

## Supporting Information

# Mechanochemically-Flavoured Three-Way Approach for the Synthesis of K-doped Cu-Fe/ZnO-Al<sub>2</sub>O<sub>3</sub> Catalysts for Converting CO<sub>2</sub> to Oxygenates

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## EXPERIMENTAL SECTION

### Methods and materials

Na<sub>2</sub>CO<sub>3</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, CuO, Fe<sub>2</sub>O<sub>3</sub>, ZnO and Al<sub>2</sub>O<sub>3</sub> were purchased from Sigma Aldrich, Fe<sub>2</sub>O<sub>3</sub> from PenReac, K<sub>2</sub>CO<sub>3</sub> from Fisher and CuO from Merck. TraceMetal™ Grade nitric acid, hydrochloric acid and hydrofluoric acid used in elemental analysis were purchased from Fisher.

### Catalyst Preparation

#### A) Solution synthesis of **CFZA (SS1) Cu<sub>0.65</sub>-Fe<sub>0.05</sub>/Zn<sub>0.2</sub>Al<sub>0.1</sub>**

Cu<sub>0.65</sub>-Fe<sub>0.05</sub>/Zn<sub>0.2</sub>Al<sub>0.1</sub> was prepared *via* co-precipitation method. An aqueous solution of 1.2 M solution of Na<sub>2</sub>CO<sub>3</sub> (125 mL) was added dropwise to 100 mL aqueous solution of stoichiometric amount of Cu(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, Zn(NO<sub>3</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub> at 70 °C for 2 h and a pH of 6-7. During precipitation, the pH of the suspension was monitored constantly using a pH meter and Na<sub>2</sub>CO<sub>3</sub> solution was added at a controlled rate to maintain the prescribed pH (6–7). The resulting precipitate was washed with 1.5 L DI water and dried for 16 h at 70 °C in oven. The dried precipitate was calcined under air flow at 5 °C/min for 4 h at 350 °C and then reduced under H<sub>2</sub> at 5 °C/min for 4 h at 450 °C.

#### B) K-promoted **KCFZA (SS1-K) Cu<sub>0.65</sub>-Fe<sub>0.05</sub>/Zn<sub>0.2</sub>Al<sub>0.1</sub>**

K<sub>2</sub>CO<sub>3</sub> (5 wt% K) was added onto the calcined catalyst prepared in (A) *via* **incipient wetness impregnation** with an aqueous solution of K<sub>2</sub>CO<sub>3</sub>. The wet mixture is then dried in an oven for 2 h at 120 °C. After drying, the solid powder is placed in a tube furnace and calcinated with an air flow at 5 °C/min for 4 h at 350 °C and then reduced under H<sub>2</sub> at 5 °C/min for 4 h at 450 °C to yield **SS1-K**.

Catalyst preparation *via* **mechanosynthesis**: Mechanosynthesis of **KCFZA** was carried out in a Retch MM400 mill at a frequency of 29 Hz using a 35 mL 440B stainless steel milling jar and three balls made of the same material (10 mm diameter).

**BM1 – Mechanosynthesis of solution-synthesized KCFZA:** K<sub>2</sub>CO<sub>3</sub> (5 wt% K, 0.1 g) and the calcined catalyst (2.0 g) prepared from (A) was added into the 35 mL milling jar and then milled neat at a frequency of 29 Hz for 1 h following by calcination under air flow at 5 °C/min for 4 h at 350 °C and then reduction under H<sub>2</sub> at 5 °C/min for 4 h at 450 °C.

**BM2 – Mechanosynthesis of KCFZA using metallic nitrate salt precursors:** Stoichiometric amount of Cu(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Al(NO<sub>3</sub>)<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> were weighed (total weight about 4.0 g) and 1 mL of DI water (as the milling media) transferred into a 35 mL milling jar and milled at 29 Hz for 3 h. After milling, the resultant solids were washed with 500 mL DI water and dried 16 h at 70 °C in oven. The dried

precipitate was calcined under air flow at 5 °C/min for 4 h at 350 °C and then reduced under H<sub>2</sub> at 5 °C/min for 4 h at 450 °C. K<sub>2</sub>CO<sub>3</sub> (5 wt% K, 0.05 g) and the calcined catalyst (1.0 g) was added into a 35 mL milling jar and milled neat at a frequency of 29 Hz for 1 h following by calcination under air flow at 5 °C/min for 4 h at 350 °C and then reduction under H<sub>2</sub> at 5 °C/min for 4 h at 450 °C.

**BM3 - Mechano-synthesis of KCFZA using metallic oxide precursors:** Stoichiometric amount of CuO, Fe<sub>2</sub>O<sub>3</sub>, ZnO and Al<sub>2</sub>O<sub>3</sub> were weighed (total weight about 4.0 g) and transferred into a 35 mL milling jar and milled neat at a frequency of 29 Hz for 3 h. The product was calcined under air flow at 5 °C/min for 4 h at 350 °C and then reduced under H<sub>2</sub> at 5 °C/min for 4 h at 450 °C. K<sub>2</sub>CO<sub>3</sub> (5 wt% K, 0.05 g) was added onto the calcined catalyst (1.0 g) ball-milled neat at a frequency of 29 Hz for 1 h following by calcination under air flow at 5 °C/min for 4 h at 350 °C and then reduction under H<sub>2</sub> at 5 °C/min for 4 h at 450 °C.

### **Catalyst characterization**

Powder X-ray diffraction (XRD) patterns of the calcined **KCFZA** catalysts were collected on a powder diffractometer (Bruker D8 Advance X-ray) with a Cu-K<sub>α</sub> source (K<sub>α</sub>=0.154nm) in the 2θ range between 20–80°. Scanning electron microscopy (SEM) was conducted using a JEOL JSM-7900F Schottky Field Emission Scanning Electron Microscope fitted with Oxford Instruments X-Max 80 EDX spectrometer. SEM Images were taken at an acceleration voltage of 10 kV while EDX analysis at an acceleration voltage of 15 kV. Samples were sputter-coated with gold, by Cressington 208HR High Resolution Sputter Coater for better conductivity. High resolution transmission electron microscopy (HRTEM) was conducted using a JEOL JEM-2200FS field emission with a high-energy electron beam operated at 200 kV. The instrument is equipped with JEOL JED-2300 Plus EDS detector for elemental analysis. Samples were prepared by drop-casting and air drying a dilute suspension of nanoparticles, after sonicating in HPLC-grade ethanol (99.8% purity), onto carbon-coated molybdenum grids. Elemental analysis of the catalysts was performed by digesting the catalysts using a Milestone ETHOS One microwave system containing 10 PTFE (polytetrafluoroethylene) Teflon digestion containers (100 mL) equipped with individual pressure safety springs and a high pressure segmented rotor (Milestone model HPR 1000/10S) with a system pressure sensor using HPR-CE-01 method in the Milestone application note, followed by analysis performed with a Varian Vista MPX CCD ICP-OES.

### **Catalysis**

All catalytic experiments were performed using a 50 mL Parr 4792 reactor with a thermocouple attached and heated over a jacketed heater. Flow reaction was performed using a vertical tube furnace with a fixed catalyst

bed. Liquid CO<sub>2</sub> hydrogenation products were analysed on Agilent 6890N GC with Agilent CP-Wax 52 CB capillary column (50 m x 0.25 mm x 0.5 μm).

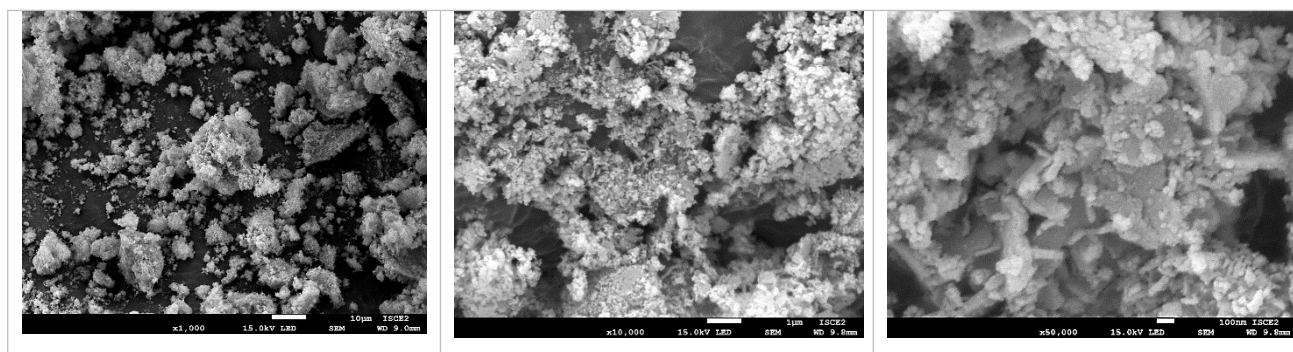
#### *General procedure for CO<sub>2</sub> hydrogenation reaction.*

For batch reaction: Into a 50 mL Parr reactor vessel with a magnetic stirrer bar was charged 100 mg catalyst and 10 mL water. The Parr reactor was sealed was purged 3 times with CO<sub>2</sub>. Subsequently, 15 bar CO<sub>2</sub> was charged into the reactor followed by 45 bar H<sub>2</sub>. The reaction was heated to 200 °C using a jacketed heater and was stirred for 16 h. The reaction was then cooled in an ice bath to room temperature and the gases were vented. 1 mL of the reaction mixture was filtered with a 0.45-micron syringe filter and then analysed with GC.

