Supporting information

Catalytic performance of Cu-Co/metakaolinite: role of structural properties in the partial oxidation of glycerol

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1. Experimental section

1.1. HPLC analysis

Detection and quantification of glycerol and the reaction products was performed by HPLC. Glycerol (Panreac >99%), glycolic acid (99%, Sigma-Aldrich), tartronic acid (≥97%, Sigma-Aldrich), sodium mesoxalate monohydrate (≥98%, Sigma-Aldrich), glyoxylic acid monohydrate (98%, Sigma-Aldrich), DL-glyceric acid hemicalcium salt (≥98%, Sigma-Aldrich), β-hydroxypyruvic acid (≥95%, Sigma), DL-Glyceraldehyde (≥90%, Sigma-Aldrich), and dihydroxyacetone (≥98%, Merck) were used as certified standard compounds. Analyses were performed on a Shimadzu Prominence equipped with a Shodex SH1821 column, UV/vis detector (210 nm) and refractive index detector. A 3.3 mM aqueous H_2SO_4 solution was used as mobile phase at a flow rate of 0.5mL/min and 60°C. Due to the high concentration of glycerol, the samples were diluted.

A refractive index detector is necessary for analyzing glycerol, and a UV detector (210 nm) is used for monitoring reaction products. The scientific literature underscores the significant challenge in achieving the separation between glycerol and dihydroxyacetone, which share the same retention time [1]. Given that glycerol does not absorb and therefore does not produce signals at the 210 nm wavelength, the UV detector becomes the sole method for quantifying dihydroxyacetone. For the quantification of glycerol, two calibration curves for dihydroxyacetone were necessary: one with the refractive index detector and another with the UV detector at 210 nm. In the case of observing a peak by the refractive index detector at the retention time of glycerol, it is possible to calculate the area corresponding only to glycerol by subtracting the area of dihydroxyacetone, which can be calculated by interpolation of the concentration obtained by the calibration curve by the UV detector in the calibration curve by the refractive index detector.

1.2. Calculation

The conversion, selectivity and carbon balance were calculated as shown below:

$$Conversion\ (\%) = \frac{(M_{gly\ t=0} - M_{gly\ t=x})}{M_{gly\ t=0}} x100$$

Where,

$M_{gly\ t=0}$: initial mol of glycerol

$M_{gly\ t=x}$: mol of glycerol after reaction

$$Selectivity\ (\%) = \frac{M_x}{M_{gly\ rx}} x100$$

Where,

M_x: mol of reaction product

$M_{gly\ rx}$: mol of glycerol transformed

$$Carbon\ balance\ (\%) = \frac{\sum M_{C3}}{M_{gly\ rx}} x100$$

Where,

M_{C3}: mole of reaction product type C3.

2. Supporting figures and tables

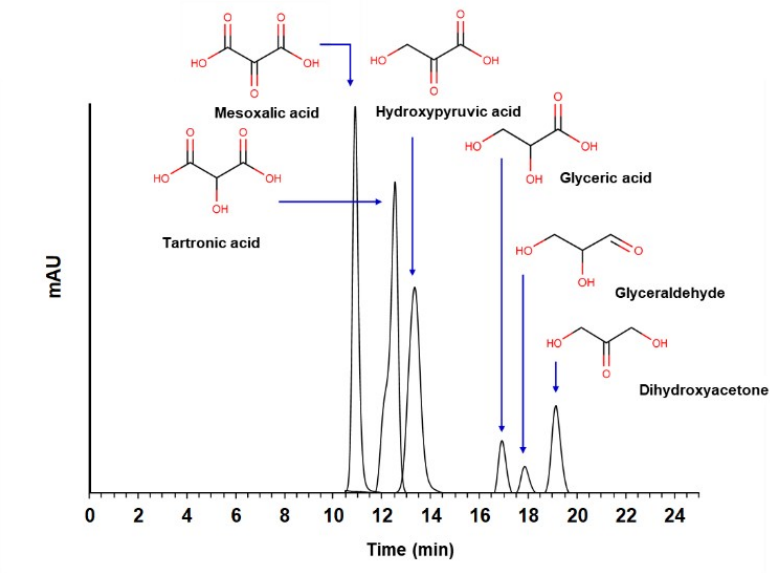

Figure S1. Chromatograms of the reaction products, UV detector at 210 nm.

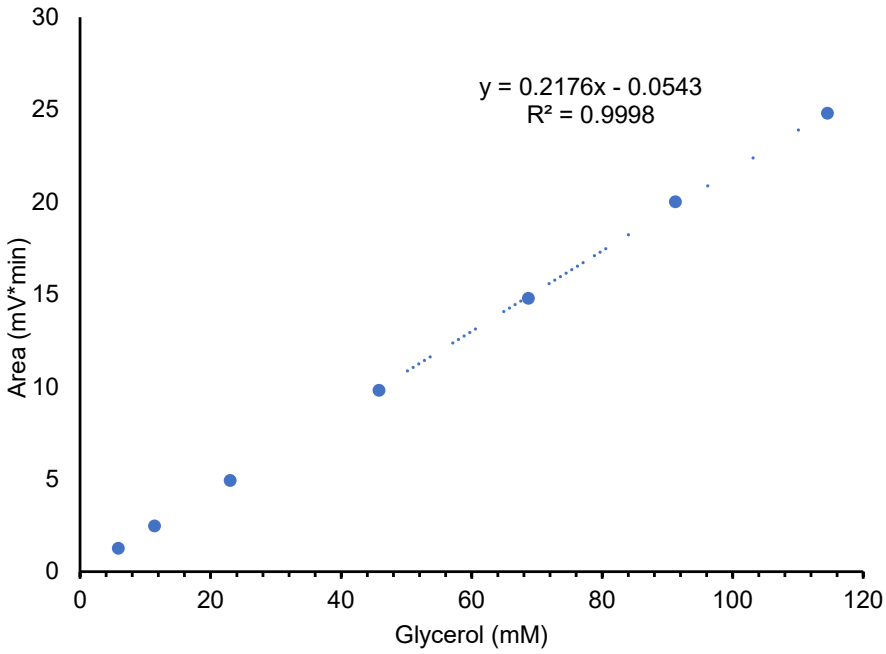

Figure S2. Glycerol calibration curve (Refractive index detector).

