>3</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>4</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>4</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>5</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>5</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>6</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>6</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>7</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>7</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>8</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>8</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>9</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>9</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>10</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>10</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>11</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>11</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>12</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>12</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>13</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>13</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%

<b>14</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>14</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>15</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>15</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>16</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>16</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>17</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>17</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>18</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>18</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>19</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>19</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>20</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>20</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>21</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>21</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>22</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>22</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>23</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>23</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>24</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>24</b>	100.0 %	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%

**Table S4:** selectivity during stability test at 623 K.

Cu/Si	Selectivity							Cu/SiM 1	Selectivity						
	S CH <sub>3</sub> CHO	S C <sub>2</sub> H <sub>4</sub>	S C <sub>4</sub> H <sub>10</sub> O	S CH <sub>4</sub>	S CH <sub>3</sub> COOH	S CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>	S C <sub>4</sub> H <sub>8</sub> O		Time (h)	S CH <sub>3</sub> CHO	S C <sub>2</sub> H <sub>4</sub>	S C <sub>4</sub> H <sub>10</sub> O	S CH <sub>4</sub>	S CH <sub>3</sub> COOH	S CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>
<b>1</b>	93.2%	3.8 %	0.1%	0.8 %	0.2%	0.0%	0.0%	<b>1</b>	91.8%	3.2 %	0.0%	1.1 %	0.0%	0.0%	0.0%
<b>2</b>	92.0%	2.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>2</b>	91.8%	3.4 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>3</b>	92.3%	2.1 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>3</b>	91.5%	3.2 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>4</b>	90.1%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>4</b>	98.8%	2.8 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>5</b>	90.4%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>5</b>	92.1%	2.7 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>6</b>	94.2%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>6</b>	96.2%	2.7 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>7</b>	89.6%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>7</b>	96.0%	2.3 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>8</b>	89.3%	2.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>8</b>	91.2%	2.6 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>9</b>	92.9%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>9</b>	92.1%	2.6 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>10</b>	91.9%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>10</b>	92.6%	2.7 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>11</b>	91.4%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>11</b>	92.9%	2.6 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>12</b>	92.8%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>12</b>	92.3%	2.7 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>13</b>	89.0%	2.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>13</b>	93.3%	2.8 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>14</b>	93.0%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>14</b>	90.7%	2.8 %	0.0%	0.0 %	0.0%	0.0%	0.0%

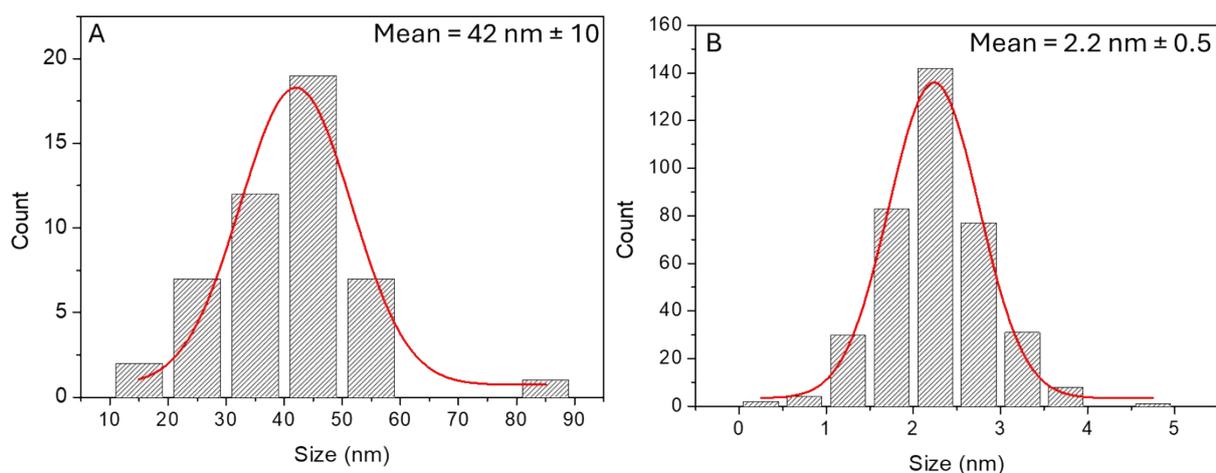
<b>15</b>	92.9%	2.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>15</b>	94.7%	2.5 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>16</b>	90.3%	2.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>16</b>	92.1%	2.6 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>17</b>	93.8%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>17</b>	76.8%	2.6 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>18</b>	93.1%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>18</b>	91.0%	2.6 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>19</b>	93.6%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>19</b>	93.3%	2.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>20</b>	90.4%	2.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>20</b>	93.8%	3.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>21</b>	93.7%	1.5 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>21</b>	92.9%	3.2 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>22</b>	93.8%	2.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>22</b>	92.0%	3.3 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>23</b>	92.7%	1.1 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>23</b>	95.7%	3.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>24</b>	92.9%	2.1 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>24</b>	92.2%	3.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%