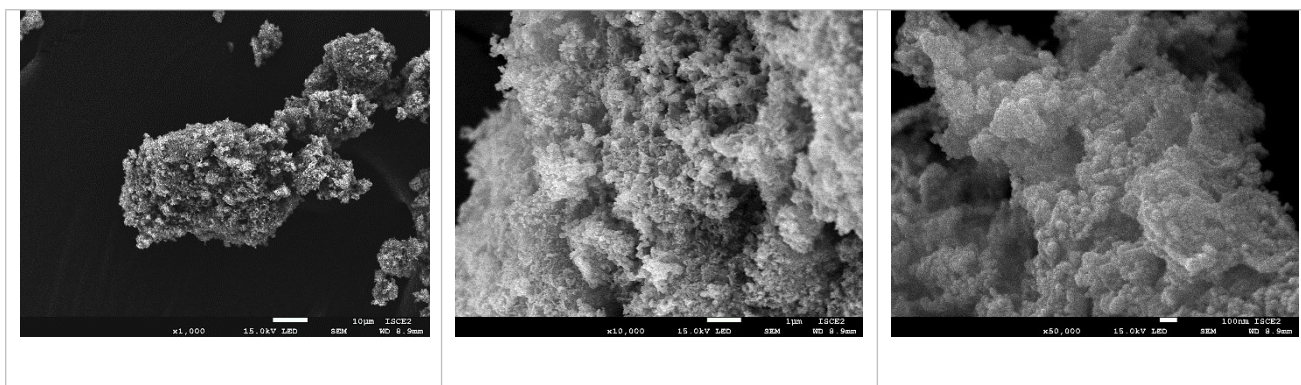
For continuous flow reaction, a 3/8" stainless tube was placed in a vertical furnace as the reactor. 0.5 g of catalyst was diluted in equal volume of SiC, supported on quartz wool as a fixed catalyst bed. The catalyst was first reduced with 50% H<sub>2</sub> at 400°C for 3 hours. Reaction gas mix (24% CO<sub>2</sub>, 72% H<sub>2</sub>, 4% Ar) was flowed through the catalyst at SV 2500 ml(gh)<sup>-1</sup> and at 50 bar. The CO<sub>2</sub> hydrogenation reaction was performed at 200 C for 16 hours. An online GC (equipped with a Thermal Conductivity Detector and Flame Ionisation Detector) was employed to analyse the reaction products.

## SUPPORTING INFORMATION

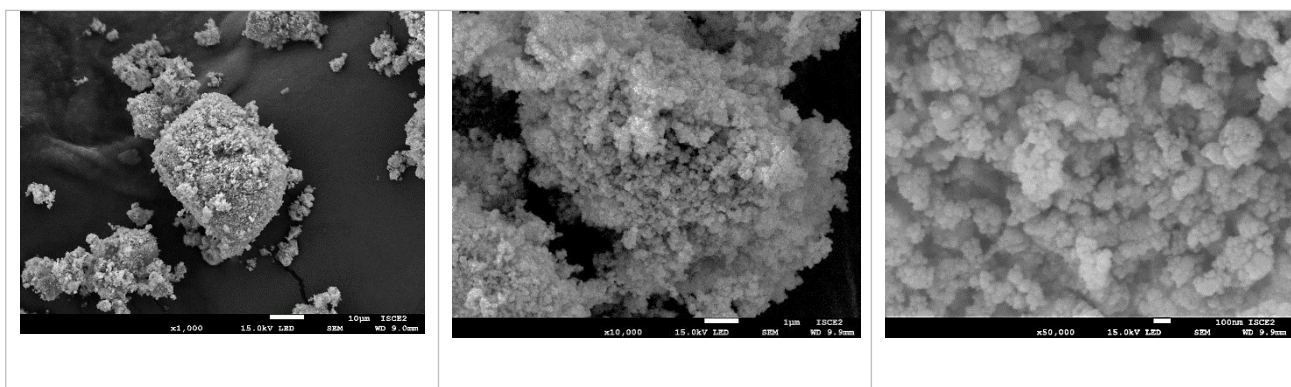
### SEM Micrograph/ SEM-EDX elemental mapping



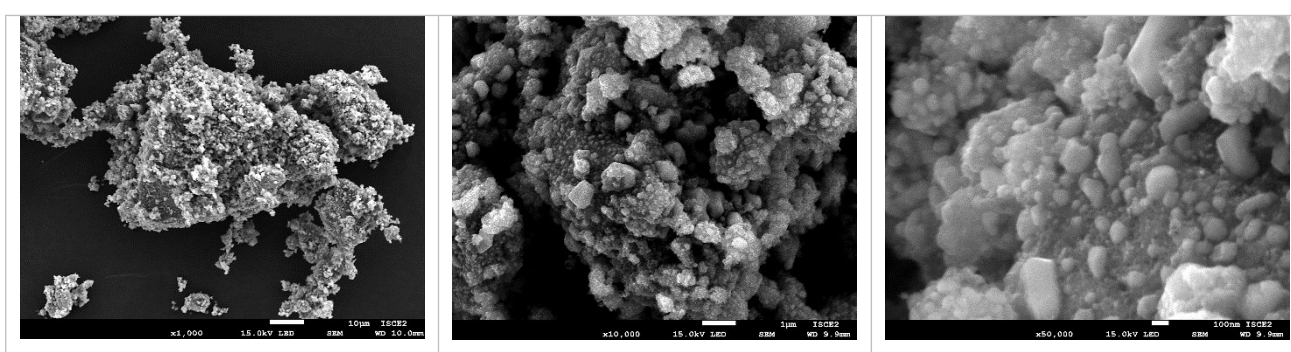
**Supp. Info. 1.** SEM micrographs of solution synthesized Cu-Fe/Zn/Al (**SS1**) catalyst, 1k magnification (left), 10k magnification (middle) and 50k magnification (right).



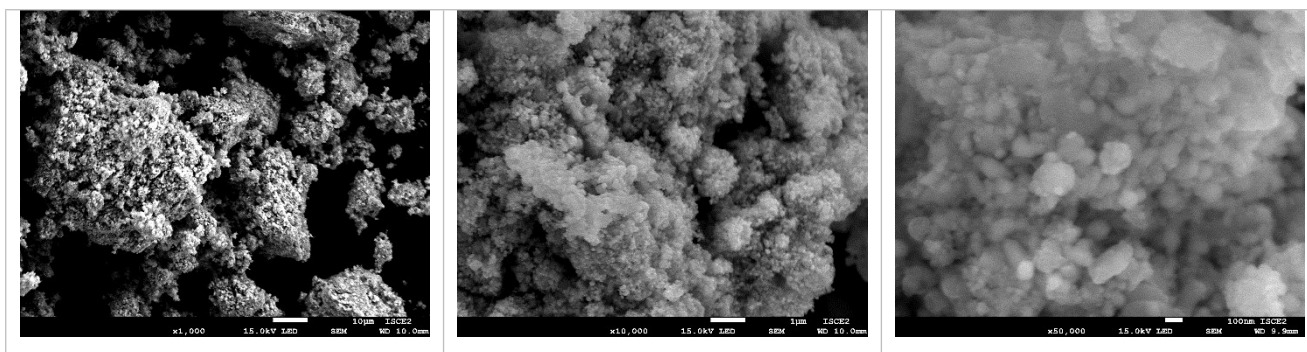
**Supp. Info. 2.** SEM micrographs of K-doped Cu-Fe/Zn/Al catalyst *via* wet impregnation (**SS1-K**), 1k magnification (left), 10k magnification (middle) and 50k magnification (right).



