Supplementary Information (SI) for Energy Advances.

Supplementary Information

Boosting Ethylene Yield via Synergistic 2D/0D Nanostructured VCu Layered Double Hydroxide/TiO_2 Catalyst in Electrochemical CO_2 Reduction

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1. **ICP-OES**

1.1 Sample preparation for ICP for VCu LDH/TiO2

4 mg of sample dissolved in 50 ml HNO_3

200 µl out of 50 ml was taken and diluted in 25 ml H2O = 25000/200 times

4 mg of sample present in 50 ml

Therefore, 200 µl of sample contains =4*200/50000 = 16 µg

→ 2 ml of sample taken for analysis.

16 µg of catalyst present in 25 ml of sample

1.2 ICP data

V= 0.277 mg/L

Cu= 0.042 mg/L

Ti= 0.049 mg/L

For Vanadium,

1000 ml → 0.277 mg = 277 µg

25 ml = 277*25/1000 = 6.925 µg of V

For Copper,

1000 ml → 0.042 mg = 42 µg

25 ml = 42*25/1000 = 1.05 µg of Cu

For Titanium,

1000 ml → 0.049 mg = 49 µg

25 ml = 49*25/1000 = 1.225 µg of Ti

16 µg of sample contains

% of V= 6.925/16 = 43.28 wt%

% of Cu= 1.05/16 = 6.56 wt%

% of Ti= 1.225/16 = 7.65 wt%

1.3 Electrode Preparation

Slurry: 5 mg of sample + 1000 µl IPA + 10 µl Nafion

50 µl solution dropcasted

Mass of catalyst

= 5000*50/1010

=247 µg

% of V = 247*43.28% = 10690 µg

Molecular weight of V = 51

51 g of V = 1 mol V

51 µg of V = 1 µmol of V

10690 µg of V = 10690/51 µmol of V

= 2.096×10^{-4} mol of V

% of Cu = 247*6.56% = 37.65 µg

Molecular weight of Cu = 63.5

63.5 g of V = 1 mol V

63.5 µg of V = 1 µmol of V

37.65 µg of Cu = 37.65/63.5 µmol of Cu

= 5.9×10^{-7} mol of Cu

% of Ti = 247*7.65% = 32.28 µg

Molecular weight of Ti = 204.3

204.3 g of V = 1 mol V

204.3 µg of V = 1 µmol of V

32.28 µg of Cu = 32.28/204.3 µmol of Cu

= 1.579×10^{-7} mol of Ti

2. Turnover Frequency (TOF)

Turn over frequency (TOF) was calculated for CO, CH_4 and C_2H_4 using formula,

$$TOF = \frac{\left(\frac{j}{N \times F}\right)}{\left(\frac{m}{M}\right)} \qquad (1)$$

Where,

j = Partial current at given potential

N = number of electrons transferred

F = Faraday's number (96485 C/mol)

m = Mass of metal sites present on the electrode

M = Atomic mass of metals

'm' can be calculated as following Equation (2),

$$m = m_{cat} \times w \qquad (2)$$

Where, m_{cat} is the mass of catalyst loaded (i.e. 247 µg) and w is the content of metals obtained from ICP data (wt%)