**Table S5:** selectivity during ramping and stability test at 623 K.

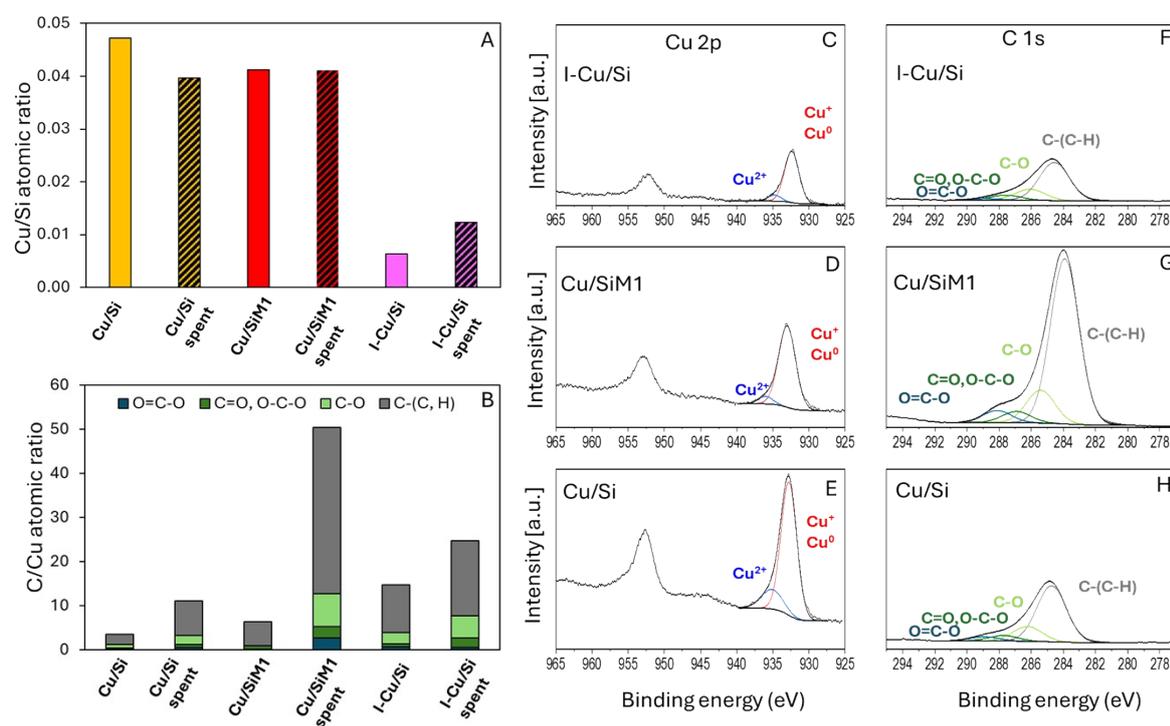
<b>Cu/Si</b>	<b>Selectivity</b>							<b>Cu/SiM 1</b>	<b>Selectivity</b>						