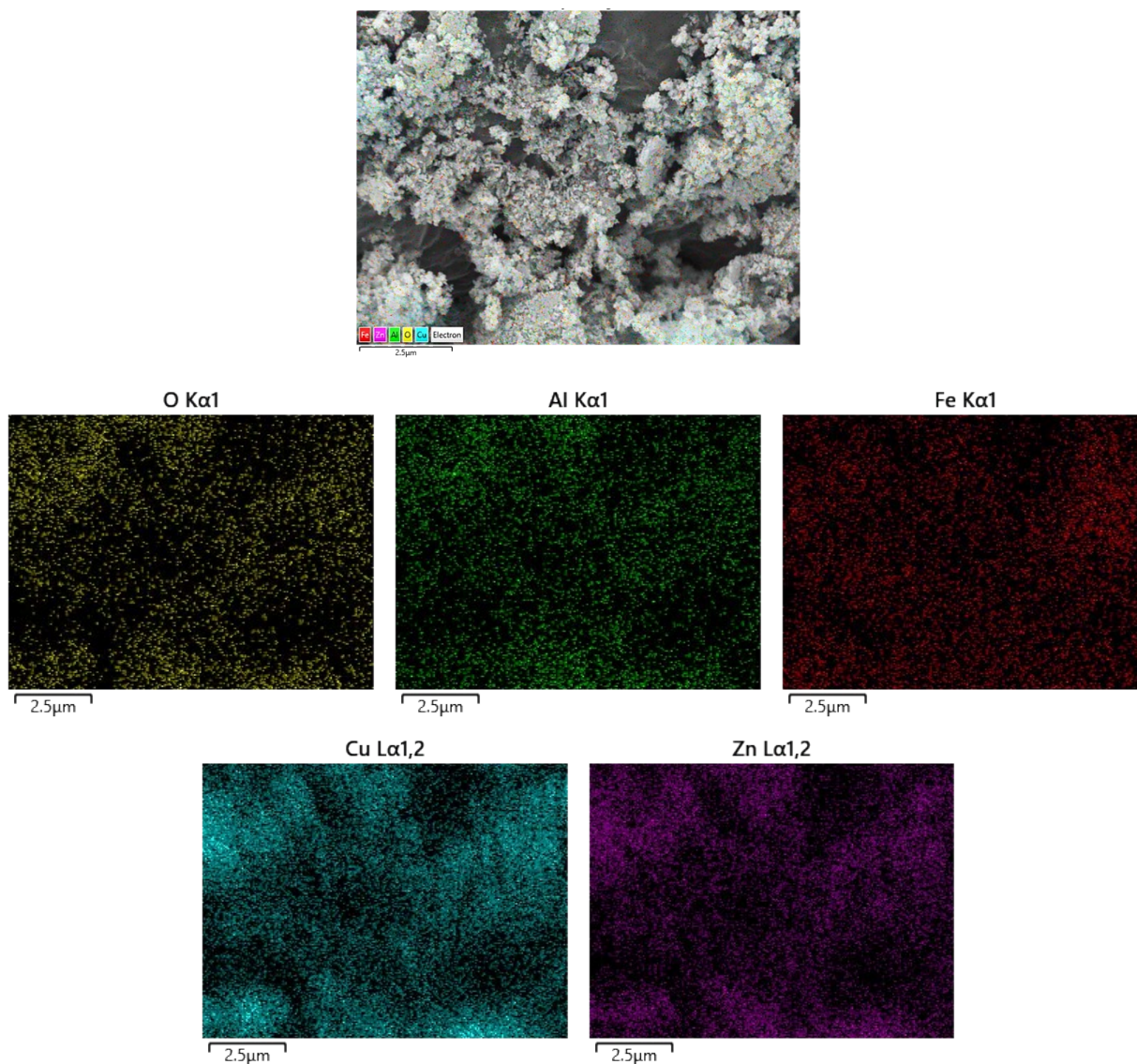
**Supp. Info. 3.** SEM micrographs of K-doped Cu-Fe/Zn/Al (KCFZA) catalyst *via* mechanosynthesis (**BM1**), 1k magnification (left), 10k magnification (middle) and 50k magnification (right).



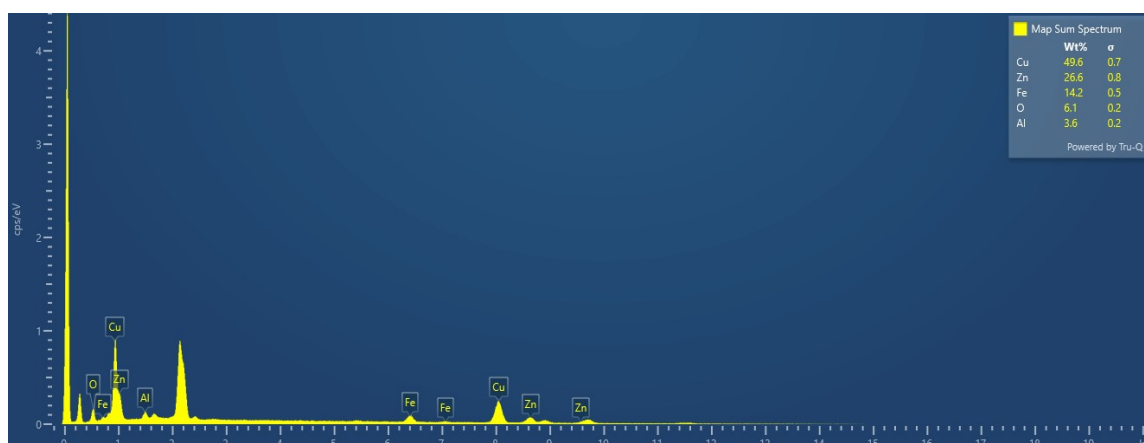
**Supp. Info. 4.** SEM micrographs of K-doped Cu-Fe/Zn/Al (KCFZA) catalyst using metallic nitrate salt precursors (**BM2**), 1k magnification (left), 10k magnification (middle) and 50k magnification (right).



**Supp. Info. 5.** SEM micrographs of K-doped Cu-Fe/Zn/Al (**KCFZA**) catalyst using metallic oxide precursors (**BM3**), 1k magnification (left), 10k magnification (middle) and 50k magnification (right).



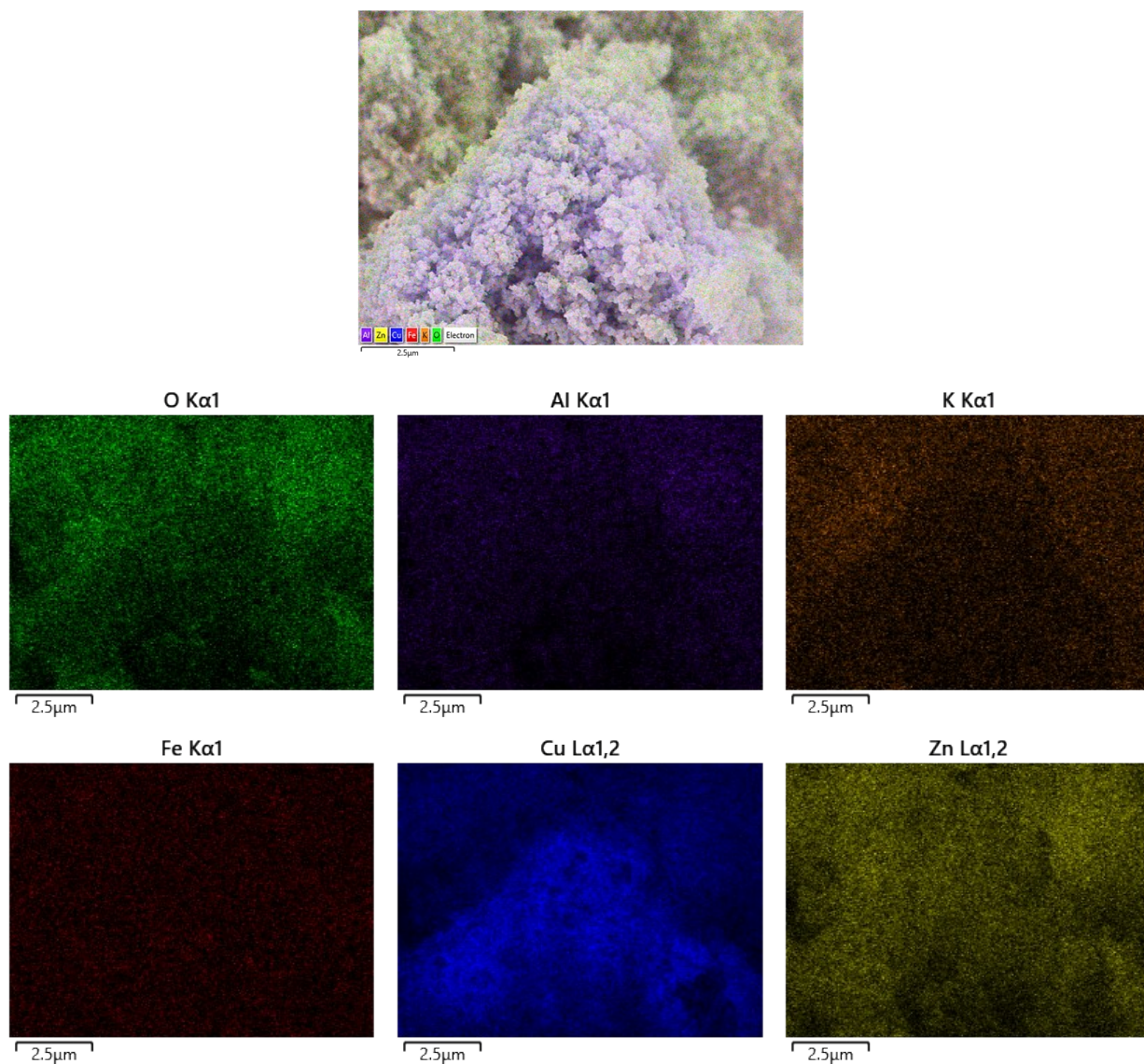
(A)