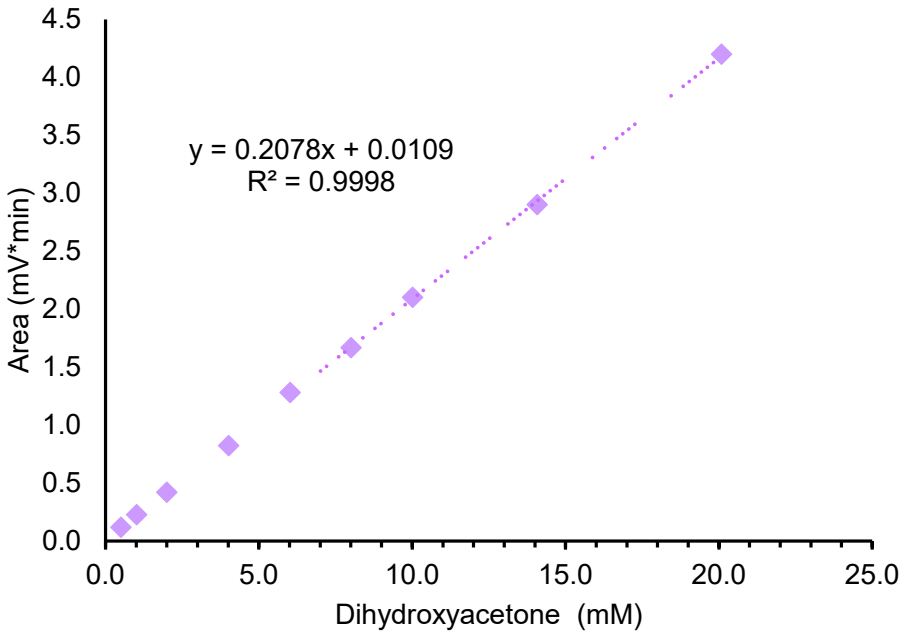

Figure S3.Dihydroxyacetone calibration curve (Refractive index detector).

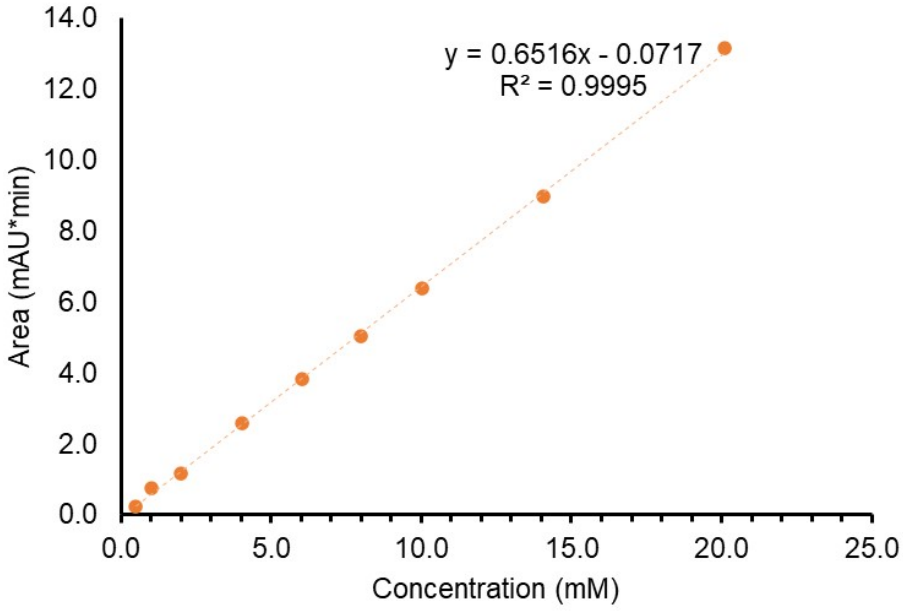

Figure S4. Dihydroxyacetone calibration curve (UV detector).

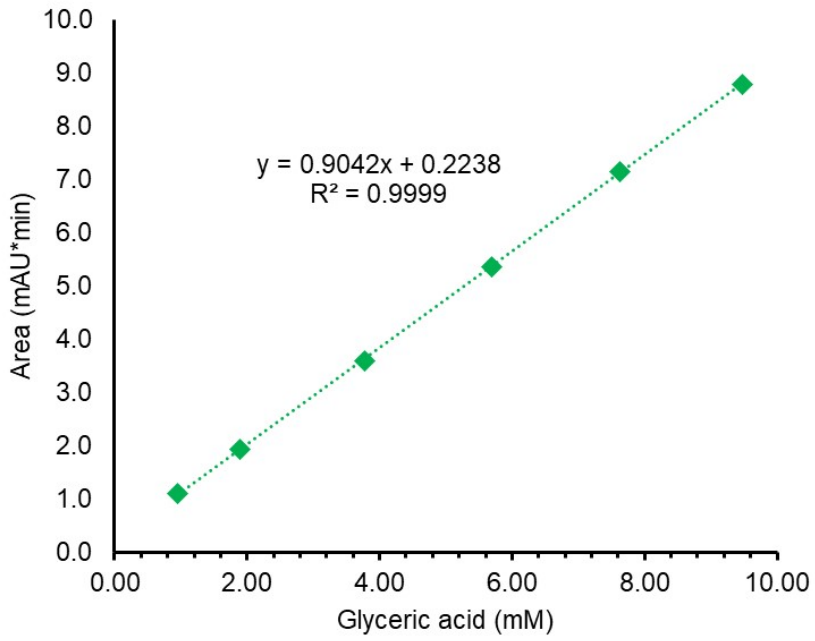

Figure S5. Glyceric acid calibration curve (UV detector).

