Supporting Information: Alumina supported Cu nanoparticles derived from MOF crystallites for CO₂ hydrogenation.

Adele T. Chalmers[1], Zonggao Hu[2], Nicholas F. Dummer[2], Kieran J. Aggett[2], David J. Morgan[2], Michael Bowker[2], Graham Hutchings[2], Kara Stowers[1]*

[1] C100 Benson Building, Department of Chemistry and Biochemistry, Brigham Young University, Provo UT 84602

[2] Max Planck-Cardiff Centre on the fundamentals of heterogeneous catalysis FUNCAT, Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Translational Research Hub, Cardiff, CF24 4HQ, UK.

*Corresponding author. Email: kara.stowers@byu.edu

Table of Contents: Page:

Experimental

Bulk HKUST-1 Synthesis

Bulk HKUST-1 was synthesized according to the procedure by Ma et al. (S1)where 2.16 g of $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in 30 ml of DI water and 1.05 g of BTC was dissolved in 30 mL of ethanol. The solutions were combined and stirred for 30 minutes before being transferred to a teflon lined autoclave. The solution was heated, in the autoclave, for 6 hours at 120°C with a 3°C/min ramp rate. After cooling, the solid was filtered using VWR 413 filter paper and washed with ethanol. BET analysis showed a relatively low surface area (369 m^2/g) and this is due to the sample being unactivated.

Table S1. Comparison of reaction conditions and methanol productivity/selectivity for Cu/Al$_2$O$_3$ and CZA catalysts from this paper and from literature examples.

Catalyst Name from Literature	Temp (°C)	pressure (bar)	Cu wt%	NP size (nm)	Methanol Productivity (mmol h^{-1} kg^{-1})	Methanol Selectivity (%)	Reference
LBL10D	230	20	10	11	870	18.6	This Work
	250	20	10	11	1380	12.0	
	270	20	10	11	1700	8.2	
10%Cu/γ-Al$_2$O$_3$	230	20	10	15	875	16.3	This Work
	250	20	20	15	1210	10.4	
	270	20	20	15	1550	7.3	
CA	250	20	10	4.65	-	13.44	S2
12Cu/γ-Al$_2$O$_3$	240	30	10	-	-	16.9	S3
	260	30	10	-	-	10.7	
30Cu	300	60	30	-	-	9.62	S4
Cu/H-600	280	30	10	-	2500	-	S5
Cu/Al$_2$O$_3$	280	40	15	19	2500	<59	S6
10wt%Cu/UAI	260	30	10	NA	-	23.1	S7
10wt%Cu/HAI	260	30	10	NA	-	30.3	
Cu/Al$_2$O$_3$-ow	350	40	5	2.2	-	78.6	S8
CZA-CP	250	20	50	14	6.93*	~11.5	S9
CZA-US	250	20	~50	9	9.28*	~11	
CZA-SC	250	20	50	11	5.02*	~7.5	
CZA-SS	250	20	50	16	2.54*	~5	
CZnA	250	20	10	5.12	-	17.37	S2
CZA-1	220	40	6.4	-	35.9	35.9	S10
CZA-2	220	40	14.7	CuO: 11.6 Cu: 12.5	-	56.2	
CZA-3	220	40	21.7	CuO: 12.3 Cu: 13.3	-	58.7	
CZA-4	220	40	28.7	CuO: 13.8 Cu: 14.4	-	58.9	

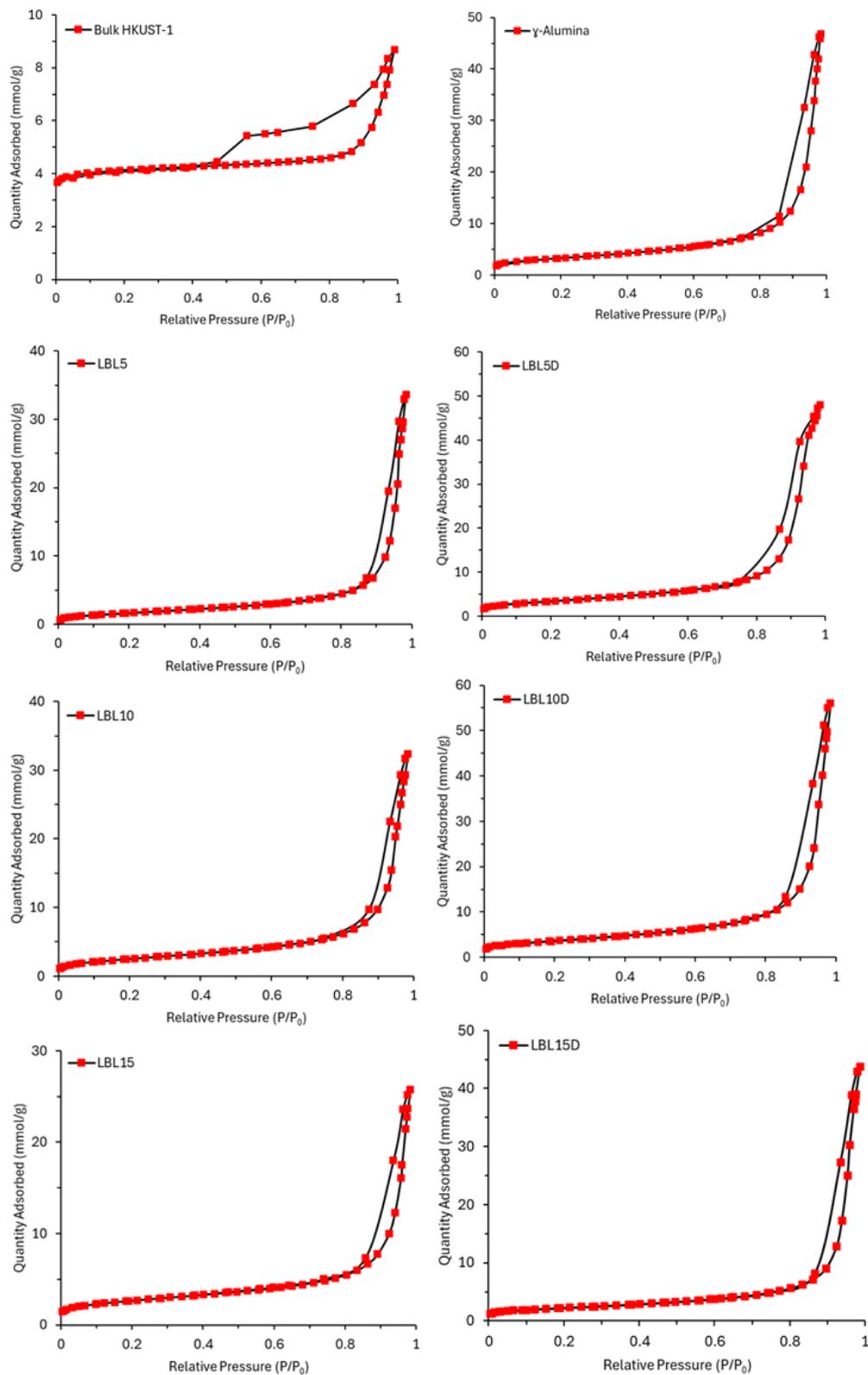*In units of mg MeOH/(ml cat*2000 h)

