Electronic Supplementary Material (ESI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2024

Supporting Information

Performance of nanowire-like aluminium-based organometallic complex with

high activity electrocatalysis of CO₂ to CO

Boming Lu¹, Tianxia Liu^{1,2*}, Xuejiao Ma¹, Yaping Zhang³

1. School of Chemisry and Chemical Engineering, North Minzu University, Yinchuan

750021, P.R.China

2. Key Laboratory for Chemical Engineering and Technology, State Ethnic Affairs

Commission, North Minzu University, Yinchuan 750021, P.R.China

3. School of Materials Science and Chemistry, Southwest University of Science and

Technology, Mianyang, 621010, P.R.China

*Corresponding author.

E-mail address: 2005053@nmu.edu.cn (Tianxia Liu)

The gas chromatograph (GC) uses a three-valve, three-column system to achieve simultaneous analysis of multiple components in one injection, using a column (capillary column) to separate the sample, and the separated components enter the detector in turn, a hydrogen flame ionization detector (FID), a thermal conductivity detector (TCD), with the specific conditions shown in Table S1. Qualitative analysis is to determine which substances the components are by retention time, and quantitative analysis is to determine the content of each component by peak area. The standard gases are a mixture of methane (CH₄), ethylene (C₂H₄), ethane (C₂H₆), carbon monoxide (CO), hydrogen (H₂) and oxygen (O₂) at different concentrations, and the FID detector determines the content of hydrogen and oxygen. The standard spectra are shown in Fig. S1, and the parameters are shown in Table S2. All the gas control of the inlet and detector are controlled by using electric pneumatic control (EPC), and the gas pressure control accuracy reaches 0.001 psi, so the automation degree of the equipment and the repeatability and accuracy of the experiment are guaranteed.

The products of 2-Ml/Al-F-N catalysts in this work in the electrocatalytic reduction of CO_2 were determined by gas chromatography. The Faraday efficiency (FE) of these three materials was obtained by averaging the test results of three times at each potential. Calculation formula is shown below, and only one spectrogram at - 1.1 V vs. RHE potential is given (Fig. S2 and Table S3,).

Faraday efficiency (FE) calculation formula, using CO as an example:

$$FE_{CO} = \frac{n_{CO} \times Z \times F}{Q} = \frac{n_{CO} \times 2 \times 96485}{t \times I}$$

n_{co}: The amount of carbon monoxide substance;

Z: Number of transferred electrons (H₂ is 2e, CO is 2e, CH₄ is 8e, C₂H₄ is 12e, so Z = 2):

F: Faraday's constant ($F = 96485 C mol^{-1}$);

- Q: The total amount of charge $(Q = I \times t)$;
- I: The current on the electrochemical workstation, generally in mA, needs to be

converted into A in calculation.

t: General take 1s directly (t = 1s).

$P \times V_{CO} = 101325 Pa \times V_{CO}$
$n_{CO} = \frac{P \times V_{CO}}{R \times T} = \frac{101325 Pa \times V_{CO}}{8.314J mol^{-1} K^{-1} \times 298.15 K}$
$V_{CO} = V \times C_{CO} = V_{MFC} \times t$
P: Pressure $(P = 101325 Pa);$
R: Gas constant ($R = 8.314J mol^{-1} K^{-1}$)
T: Temperature $(T = 298.15K)$
V _{CO} : Carbon monoxide volume;
C _{CO} : Carbon monoxide concentration measured by GC (ppm);
V_{MFC} : The mass controller controls the gas flow rate and the un

V_{MFC}: The mass controller controls the gas flow rate and the unit must be converted to m³ s⁻¹, but the unit usually obtained is mL min⁻¹. (For example, the CO₂ flow rate in this paper is 20 mL min⁻¹, so $V_{MFC} = \frac{1}{3} \times 10^{-6} m^3 s^{-1}$).

Detector	FID	TCD	
Chromatographic column	HP-PLOT-Q $30m \times 0.32mm \times 20\mu m$		
Column temperature (°C)	80.0	80.0	
Detector temperature (°C)	250.0	160.0	
Sample inlet temperature (°C)	250.0		
Column flow (mL/min) (constant flow)	3.0	3.0	
Air flow (mL/min)	400.0	400.0	
Hydrogen flow (mL/min)	60.0	60.0	
Make-up gas (mL/min)	10.0	2.0	
Split Ratio	10.0: 1	10.0: 1	
Carrier gas	P	Ar	



Fig. S1 Gas chromatogram for (a) FID detector and (b) TCD detector of standard gas.

Gas composition	CH ₄	C_2H_4	C_2H_6	СО	H_2	O ₂
Retention time (min)	1.331	1.735	1.936	6.576	2.093	2.740
Peak height (Pa/250uV)	67.33	125.51	118.91	116.85	9.45	4.74
Peak area (Pa*s/250uV*s)	125.54	245.94	243.71	3365.82	74.82	41.29
Concentration (ppm)	205	196	199	194	201	500

Table S2 The data of each substance in the gas chromatogram of standard gas



Fig. S2 Gas chromatogram for (a) FID detector and (b) TCD detector of 2-Ml/Al-F-N.