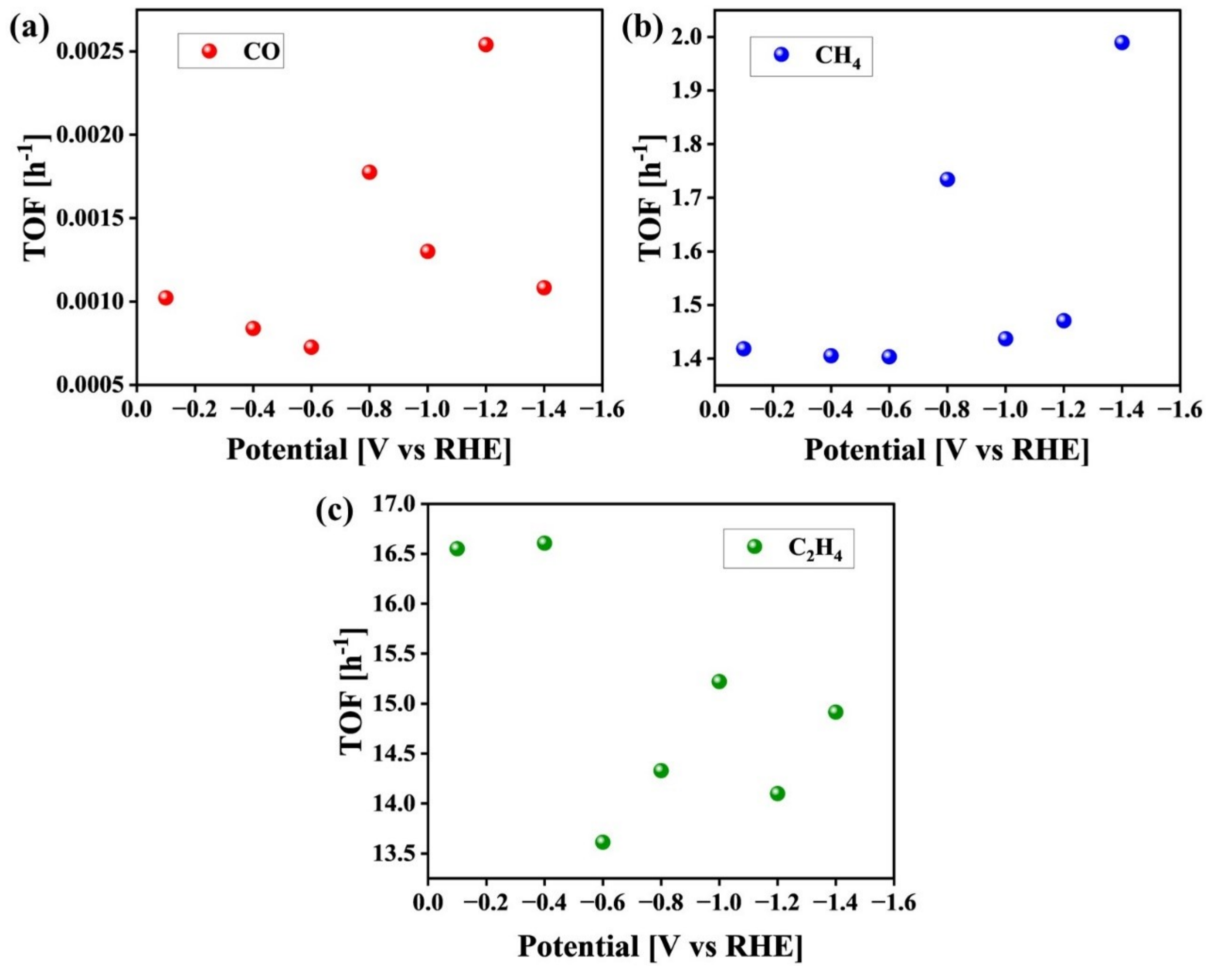

Figure S 1: TOF values of VCu LDH/TiO_2 for (a) CO, (b) CH_4 and (c) C_2H_4 w.r.t. applied potential