Time (h)	S CH <sub>3</sub> CHO	S C <sub>2</sub> H <sub>4</sub>	S C <sub>4</sub> H <sub>10</sub> O	S CH <sub>4</sub>	S CH <sub>3</sub> COOH	S CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>	S C <sub>4</sub> H <sub>8</sub> O	Time (h)	S CH <sub>3</sub> CHO	S C <sub>2</sub> H <sub>4</sub>	S C <sub>4</sub> H <sub>10</sub> O	S CH <sub>4</sub>	S CH <sub>3</sub> COOH	S CH <sub>3</sub> COOCH <sub>2</sub> CH <sub>3</sub>	S C <sub>4</sub> H <sub>8</sub> O
<b>1</b>	93.2%	3.8%	0.1%	0.8%	0.2%	0.0%	0.0%	<b>1</b>	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
<b>2</b>	92.0%	2.0%	0.0%	0.0%	0.0%	0.0%	0.0%	<b>2</b>	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
<b>3</b>	92.3%	2.1%	0.0%	0.0%	0.0%	0.0%	0.0%	<b>3</b>	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
<b>4</b>	90.1%	1.9%	0.0%	0.0%	0.0%	0.0%	0.0%	<b>4</b>	100.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
<b>5</b>	90.4%	1.9%	0.0%	0.0%	0.0%	0.0%	0.0%	<b>5</b>	93.8%	2.2%	0.0%	0.0%	0.0%	0.0%	0.0%
<b>6</b>	94.2%	1.9%	0.0%	0.0%	0.0%	0.0%	0.0%	<b>6</b>	92.0%	2.0%	0.0%	0.0%	0.0%	0.0%	0.0%
<b>7</b>	89.6%	1.9%	0.0%	0.0%	0.0%	0.0%	0.0%	<b>7</b>	94.5%	2.0%	0.0%	0.0%	0.0%	0.0%	0.0%
<b>8</b>	89.3%	2.0%	0.0%	0.0%	0.0%	0.0%	0.0%	<b>8</b>	97.6%	2.2%	0.0%	0.0%	0.0%	0.0%	0.0%
<b>9</b>	92.9%	1.9%	0.0%	0.0%	0.0%	0.0%	0.0%	<b>9</b>	93.0%	2.0%	0.0%	0.0%	0.0%	0.0%	0.0%
<b>10</b>	91.9%	1.9%	0.0%	0.0%	0.0%	0.0%	0.0%	<b>10</b>	92.3%	1.9%	0.0%	0.0%	0.0%	0.0%	0.0%
<b>11</b>	91.4%	1.9%	0.0%	0.0%	0.0%	0.0%	0.0%	<b>11</b>	95.5%	1.9%	0.0%	0.0%	0.0%	0.0%	0.0%
<b>12</b>	92.8%	1.9%	0.0%	0.0%	0.0%	0.0%	0.0%	<b>12</b>	91.6%	1.7%	0.0%	0.0%	0.0%	0.0%	0.0%
<b>13</b>	89.0%	2.0%	0.0%	0.0%	0.0%	0.0%	0.0%	<b>13</b>	94.5%	1.6%	0.0%	0.0%	0.0%	0.0%	0.0%
<b>14</b>	93.0%	1.9%	0.0%	0.0%	0.0%	0.0%	0.0%	<b>14</b>	9.9%	1.4%	0.0%	0.0%	0.0%	0.0%	0.0%
<b>15</b>	92.9%	2.0%	0.0%	0.0%	0.0%	0.0%	0.0%	<b>15</b>	92.1%	1.4%	0.0%	0.0%	0.0%	0.0%	0.0%