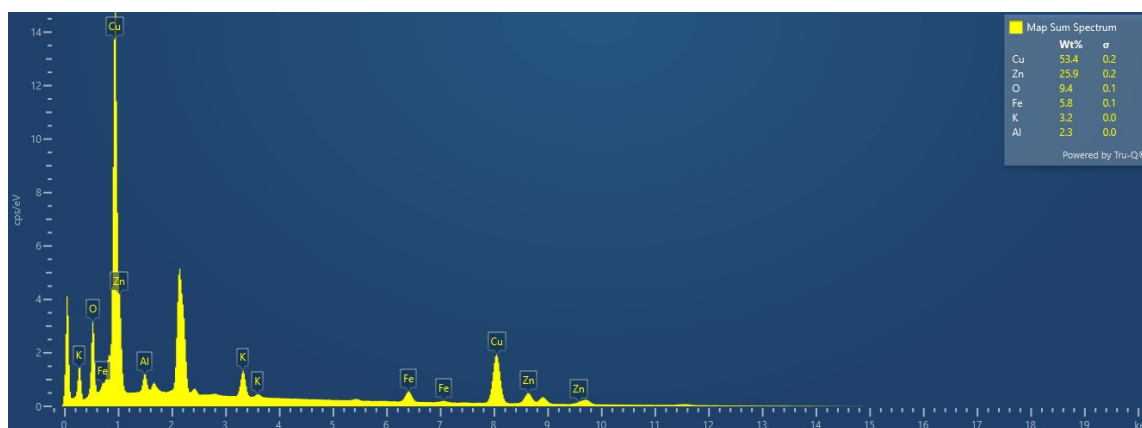
(B)

**Supp. Info. 6.** (A) SEM-EDX elemental mapping of solution synthesized Cu-Fe/Zn/Al (SS1) catalyst, (B) elemental composition of solution synthesized Cu-Fe/Zn/Al (SS1) catalyst.



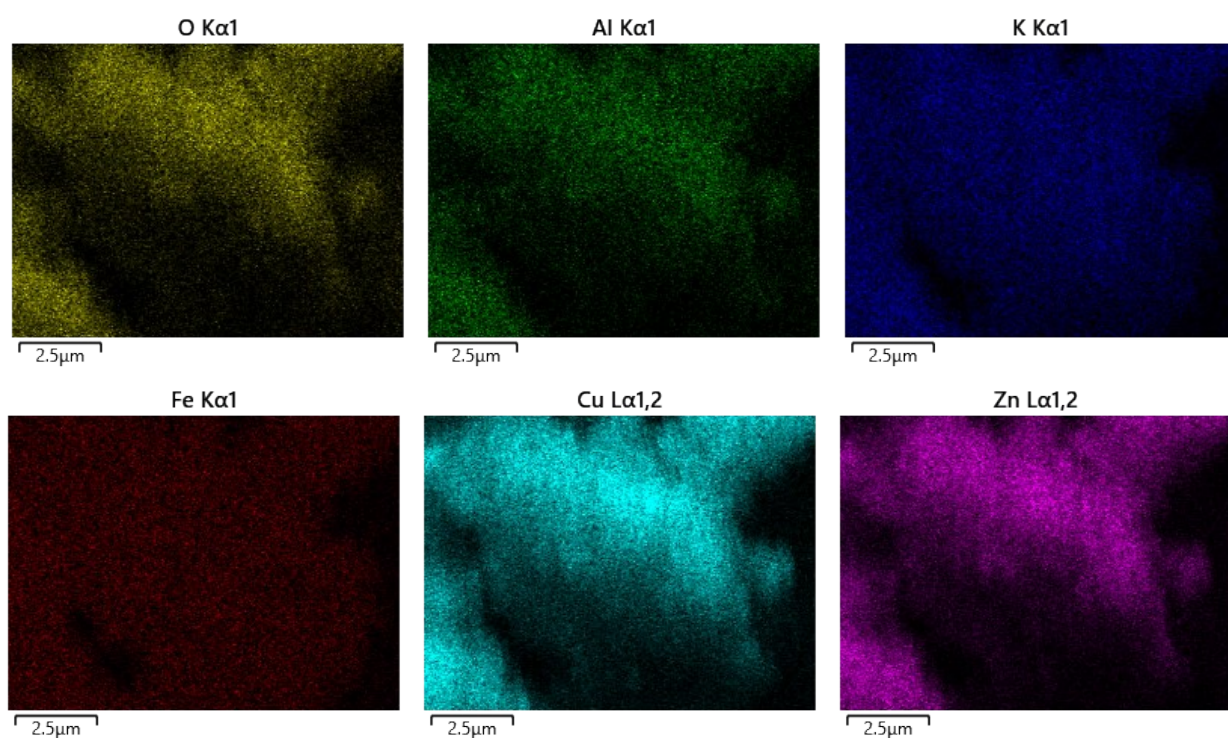
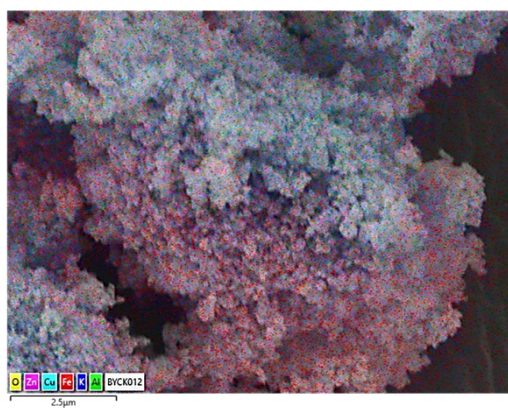


(A)

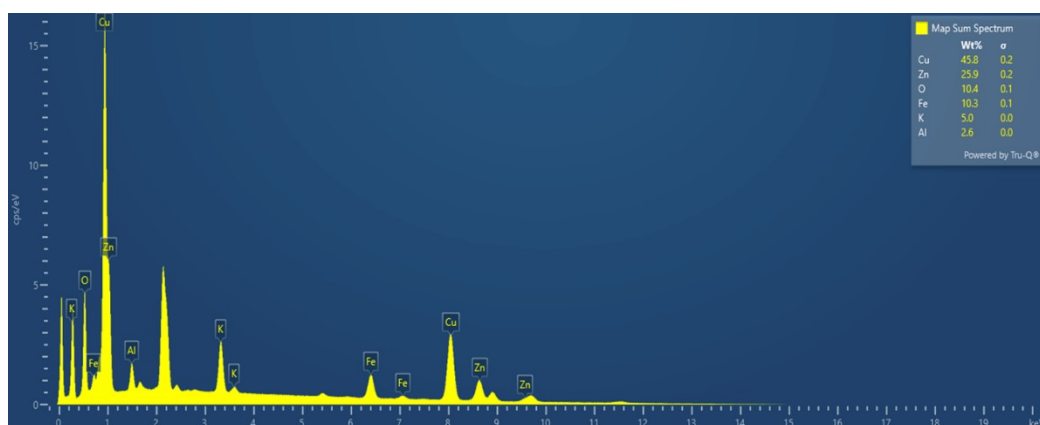


(B)

**Supp. Info. 7.** (A) SEM-EDX elemental mapping of K-doped Cu-Fe/Zn/Al catalyst *via* wet impregnation (**SS1-K**), (B) elemental composition of K-doped Cu-Fe/Zn/Al catalyst *via* wet impregnation (**SS1-K**).