3. FESEM

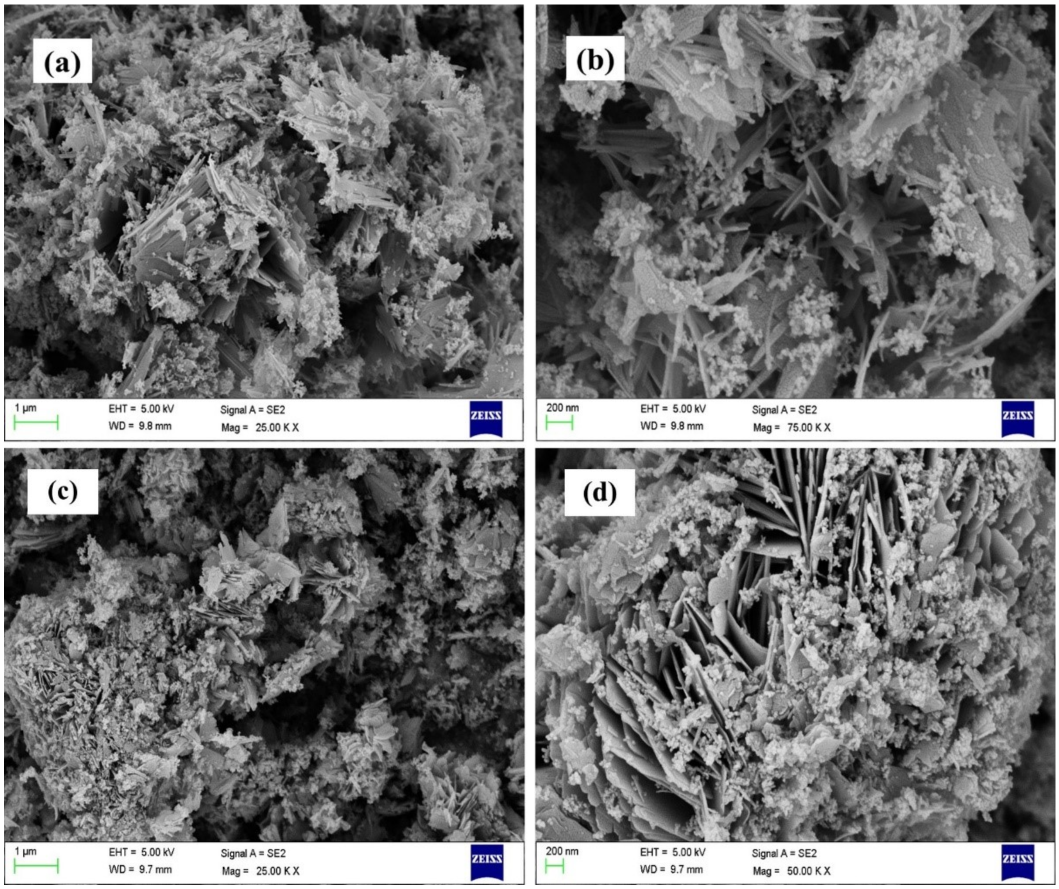

Figure S 2: FESEM images of VCu LDH/TiO_2 with reaction time of (a,b) 3 h and (c,d) 6 h