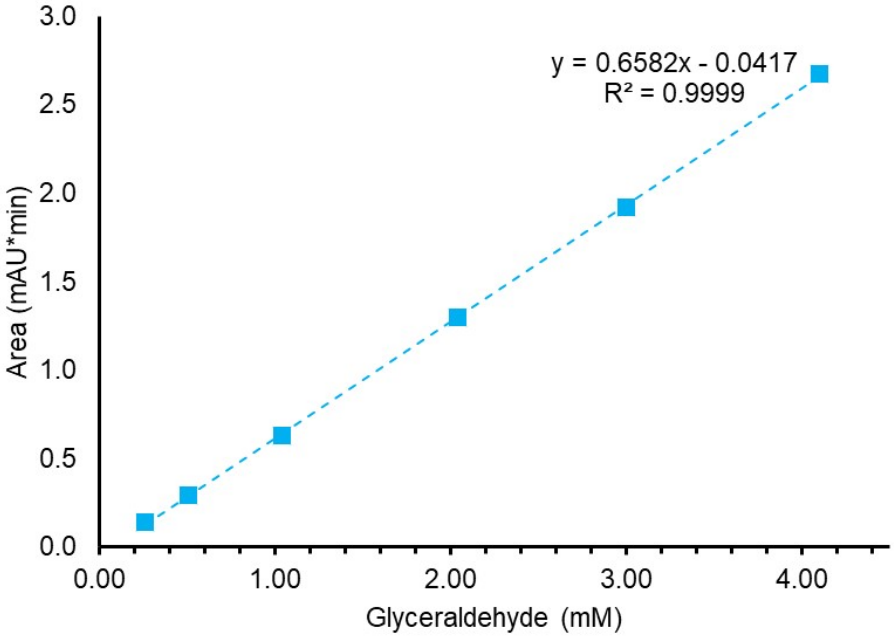

Figure S6. Glyceraldehyde calibration curve (UV detector).

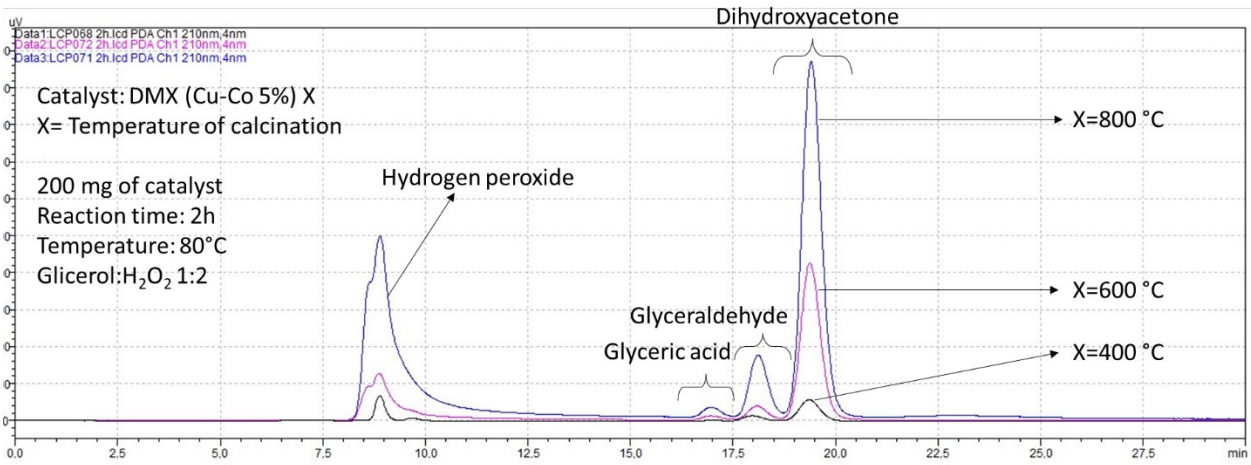

Figure S7. Typical chromatograms of the samples solution after the reaction.