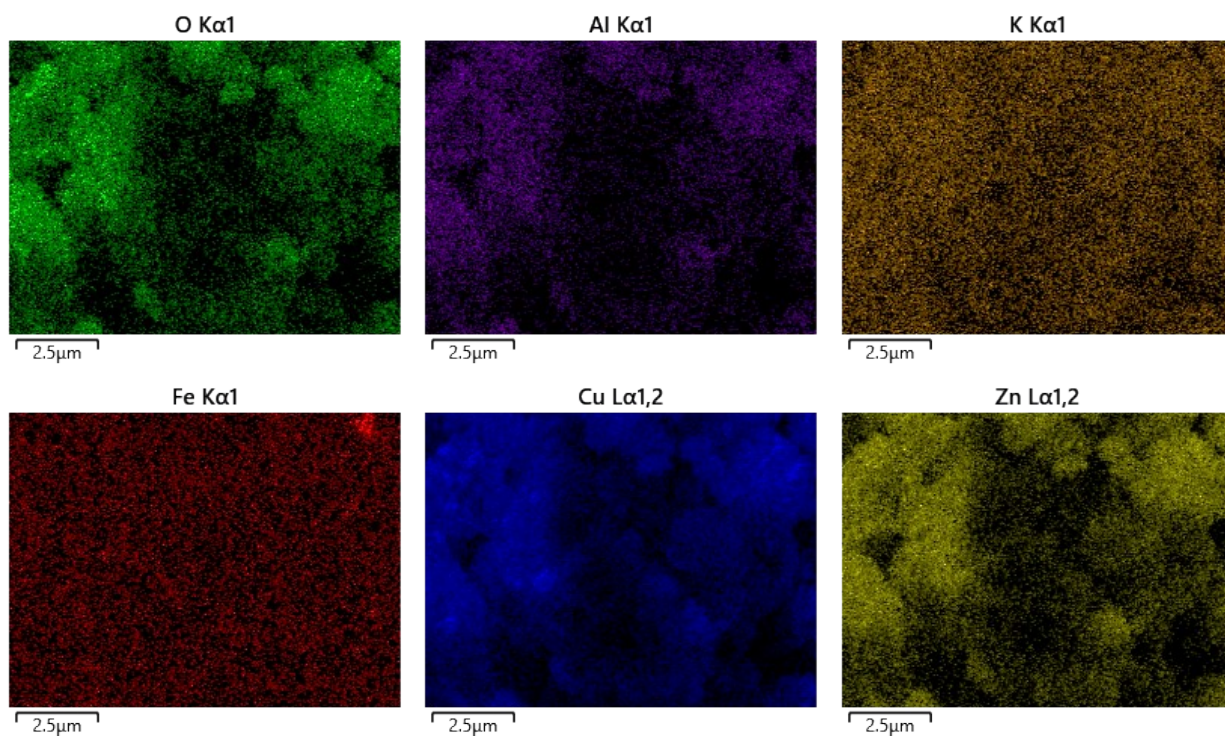


(A)

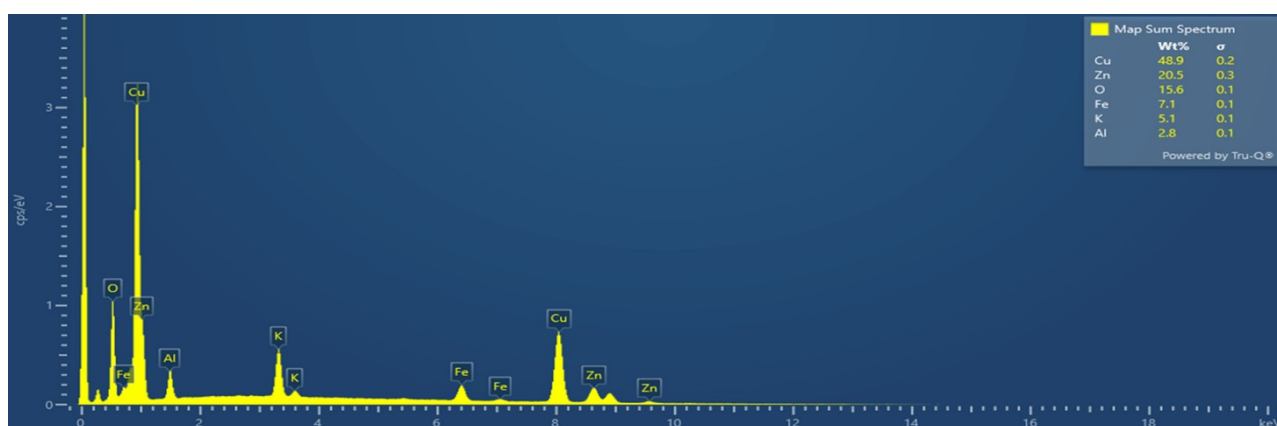


(B)

**Supp. Info. 8.** (A) SEM-EDX elemental mapping of K-doped Cu-Fe/Zn/Al (**KCFZA**) catalyst via ball milling (**BM1**), (B) elemental composition of K-doped Cu-Fe/Zn/Al (**KCFZA**) catalyst via ball milling (**BM1**).

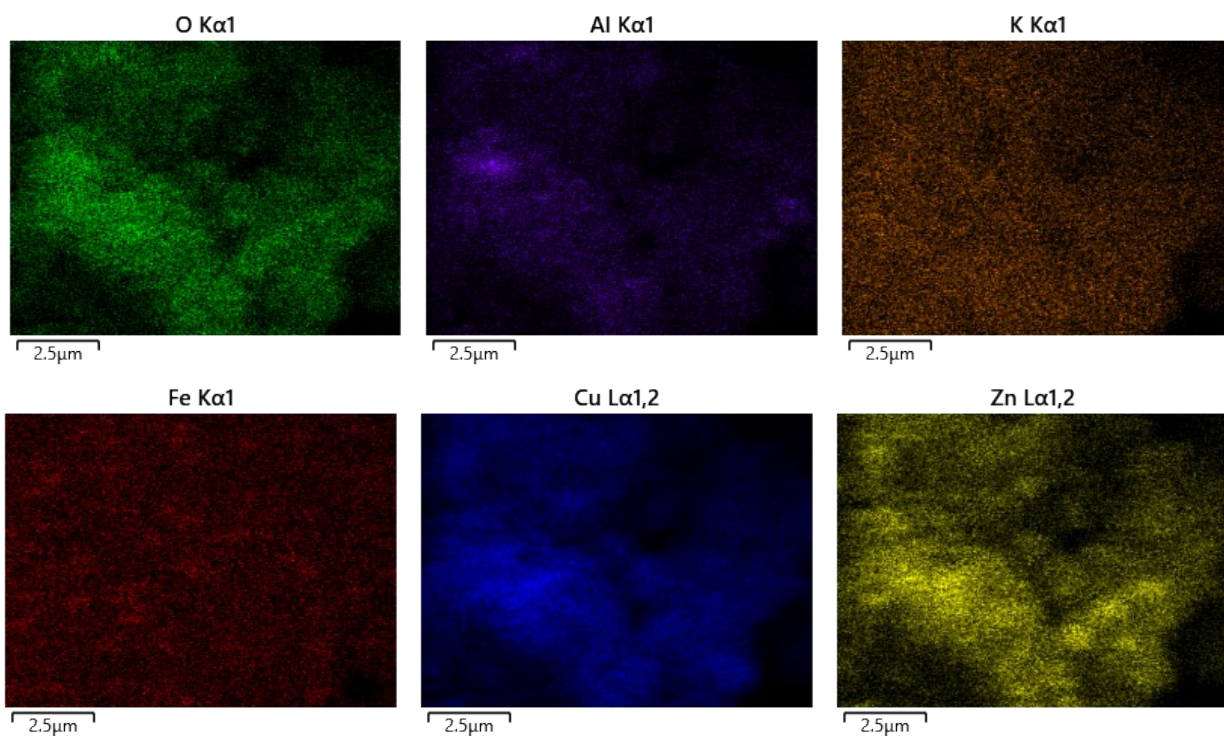
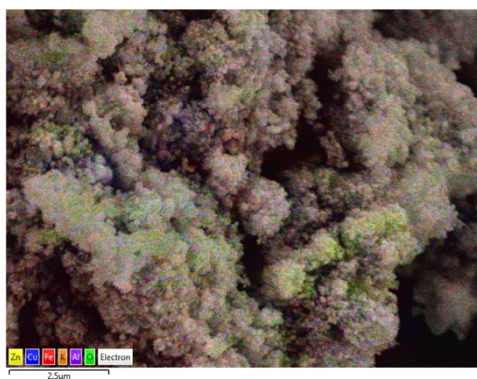