4. XRD

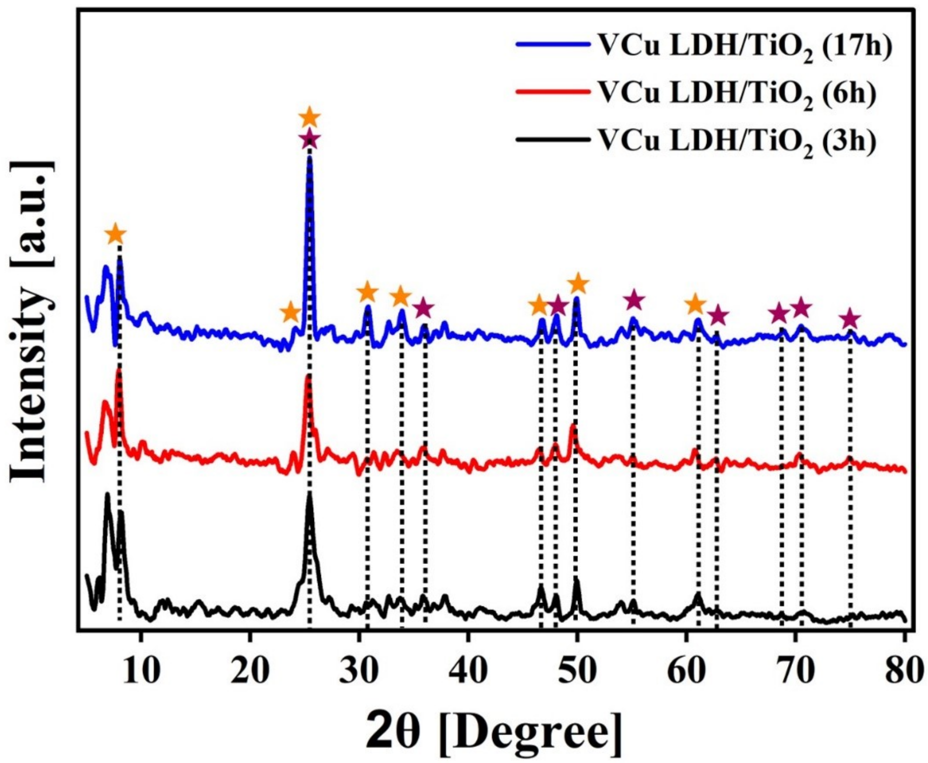

Figure S 3: XRD of VCu LDH/TiO_2 with reaction time of 3, 6 and 17 h

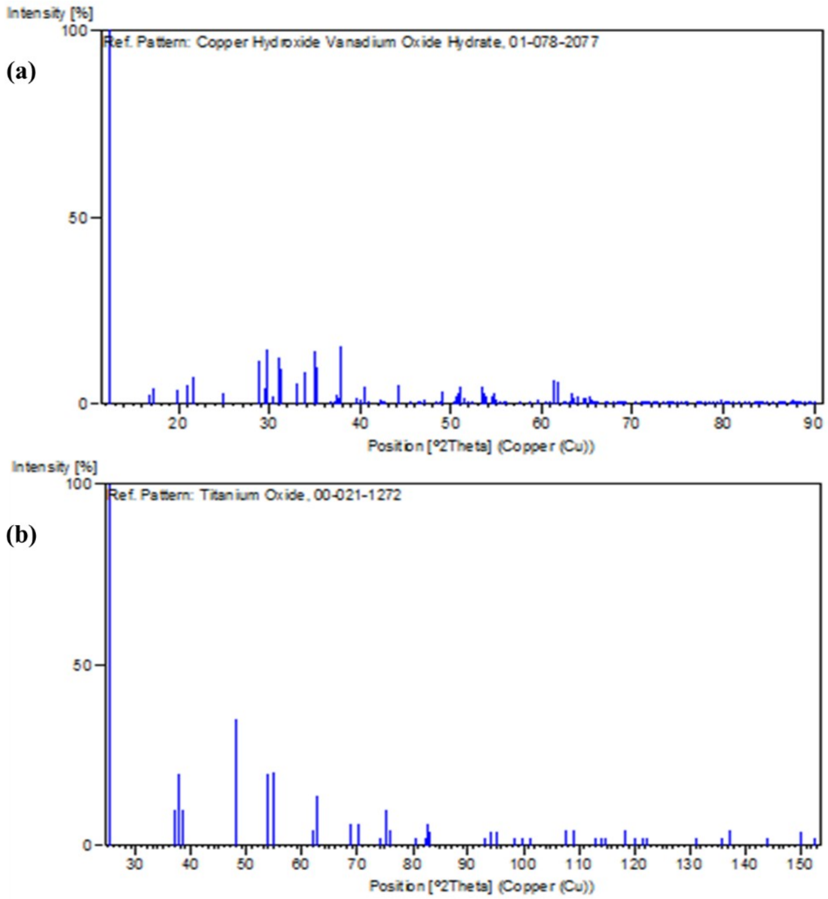

Figure S 4: XRD standard reference JCPDS cards of (a) VCu LDH, and (b) TiO_2