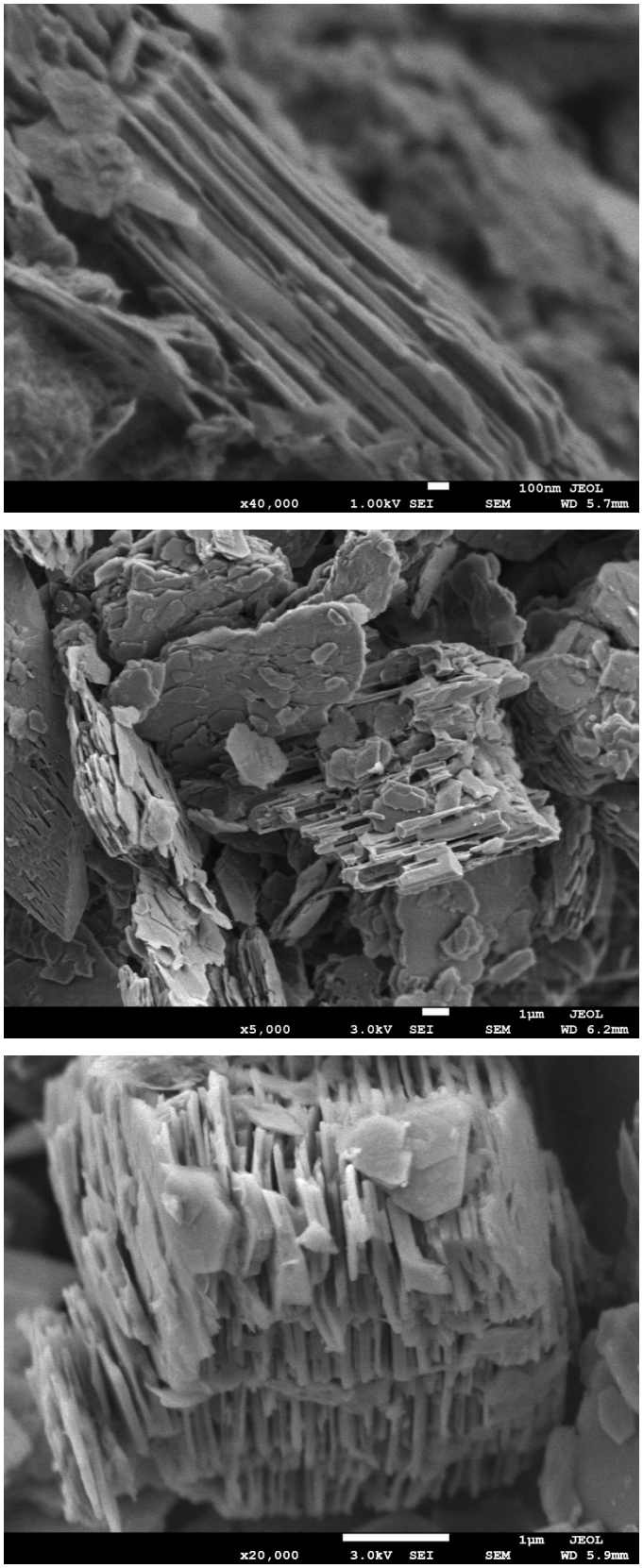

Figure S8. SEM images of the catalytic support (DM400).

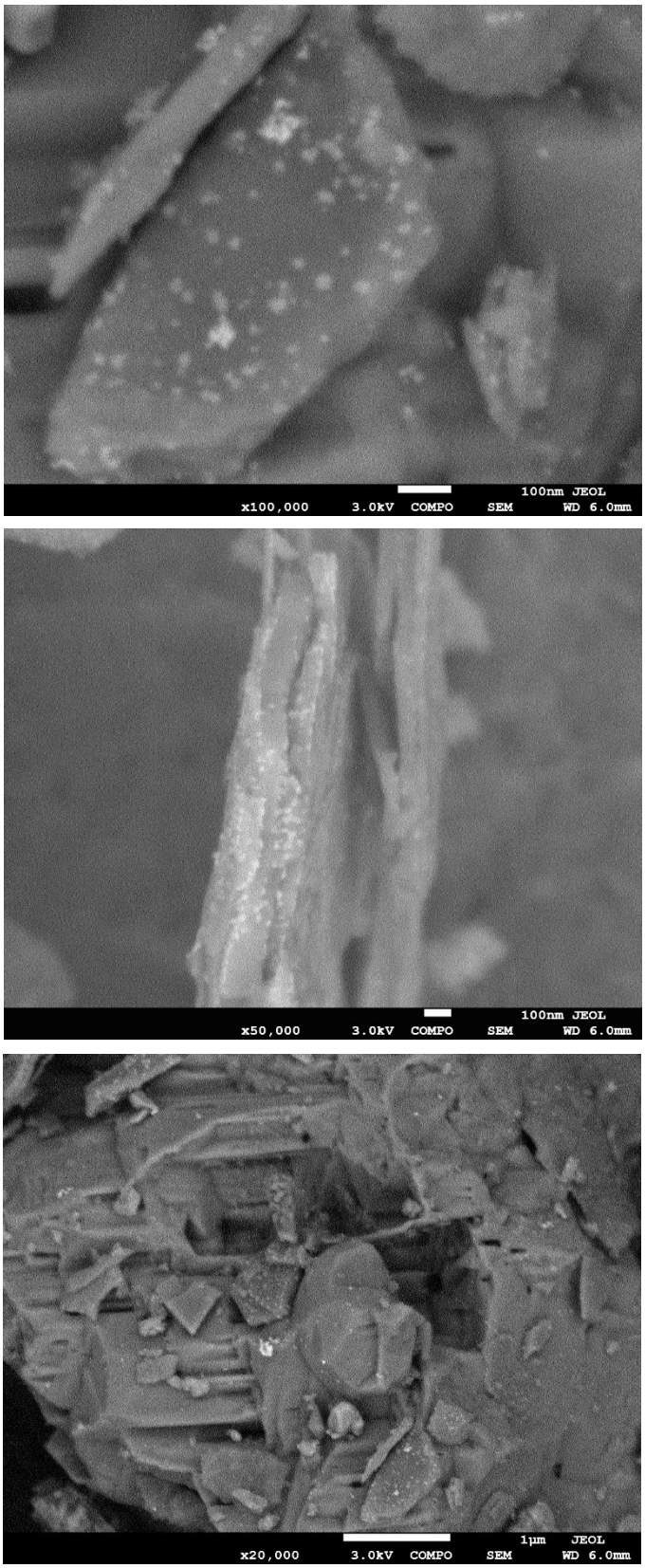

Figure S9.SEM images of DM400 (Cu-Co 5%) 400.