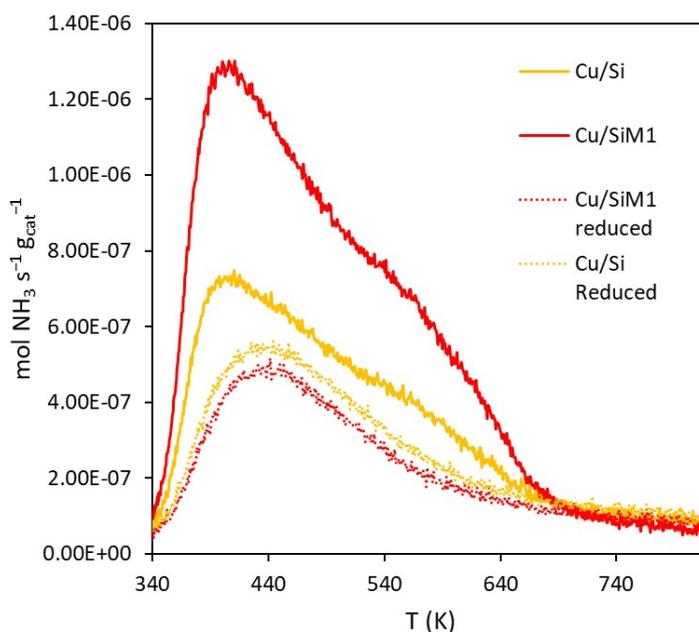
<b>16</b>	90.3%	2.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>16</b>	95.4%	1.5 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>17</b>	93.8%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>17</b>	93.7%	1.5 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>18</b>	93.1%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>18</b>	92.7%	1.5 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>19</b>	93.6%	1.9 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>19</b>	95.9%	1.5 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>20</b>	90.4%	2.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>20</b>	98.3%	1.7 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>21</b>	93.7%	1.5 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>21</b>	94.3%	1.5 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>22</b>	93.8%	2.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>22</b>	93.8%	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%
<b>23</b>	92.7%	1.1 %	0.0%	0.0 %	0.0%	0.0%	0.0%	<b>23</b>	92.0%	0.0 %	0.0%	0.0 %	0.0%	0.0%	0.0%



**Figure S6:** Particle size distribution of spent Cu/Si (A) and spent Cu/SiM1 (B)



**Figure S7:** XPS quantitative analyses of fresh and spent catalysts for Cu/Si at. Ratio (panel A) and C/Cu atomic ratio (panel B). Panels C, D, E report high resolution spectra of Cu 2p region while panels F, G, H report high resolution spectra of C 1s region for spent catalysts.



**Figure S8:** NH<sub>3</sub>-TPD patterns over calcined and reduced Cu/Si and Cu/SiM1

#### REFERENCES

- (1) Gervasini, A.; Bennici, S. Dispersion and Surface States of Copper Catalysts by Temperature-Programmed-Reduction of Oxidized Surfaces (s-TPR). *Appl. Catal. A Gen.* **2005**, *281* (1–2), 199–205.
- (2) Jensen, J. R.; Johannessen, T.; Livbjerg, H. An Improved N<sub>2</sub>O-Method for Measuring Cu-Dispersion. *Appl. Catal. A Gen.* **2004**, *266* (1), 117–122.
- (3) Jacquemin, M.; Genet, M. J.; Gaigneaux, E. M.; Debecker, D. P. Calibration of the X-Ray Photoelectron Spectroscopy Binding Energy Scale for the Characterization of Heterogeneous Catalysts: Is Everything Really under Control? *ChemPhysChem* **2013**, *14* (15), 3618–3626.
- (4) Genc, A.; Marlowe, J.; Jalil, A.; Belzberg, D.; Kovarik, L.; Christopher, P. A Versatile Machine Learning Workflow for High-Throughput Analysis of Supported Metal Catalyst Particles. *Ultramicroscopy* **2025**, *271* (3), 114116.