5. Gas Chromatography Data

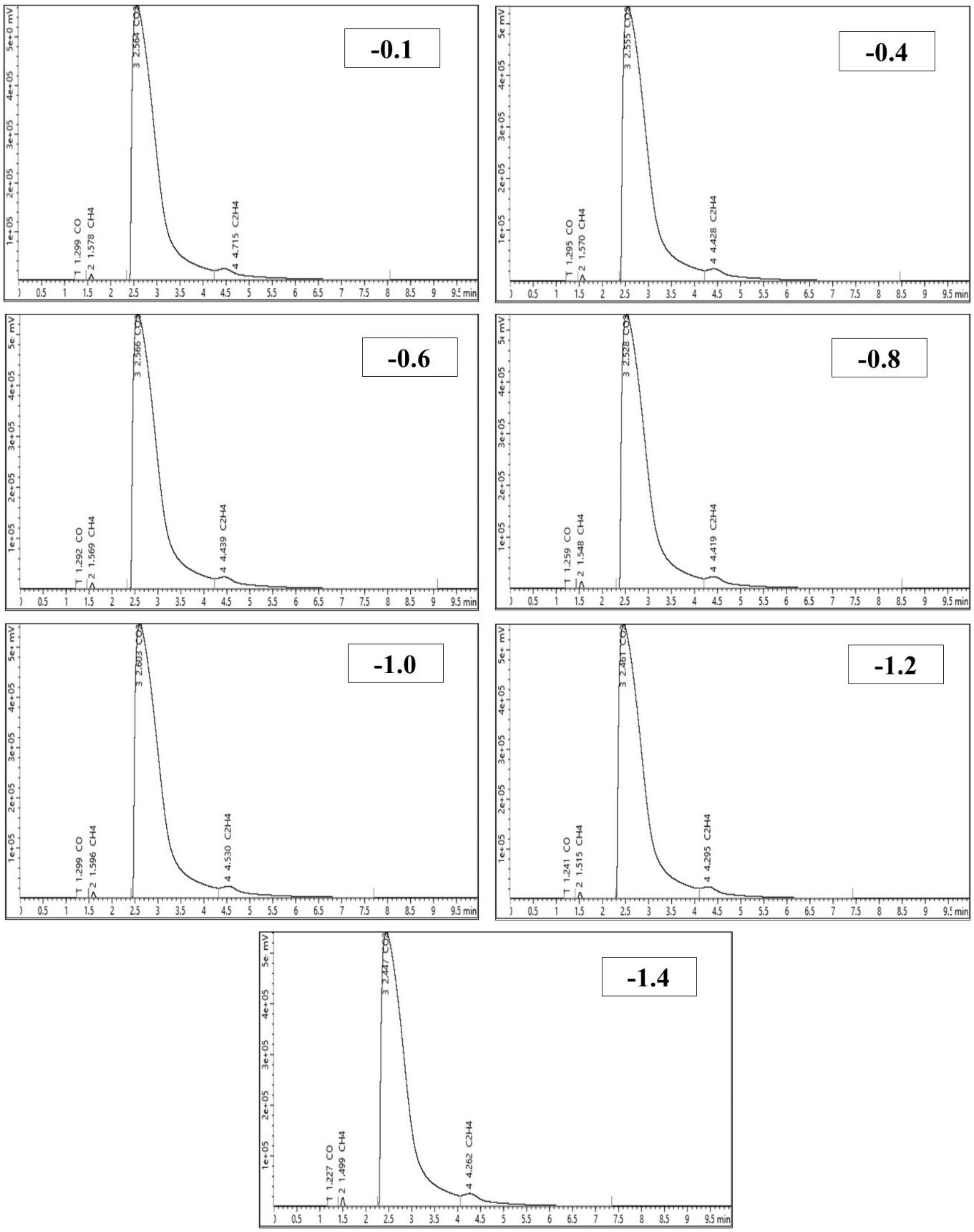

Figure S 5: Gas chromatography data (FID) obtained after chronoamperometry at different potentials (V vs RHE)