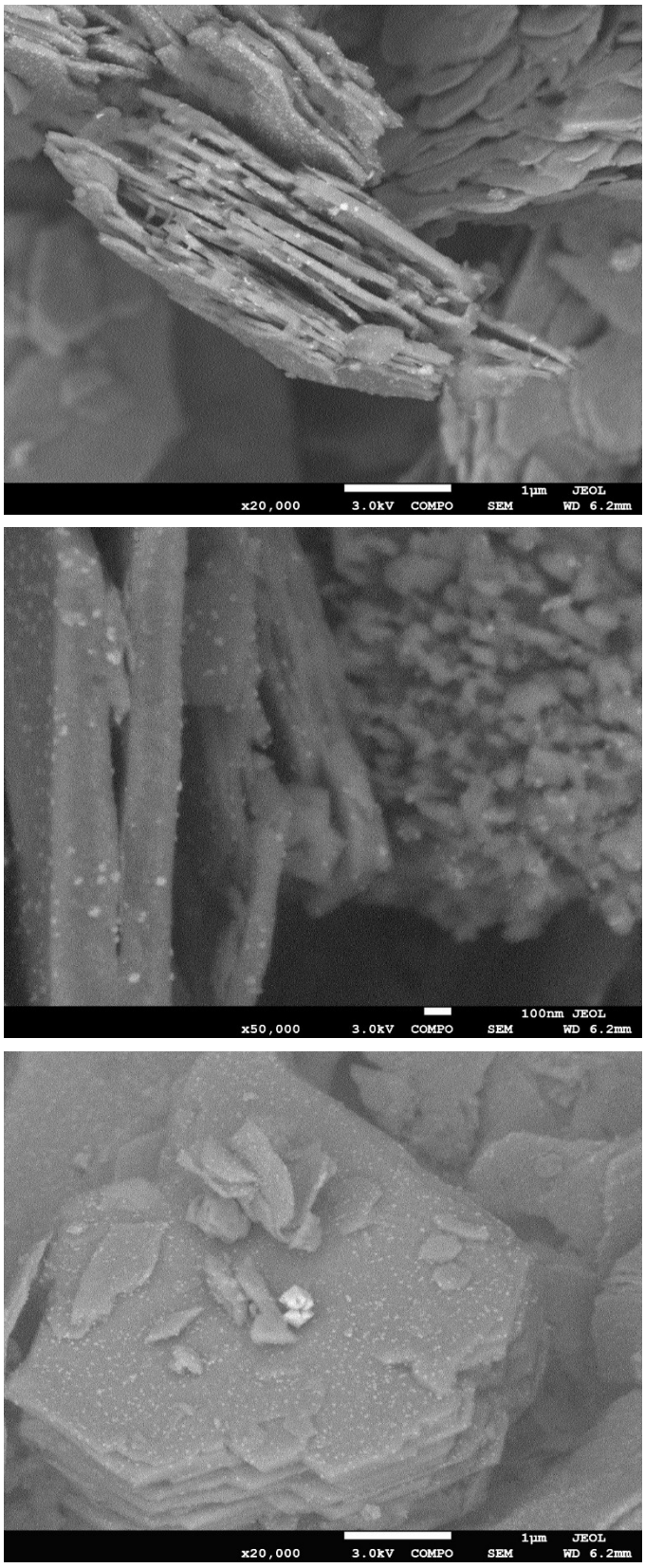

Figure S10.SEM images of DM600 (Cu-Co 5%) 600 catalyst.

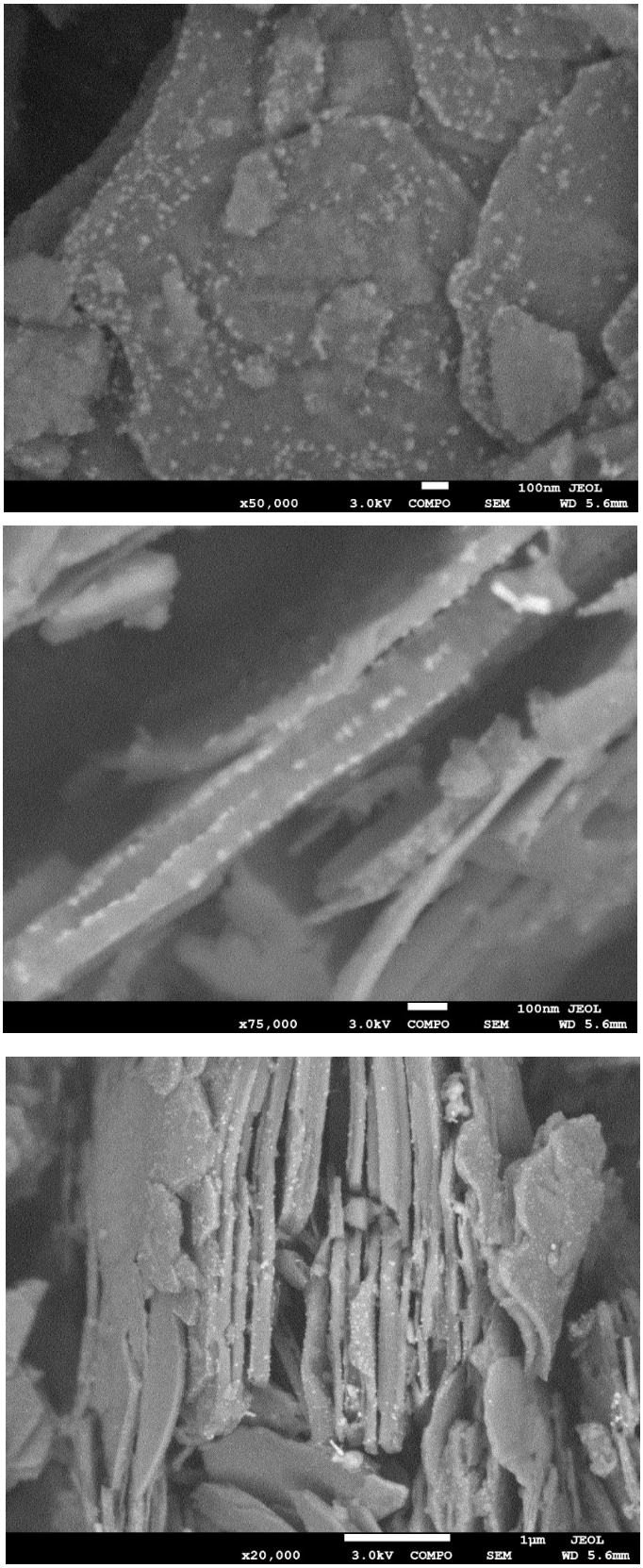

Figure S11.SEM images of DM800 (Cu-Co5%) 800 catalyst.