(A)

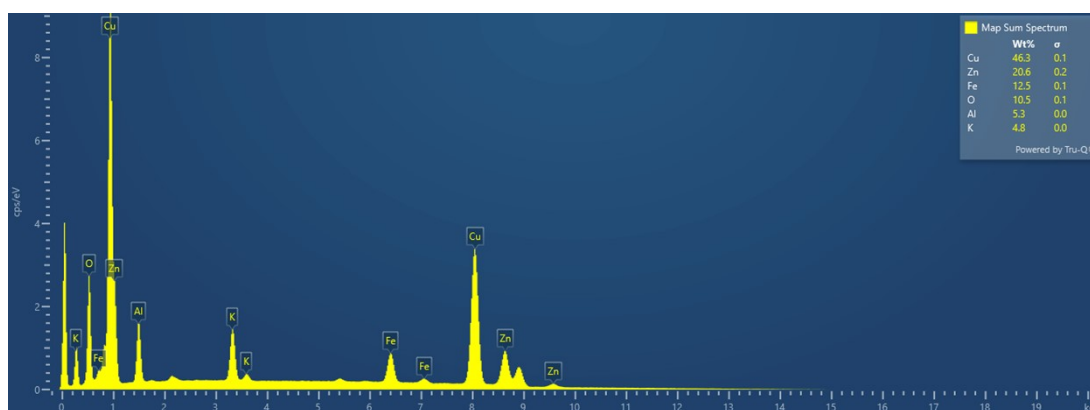


(B)

**Supp. Info. 9.** (A) SEM-EDX elemental mapping of K-doped Cu-Fe/Zn/Al (**KCFZA**) catalyst using metallic nitrate salt precursors (**BM2**), (B) elemental composition of K-doped Cu-Fe/Zn/Al (**KCFZA**) catalyst using metallic nitrate salt precursors (**BM2**).



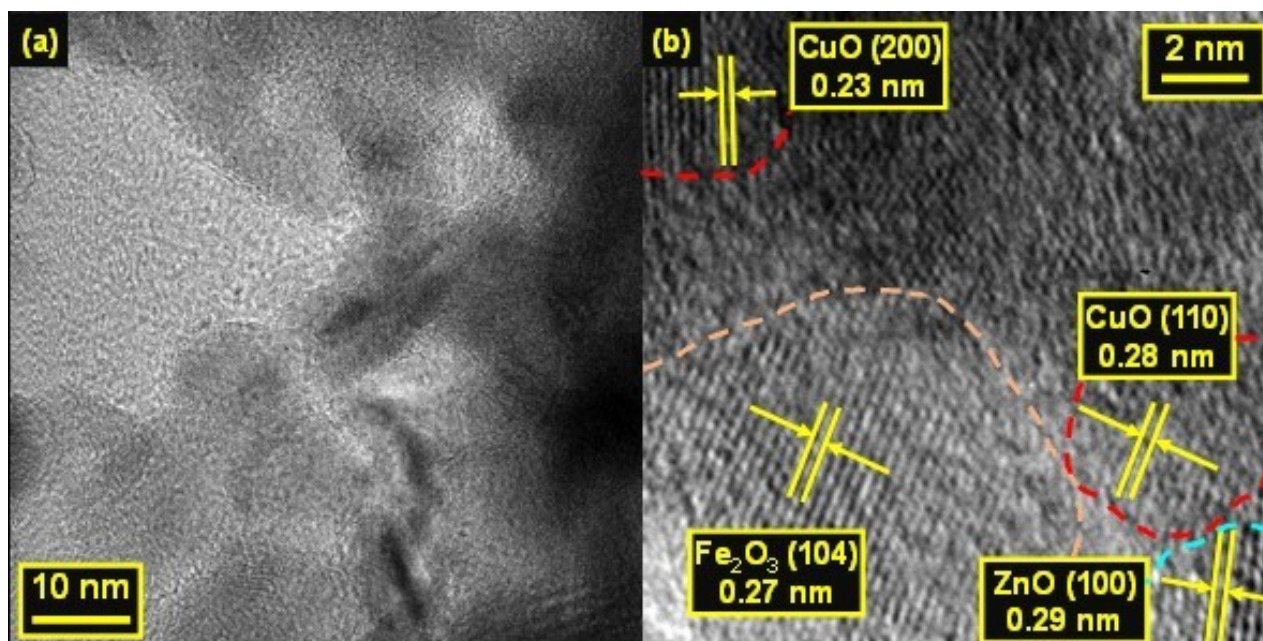
(A)



(B)

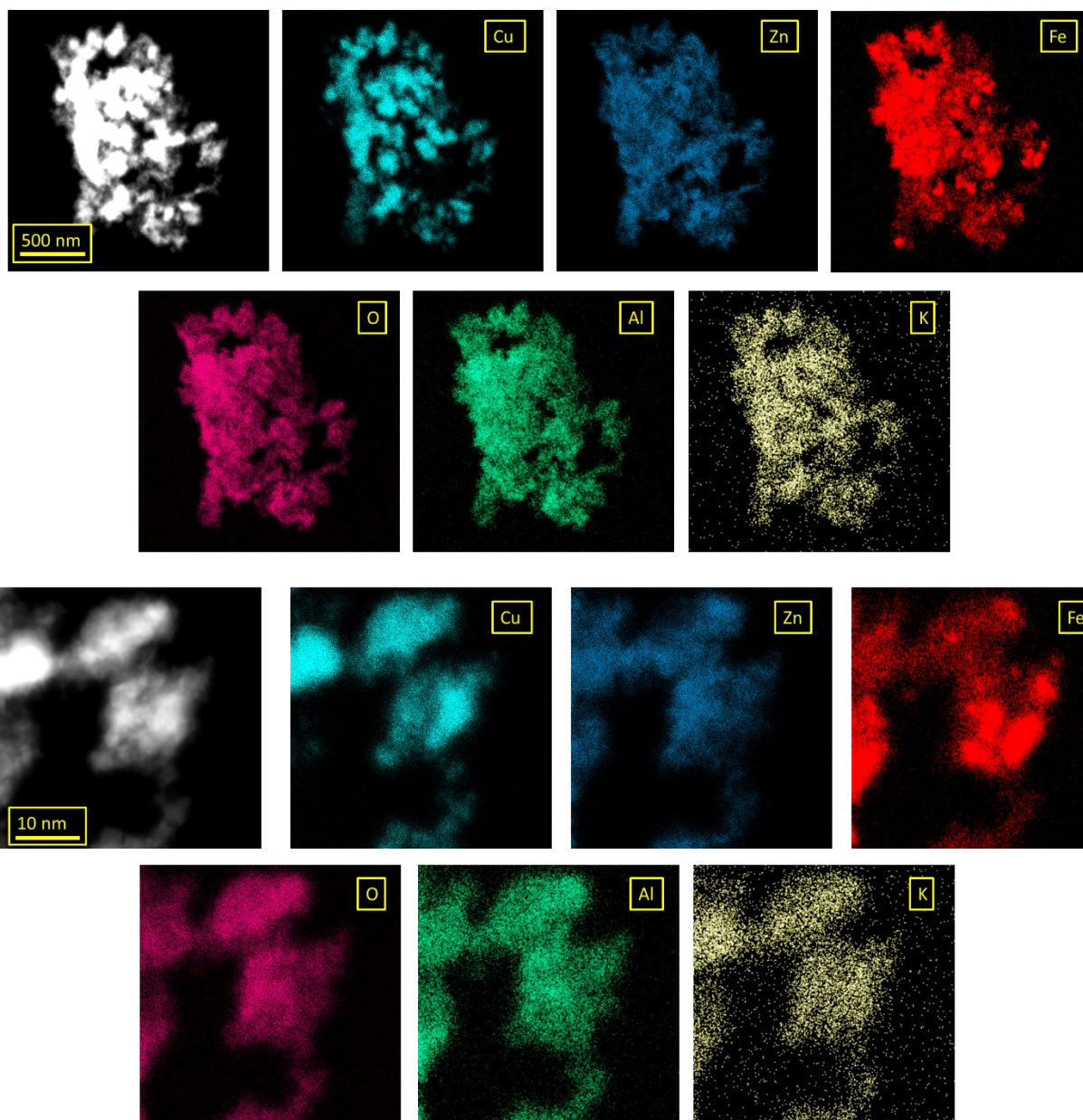
**Supp. Info. 10.**(A) SEM-EDX elemental mapping K-doped Cu-Fe/Zn/Al (**KCFZA**) catalyst using metallic oxide precursors (**BM3**), (B) elemental composition of K-doped Cu-Fe/Zn/Al (**KCFZA**) catalyst using metallic oxide precursors (**BM3**).