6. EDS with elemental mapping

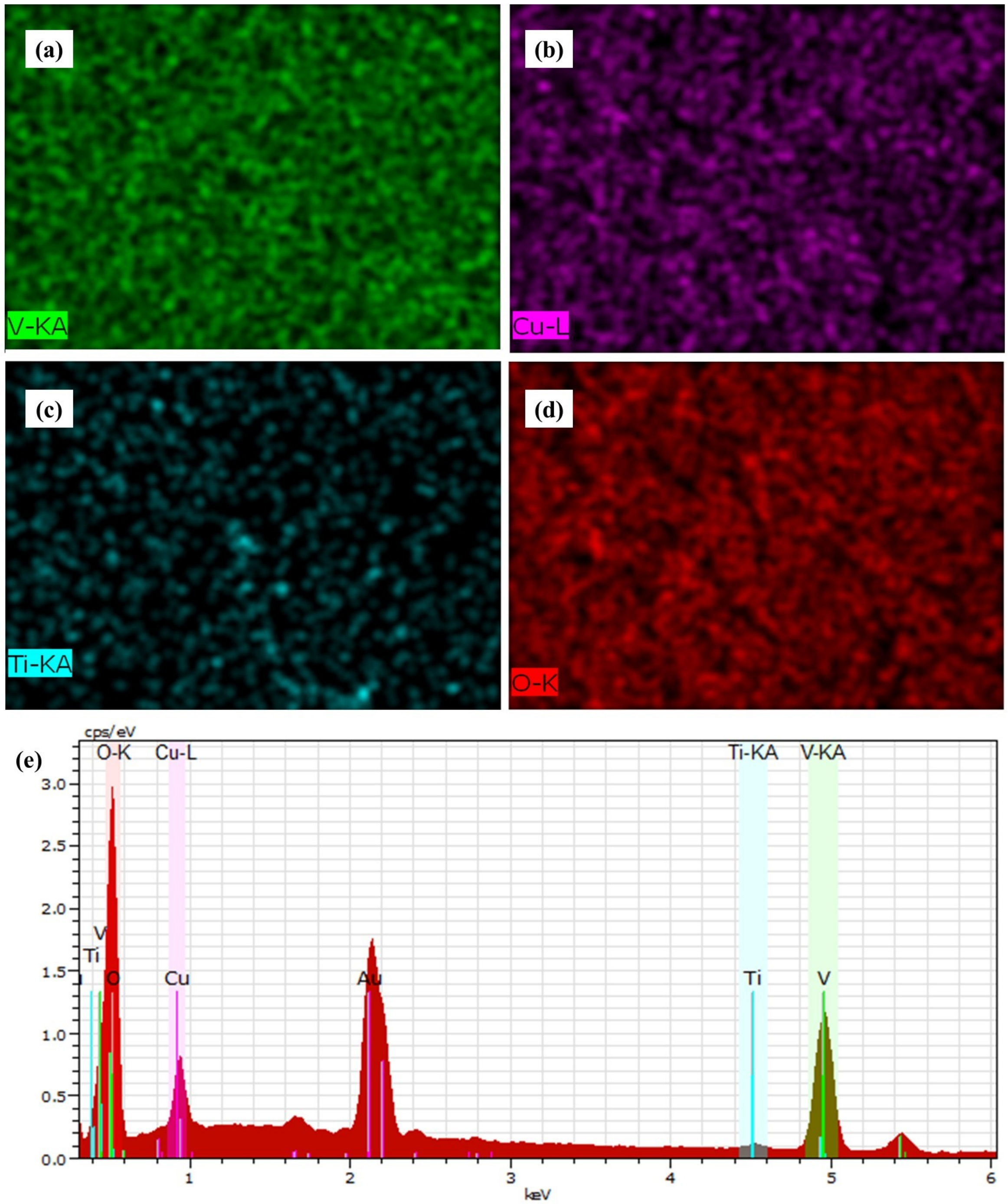

Figure S 6: Elemental mapping of (a) V, (b) Cu, (c) Ti and (d) O. Energy dispersive Spectroscopy graph for element distribution of VCu LDH/TiO_2

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
O	8	K-series	15.43	30.74	59.31	2.13
V	23	K-series	28.41	56.60	34.29	1.07
Cu	29	L-series	5.56	11.08	5.38	0.90
Ti	22	K-series	0.79	1.58	1.02	0.07
		Total:	50.20	100.00	100.00	

7. CO_2RR product analysis

The same set of reaction (mentioned in the Section 6) has been carried to validate the activity of VCu LDH as shown in Figure S7 below.