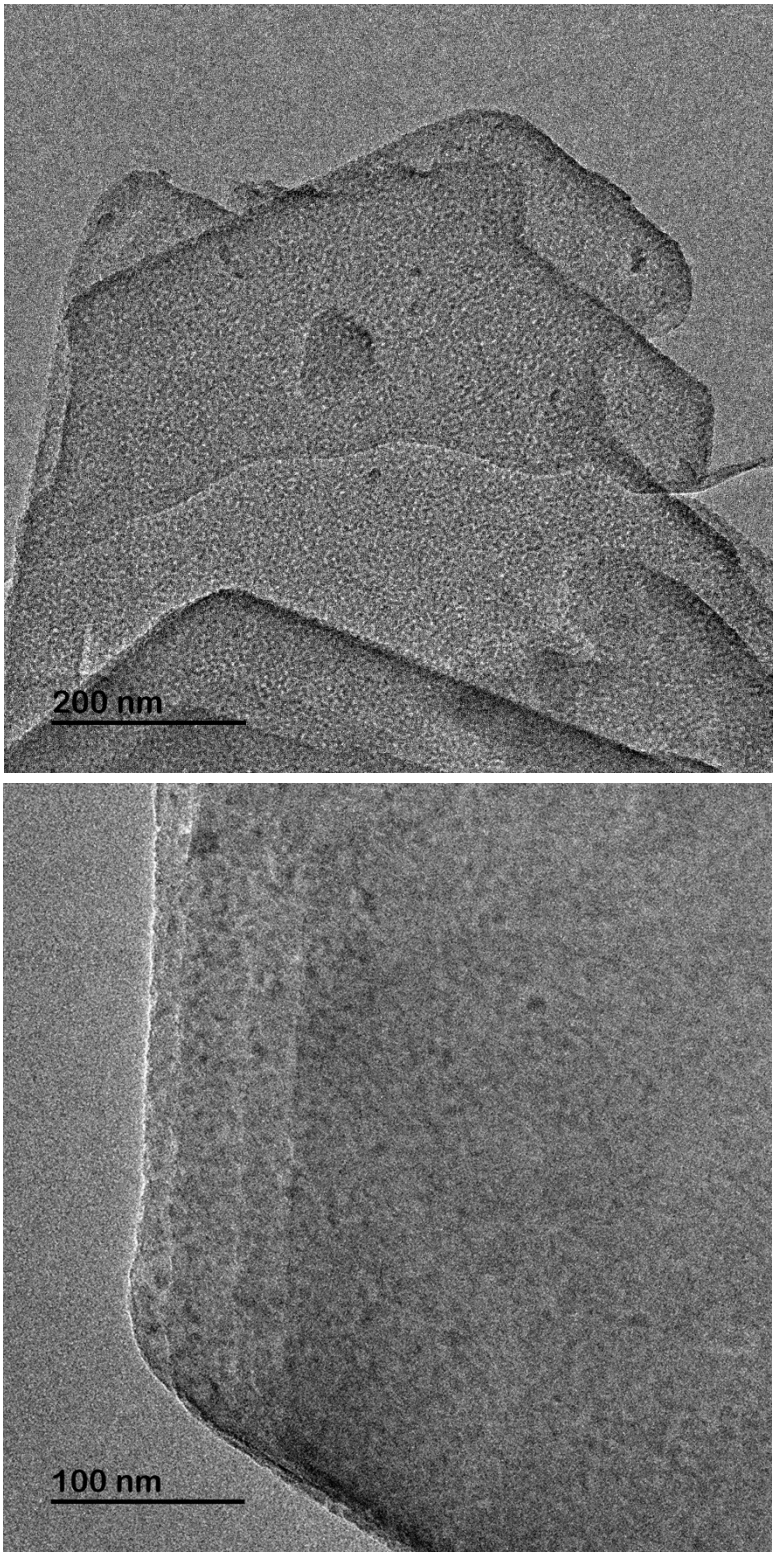

Figure S12.TEM images of the catalytic support DM 400.