## HR-TEM Micrograph/ TEM-EDX elemental mapping

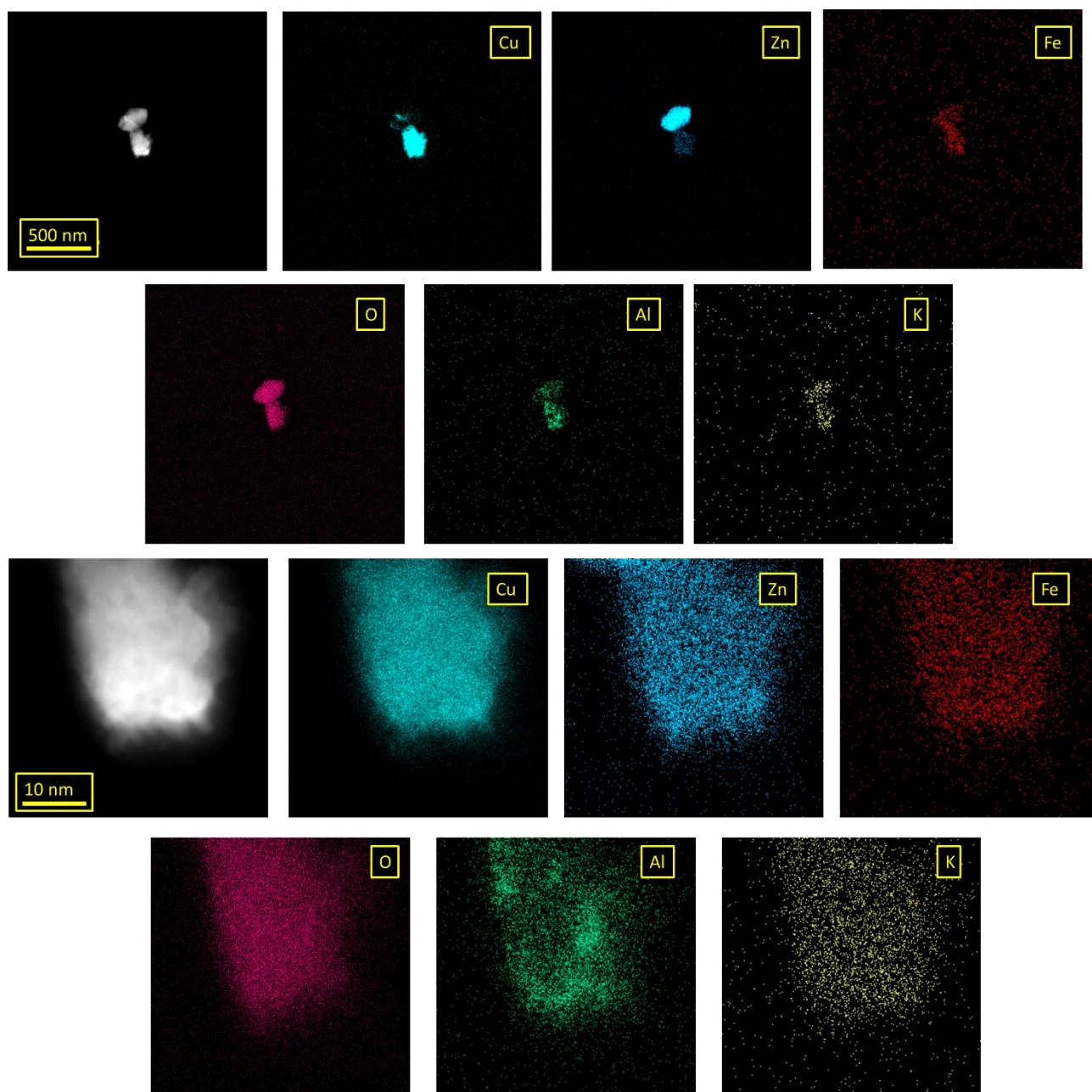


**Supp. Info. 11.** (A) TEM micrographs of K-doped Cu-Fe/Zn/Al catalyst *via* wet impregnation (SS1-K), (B) lattice d-spacing of the observed CuO, ZnO, Fe<sub>2</sub>O<sub>3</sub> particles in the sample.

TEM shows areas containing lattice d-spacing for Cu, ZnO and Fe<sub>2</sub>O<sub>3</sub> zones in close proximity for particles of SS1-K. Such multi-metallic zones could have promoted the formation of EtOH and higher alcohols.

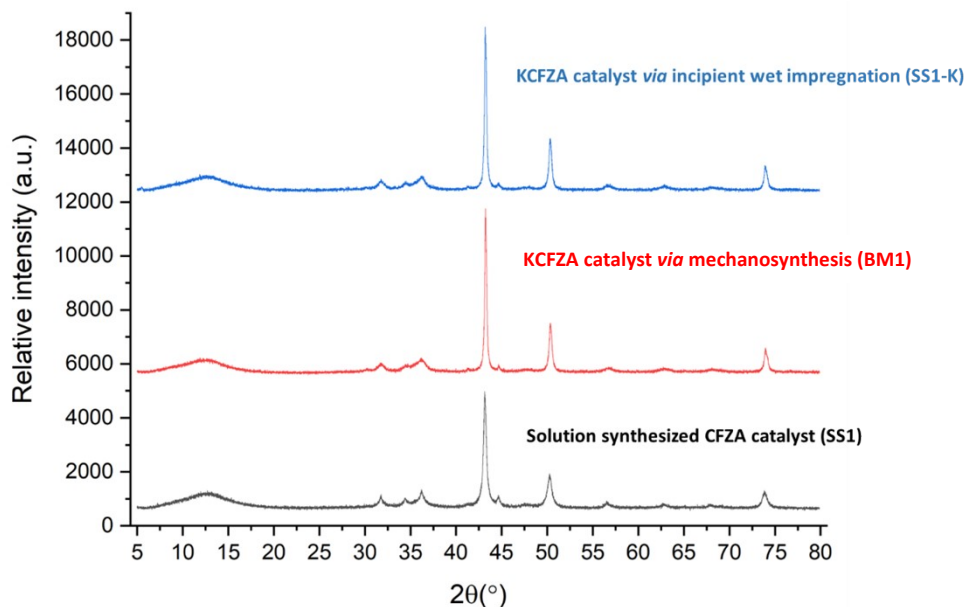


**Supp. Info. 12.** TEM-EDX elemental mapping K-doped Cu-Fe/Zn/Al (**KCFZA**) catalyst using metallic nitrate salt precursors (**SS1-K**). Brightness for images of Fe, Al and K have been increased by 65% and sharpness reduced by 30%.

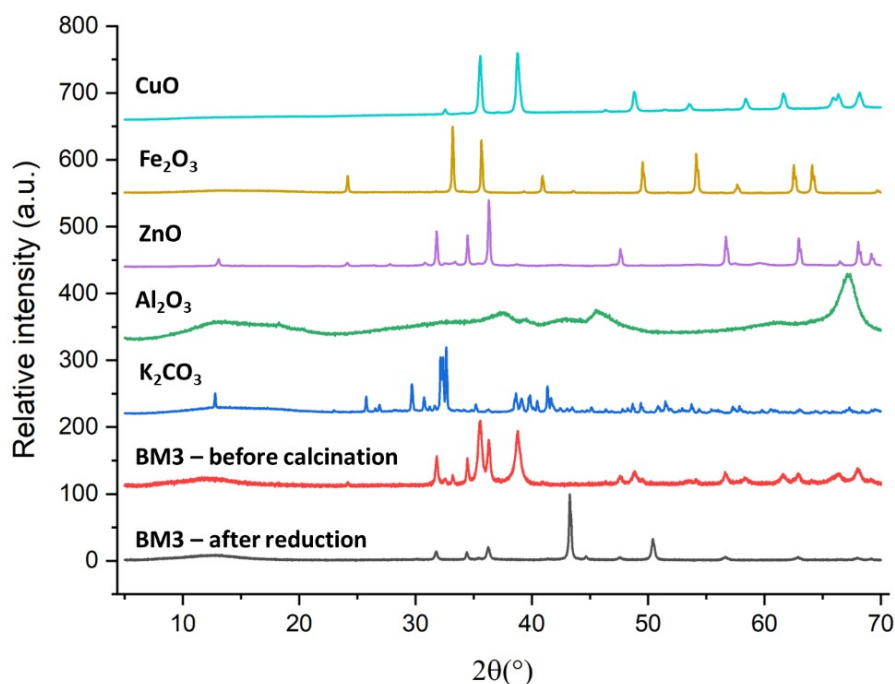


**Supp. Info. 13.** TEM-EDX elemental mapping K-doped Cu-Fe/Zn/Al (**KCFZA**) catalyst using metallic oxide precursors (**BM3**). Brightness for images of Fe, Al and K have been increased by 65% and sharpness reduced by 30%.