Gas composition	СО	H ₂
Retention time (min)	6.397	2.057
Peak height (Pa/250uV)	2829.00	44.95
Peak area (Pa*s/250uV*s)	85344.09	300.01
Concentration (ppm)	4072	545

Table S3 The data of each substance in the gas chromatogram of 2-Ml/Al-F-N

Catalyst	j (mA cm ⁻²)	V <i>vs</i> . RHE	Electrolyte (pH)	Main products	Ref.		
	0.51	1 1	0.1 M KHCO ₃	CO (90.1%),	This		
2-Ml/Al-F-N	9.51 -1.1		(6.8)	H ₂ (9.9%)	work		
Cu-Al/LDHs	50	50	5 0		1 M KHCO ₃	CO (42%),	[0]
	50		(8.4)	formate (22%)	[2]		
FePc-graphene	1.7	-0.6	0.1 M KHCO ₃	CO (89.7%),	[2]		
	1./	1./ -0.0	(6.8)	H ₂ (10.3%)	[3]		
Sn ₄ P ₃ /RGO	68.0	-1.8	0.5 M	CO (96.6%),	Г <i>4</i> Т		
	08.0	-1.8	[Bmim]PF6	H ₂ (3.4%)	[4]		
	2.3	22 00	0.1 M KHCO ₃	CO (88.2%),	[5]		
Ni(OH) ₂ @RGO	2.3 -0.9	-0.9	(6.8)	H ₂ (11.8%)	[5]		
	5 1	5.1 -0.9	0.1 M KHCO ₃	CO (92.2%),	[5]		
Ni-AlO(OH) ₃ @RGO	5.1		(6.8)	H ₂ (7.8%)	[5]		
N-NiZnAl CLDH/RGO	9.4	-0.83	0.5 M NaCl	CO (92%),	[6]		
IN-INIZIIAI CLDII/KUU	9.4	-0.85	(7.0)	H ₂ (8%)	[6]		
N-doped carbon@Ni	23	-0.97	0.5 M KHCO ₃	CO (90%),	[7]		
on rGO	23	-0.97	(7.2)	H ₂ (10%)	[7]		
Ni/NCTs	34.3	4.3 -1.0	0.5M KHCO ₃	CO (98%),	[8]		
	54.5		(7.2)	H ₂ (2%)	[8]		
N-Ta ₂ O ₅ /C	5	-0.73	0.5M NaHCO ₃	CO (87.5%),	[9]		
			(8.32)	H ₂ (12.5%)			
CN-H-CNT		-0.5	0.1 M KHCO ₃	CO (88%),	[10]		
		-0.5	(6.8)	H ₂ (12%)			

Table S4 Summary of CO2RR to CO performance on different electrocatalysts

References:

 [1] S. Jin, Z. Hao, K. Zhang, Z. Yan, J. Chen, Advances and Challenges for the Electrochemical Reduction of CO₂ to CO: From Fundamentals to Industrialization, Angew Chem Int Ed Engl 60(38) (2021) 20627-20648.

[2] K. Iwase, T. Hirano, I. Honma, Copper Aluminum Layered Double Hydroxides with Different Compositions and Morphologies as Electrocatalysts for the Carbon Dioxide Reduction Reaction, ChemSusChem 15(2) (2022) e202102340.

[3] X. Li, G. Chai, X. Xu, J. Liu, Z. Zhong, A. Cao, Z. Tao, W. You, L. Kang, Electrocatalytic reduction of CO₂ to CO over iron phthalocyanine-modified graphene nanocomposites, Carbon 167 (2020) 658-667.

[4] L. Lu, W. Guo, C. Chen, Q. Zhu, J. Ma, H. Wu, D. Yang, G. Yang, X. Sun, B. Han, Synthesis of Sn₄P₃/reduced graphene oxide nanocomposites as highly efficient electrocatalysts for CO₂ reduction, Green Chemistry 22(20) (2020) 6804-6808.

[5] E.R. Liu, T.X. Liu, X.J. Ma, Y.P. Zhang, The electrocatalytic performance of Ni-AlO(OH)(3)@RGO for the reduction of CO₂ to CO, New J. Chem. 46(25) (2022) 12023-12033.

[6] W.T. Li, P.F. Hou, Z. Wang, P. Kang, Synergistic effect of N-doped layered double hydroxide derived NiZnAl oxides in CO₂ electroreduction, Sustainable Energy & Fuels 3(6) (2019) 1455-1460.

[7] Y. Zhao, Z. Miao, F. Wang, M. Liang, Y. Liu, M. Wu, L. Diao, J. Mu, Y. Cheng, J. Zhou, Ndoped carbon-encapsulated nickel on reduced graphene oxide materials for efficient CO_2 electroreduction to syngas with potential-independent H₂/CO ratios, Journal of Environmental Chemical Engineering 9(4) (2021).

[8] Y. Hou, Y.-L. Liang, P.-C. Shi, Y.-B. Huang, R. Cao, Atomically dispersed Ni species on Ndoped carbon nanotubes for electroreduction of CO₂ with nearly 100% CO selectivity, Applied Catalysis B: Environmental 271 (2020).

[9] M. Zhang, P. Hou, Z. Wang, P. Kang, Nitrogen-Doped Ta_2O_5 Nanocomposites for the Electrocatalytic Reduction of Carbon Dioxide to CO with Photoassistance, ChemElectroChem 5(5) (2018) 799-804.

[10] X. Cui, Z. Pan, L. Zhang, H. Peng, G. Zheng, Selective Etching of Nitrogen-Doped Carbon by

Steam for Enhanced Electrochemical CO₂ Reduction, Advanced Energy Materials 7(22) (2017).