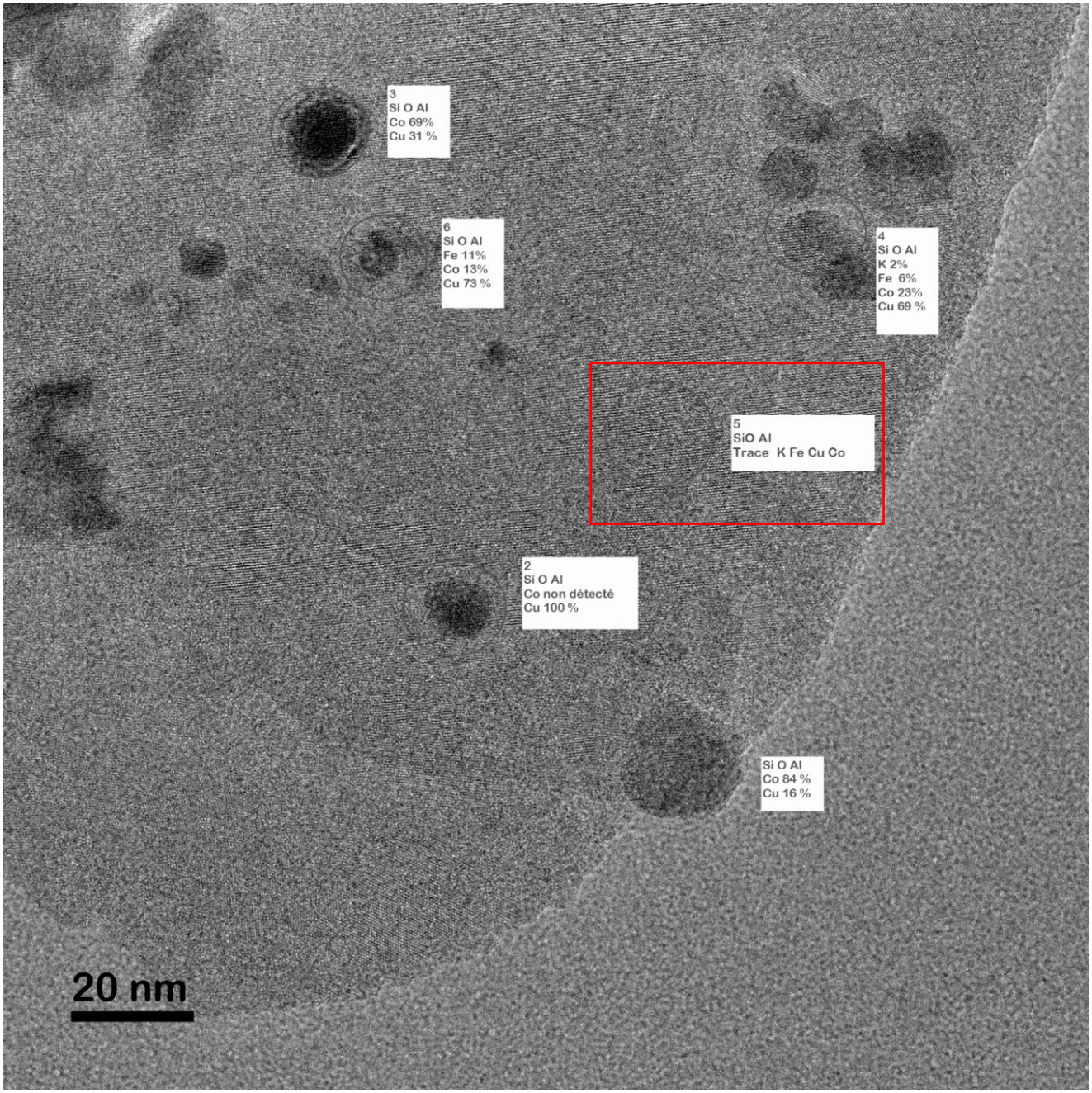

Figure S13.TEM image and EDX analysis of DM400 (Cu-Co 5%) 400.

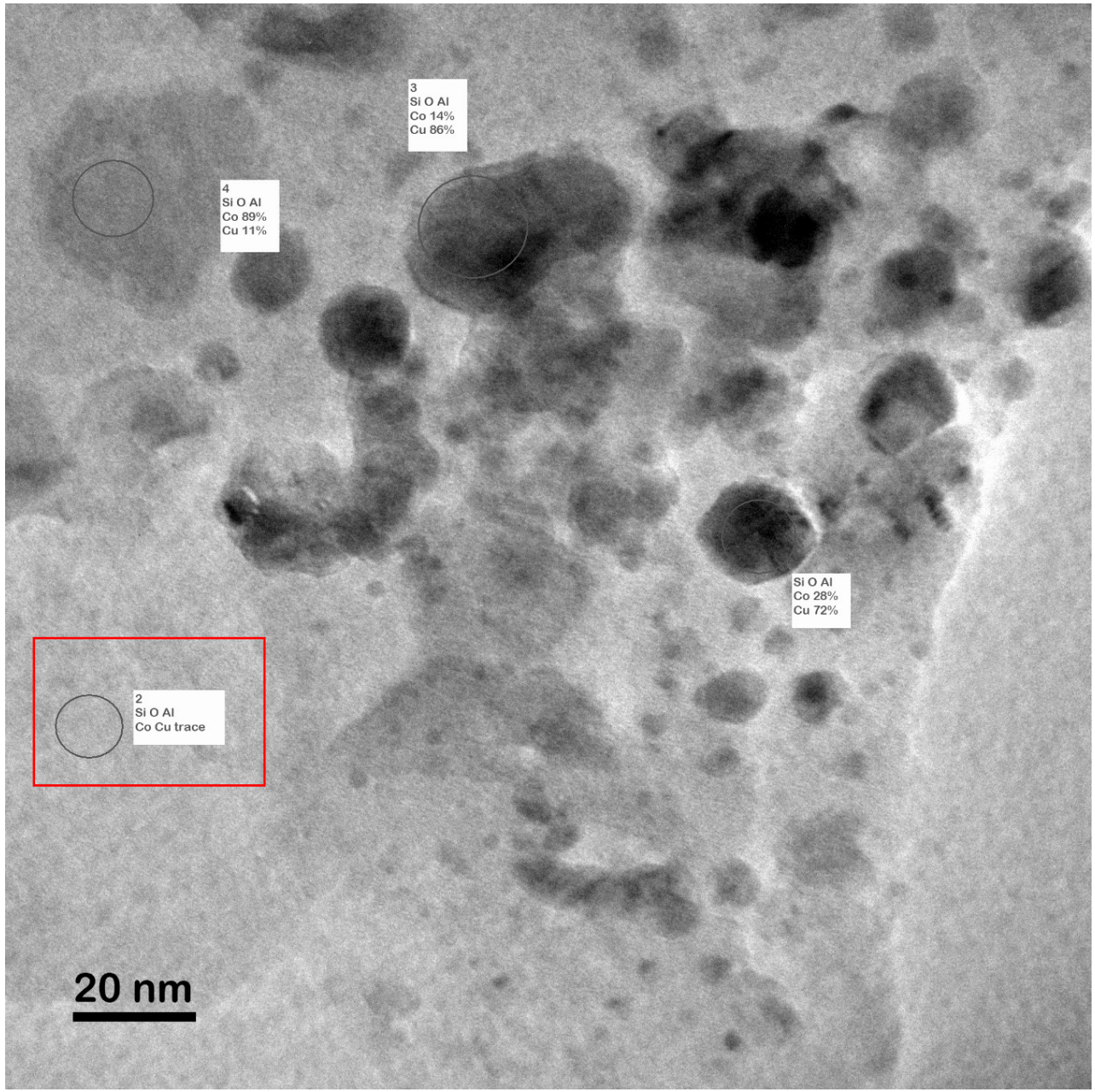

Figure S14.TEM image and EDX analysis of DM600 (Cu-Co 5%) 600.