## X-Ray Diffraction Patterns



**Supp. Info. 14.** X-ray diffraction patterns of solution synthesized **CZFA** catalyst, **SS1** (black line), and the K-promoted **KCFZA** catalysts *via* mechanosynthesis, **BM1** (red line) and incipient wet impregnation, **SS1-K** (blue line).

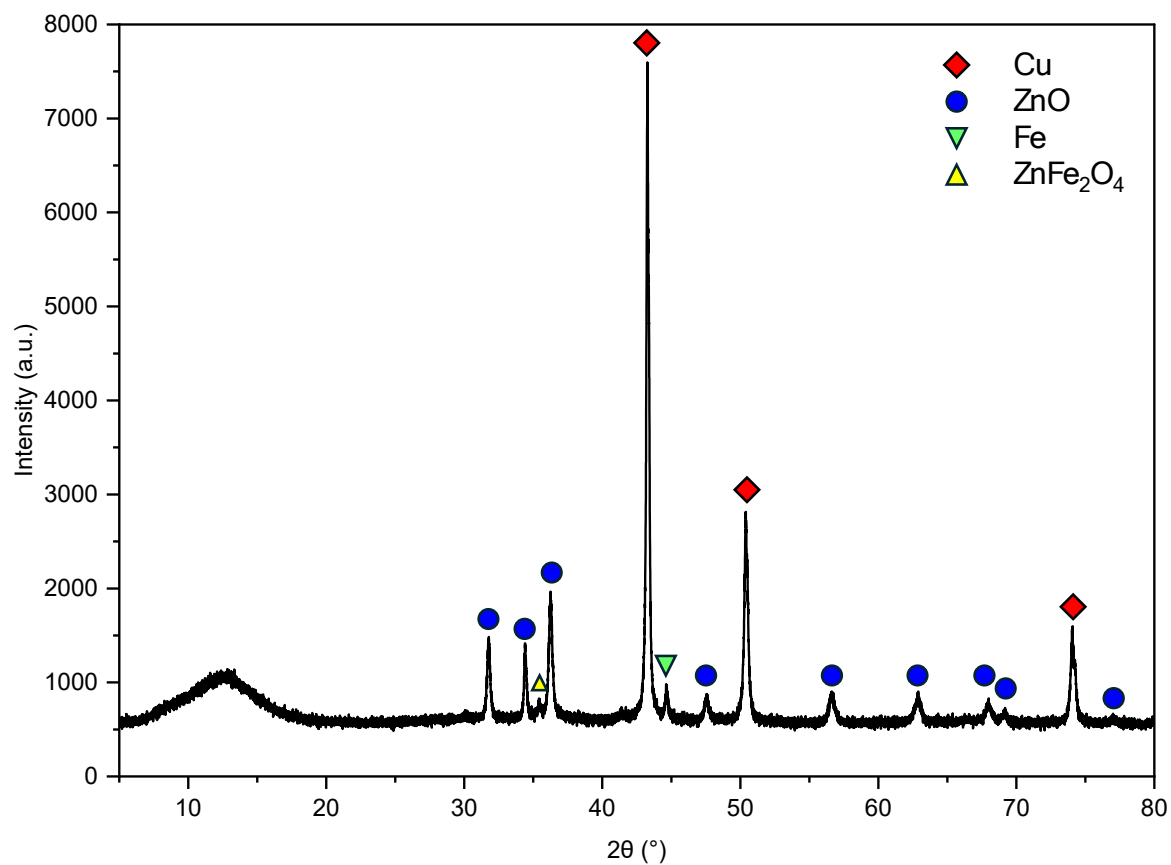


**Supp. Info. 15.** X-ray diffraction patterns of mechanosynthesized **KCZFA** catalyst using metallic oxide precursors (**BM3**) before calcination (red line), after reduction (black line) and the metallic oxides precursors CuO, Fe<sub>2</sub>O<sub>3</sub>, ZnO, Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> as the promotor.



	$\beta$	$2\theta$ (°)	D (nm)
SS1	0.3728	43.1	22.9
SS1-K	0.2256	43.2	37.9
BM1	0.2137	43.2	40.0
BM2	0.2256	43.2	37.9
BM3	0.1741	43.3	49.1

Supp. Info. 16. Crystallite size estimation of the five catalysts based on PXRD.



Supp. Info. 17. XRD analysis of BM3.

## Energy Calculation Data

The energy consumption for each method is based on the duration and relative power output of each equipment: Hotplate (825 W, max. temp. 300 °C), drying oven (1250 W, max. temp. 300 °C), tube furnace (3000 W, max. temp. 1200 °C) and ball mill (165 W, max. 30 Hz).

Method	Mass of catalyst (g)	Energy consumed synthesis + doping (J)	Energy consumed calcination + reduction (J)	Total Energy Consumed (J)	Liquid Waste (mL)*	Energy per gram catalyst (J/g)	Energy per gram catalyst** (J/g)	E-Factor***
SS1-K	3.0	4758.8	7729.0	12487.8	1725.0	4162.6	1586.3	575
BM1	3.0	4025.5	7729.0	11754.5	1725.0	3918.2	1341.8	575
BM2	3.0	4209.4	7729.0	11938.4	500.0	3979.5	1403.1	167
BM3	3.0	638.0	7729.0	8367.0	1.0	2789.0	212.7	0.33

\*Assuming density of the liquid washings waste, which includes solution of unreacted carbonate and nitrate salts, is same as water (1 g/mL). \*\*Without considering energy consumed for calcination and reduction. \*\*\*E-factor is calculated by the (total mass of waste) / (total mass of product); the lower the magnitude of E-factor, the greener the process.

**Supp. Info. 18.** Energy calculations on the various methods of synthesizing KCFZA.

## Fixed Bed Reaction Data

Sample	GC Analysis (% selectivity)									
	Acetone	Methanol	Isopropanol	Ethanol	1-propanol	1-butanol	1-pentanol	1-hexanol	1-heptanol	AcOH
BM3_200C_50bar_SV25_00_Run1	0.00	33.11	1.56	28.28	2.15	1.17	1.16	1.78	0.82	30.00
BM3_200C_50bar_SV25_00_Run2	0.00	28.65	1.37	23.98	1.88	1.01	1.01	1.54	0.68	40.00
Average (Run1+Run2)/2	0.00	30.88	1.47	26.13	2.02	1.09	1.09	1.66	0.75	35.00

**Supp. Info. 19.** Online GC analysis data of the flow reactor, showing the normalized % selectivity of the observed products for BM3.

## ICP-OES analysis

	SS1	SS1-K	BM1	BM2	BM3
Cu (%)	65.2	62.8	62.7	66.3	63.3
Zn (%)	27.0	26.4	26.2	21.6	26.0
Fe (%)	5.3	5.1	5.1	4.5	5.0
Al (%)	2.4	2.2	2.3	3.6	2.2
K (%)	0.0	3.5	3.6	4.0	3.5

**Supp. Info. 20.** ICP-OES analysis of the five catalysts in the study.

## **AUTHOR CONTRIBUTIONS**

B. Y. Tay, C. Kan and D. Tan designed and synthesised the catalysts and conducted the batch reactor experiments. J. Ong, R. J. Wong and D. Tan conducted the fixed bed reactor experiments. B. Y. Tay and D. Tan drafted the manuscript. B. Y. Tay, C. Kan, R. J. Wong and D. Tan characterized the catalysts and analysed the results. S. Dighe and A. Hengne contributed to the discussions of GC results. K. W. Huang and L. Zhang contributed to the discussions and editing of the manuscript.