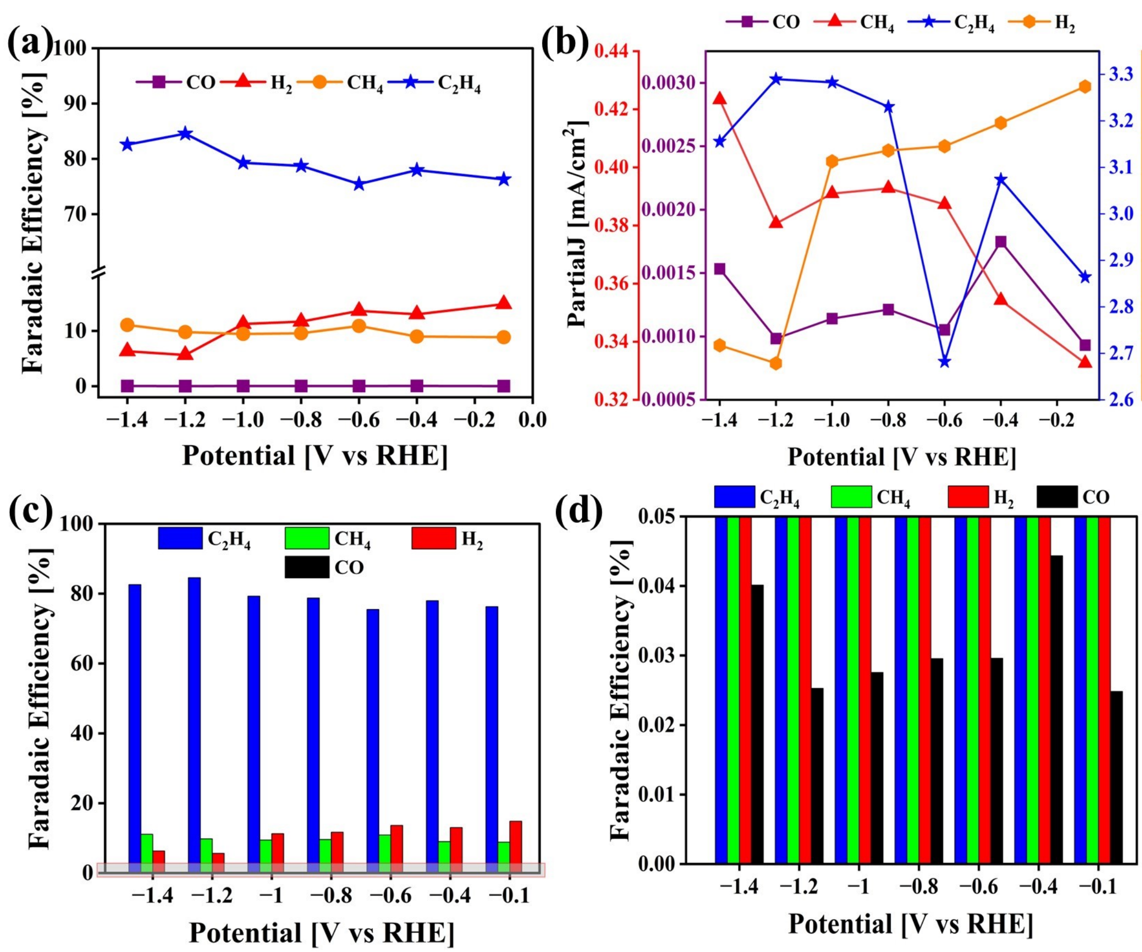

Figure S 7: Analysis of CO_2 reduction end products obtained using VCu LDH catalyst (a) Line + Symbol plot of FEs of CO, H_2, CH_4 and C_2H_4, (b) Line + Symbol plot of Partial Current Densities of CO, H_2, CH_4 and C_2H_4, (c) Bar plot of FEs and (d) Zoom in of (c) bar plot

8. FE calculations

Amount of CH_4 product = 'X' mol/L

Recorded current = 2.16×10^4 A

Flow rate of CO_2 (ϑ) = 50 sccm

Number of electrons, n_i = 2 for CO, 2 for H_2, 8 for CH_4, 12 for C_2H_4

p_0 = 101.3 kPa

Faraday constant = 96485 C/mol

Gas constant (R) = 8.314 J/mol.K

Partial current density and Faradaic Efficiency (FE) is calculated from the equation 3 and 4 as below,

$$j_i = x_i \times \vartheta \times \frac{n_i F p_0}{RT} \times (electrode\ area)^{-1} \qquad (3)$$

$j_{i\,(CO)} = 0.0012$

$j_{i\,(CH4)} = 0.41$

$j_{i\,(C2H4)} = 3.22$

$j_{i\,(H2)} = 0.22$

The corresponding FE for each potential is calculated as,

$$FE = {}^{j_i}\!/_{j_{total}} \times 100\,\% \qquad (4)$$

$FE_{(CO)} = 0.030$

$FE_{(CH4)} = 10.73$

$FE_{(C2H4)} = 83.49$

$FE_{(H2)} = 5.74$

Table S 1: Faradaic efficiency values of VCu LDH and VCu LDH/TiO_2

Potential [V vs RHE]	Faradaic Efficiency [%]							
	VCu LDH				VCu LDH/TiO_2			
	H_2	CO	CH_4	C_2H_4	H_2	CO	CH_4	C_2H_4
-0.1	14.832	0.02482	8.85927	76.2839	5.74512	0.03094	10.7323	83.4917
-0.4	13.0015	0.04434	8.98567	77.9685	5.1572	0.02549	10.6794	84.1379
-0.6	13.6189	0.0296	10.8947	75.4568	6.81481	0.02581	12.4754	80.684
-0.8	11.6704	0.02954	9.57353	78.7265	6.32047	0.05889	14.3834	79.2372
-1	11.2465	0.02755	9.44286	79.2831	6.65514	0.0419	11.5735	81.7294
-1.2	5.64137	0.02526	9.78376	84.5496	6.44835	0.08735	12.6449	80.8194
-1.4	6.31609	0.04011	11.0761	82.5677	6.13427	0.03405	15.6431	78.1886