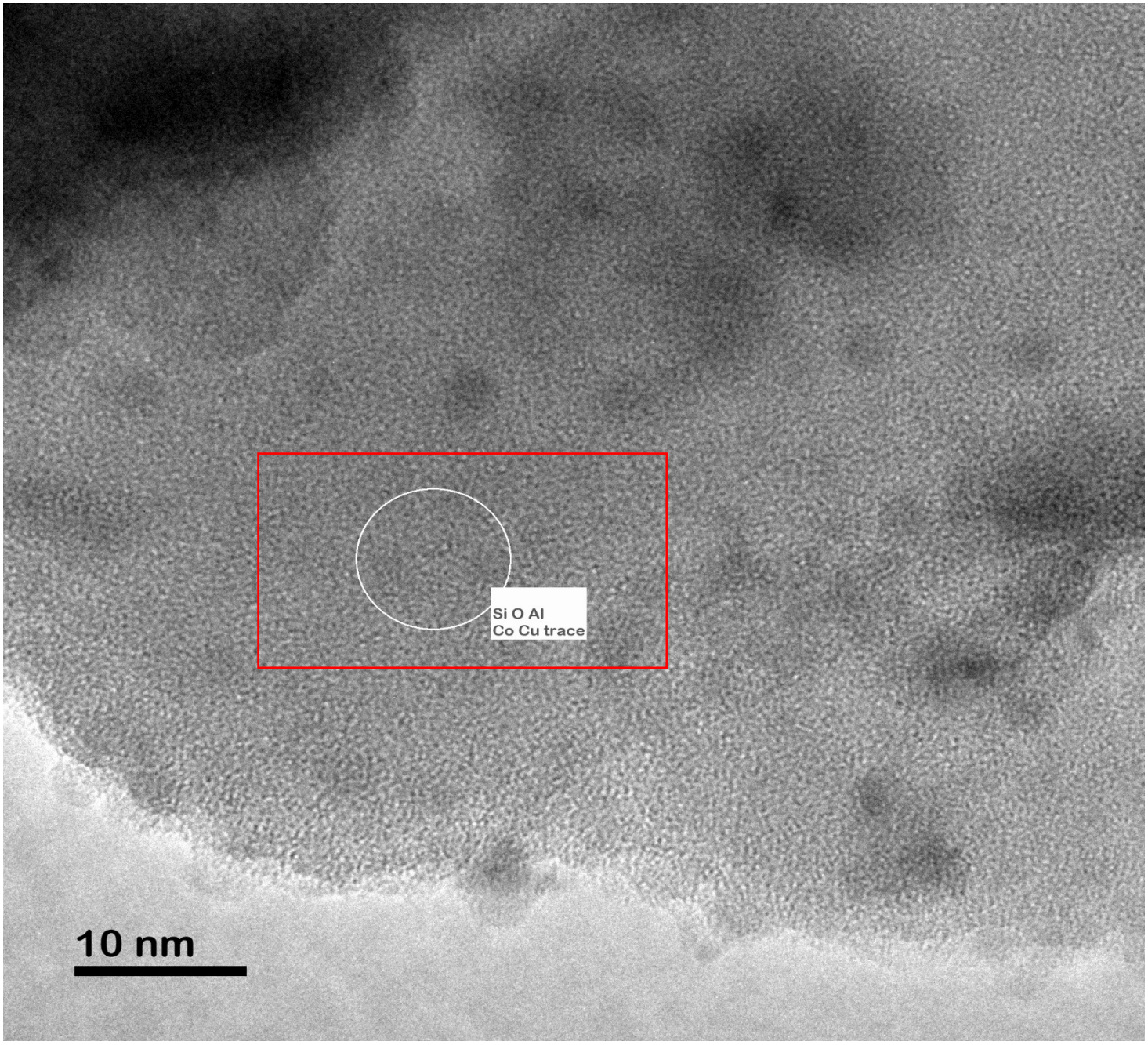

Figure S15.TEM image and EDX analysis of DM800 (Cu-Co 5%) 800.

Catalysts and Results for Glycerol Oxidation over Precious and Non-Precious Metal Catalysts.

Type of catalyst	Catalyst	Glycerol (M)	Conversion (%)	Selectivity	Source of oxygen	T (˚C)	Time of reaction (h)	NaOH:glycerol	Authors and year	Ref
Non-precious metal catalysts	DM800 (Cu-Co 5%) 800	0.54	99	Dihydroxyacetone (92 %)	H_2O_2 2:1	80	4	-	This study	
	CuO	0.54	98	Oxalic acid (39 %)	H_2O_2 2:1	80	7	-	Amaniampong et al. 2018	[2]
	$Co_{0.15}/Mg_3Al$-s	0.22	100	Tartronic acid (63 %)	0.1 MPa	70	24	6.8:1	Jin et al. 2016	[3]
	Cu/CoO	0.05	85	Glycolic acid (35 %)	1.0 MPa	90	5	4:1	Deng et al. 2015	[4]
	Cu(II) sulfonato-salen complex-intercalated LDH	0.54	40	Dihydroxyacetone (53 %)	H_2O_2 1.6:1	60	4	-	Luo et al. 2015	[5]
Precious based catalysts	Au/CuO-ZnO	0.10	70	Dihydroxyacetone (80 %)	0.2 MPa	50	4	-	Wang et al. 2024	[6]
	Au/ZnO-D	0.10	58	Dihydroxyacetone (70 %)	1.0 MPa	60	4	-	Yan et al. 2024	[7]
	$PtBi/ZrO_2$	0.10	76	Dihydroxyacetone (60 %)	Air filled in the flask	80	6	-	Luo et al. 2023	[8]
	Pt/Si-C-3	0.10	74	Glyceric acid (87 %)	0.1 MPa	60	6	-	Huang et al. 2023	[9]
	AuCu–ZnO	0.10	91	Dihydroxyacetone (83 %)	1.5 MPa	60	5	-	Zhao et al. 2022	[10]
	Pt_1/HAP	0.05	92	Glyceric acid (87 %)	1.0 MPa	50	16	10:1	Yan et al. 2022	[11]
	0.98%Au/ZnGa-LDH	0.10	73	Dihydroxyacetone (64 %)	0.5 MPa	60	4	-	An et al. 2020	[12]

3. References

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