Figure S1. N_2 adsorption/desorption isotherms of bulk HKUST-1, γ-Al_2O_3, LBL5-15, and LBL5D-15D.
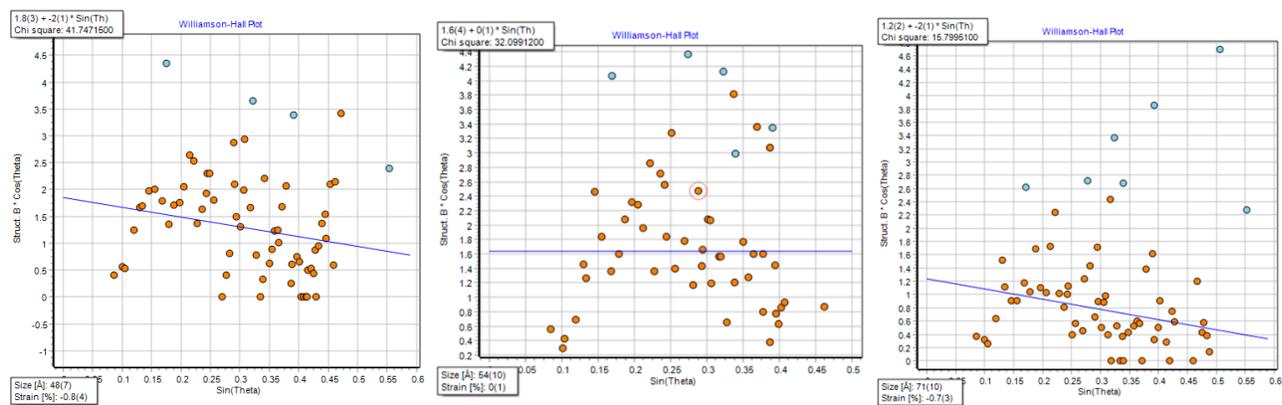
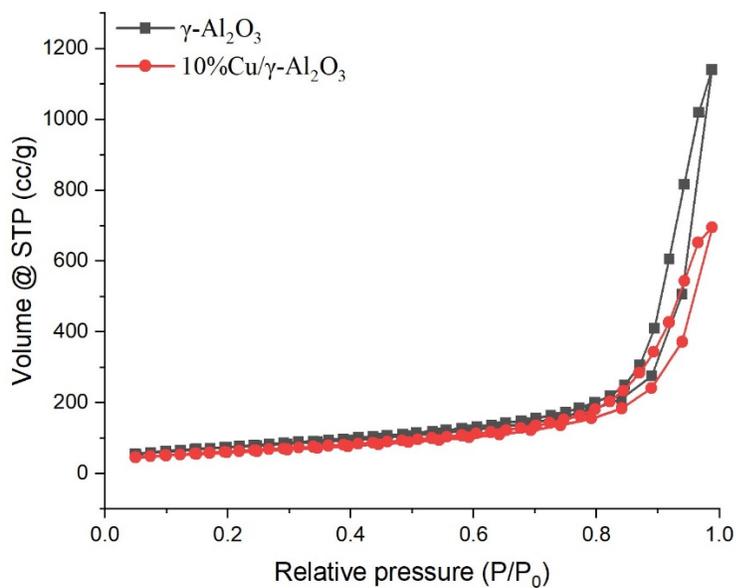**Figure S2.** Williamson-Hall plots for (left to right) LBL5, LBL10, and LBL15.

Figure S3. N_2 adsorption/desorption isotherms of γ-Al_2O_3 and 10%Cu/γ-Al_2O_3 catalyst.
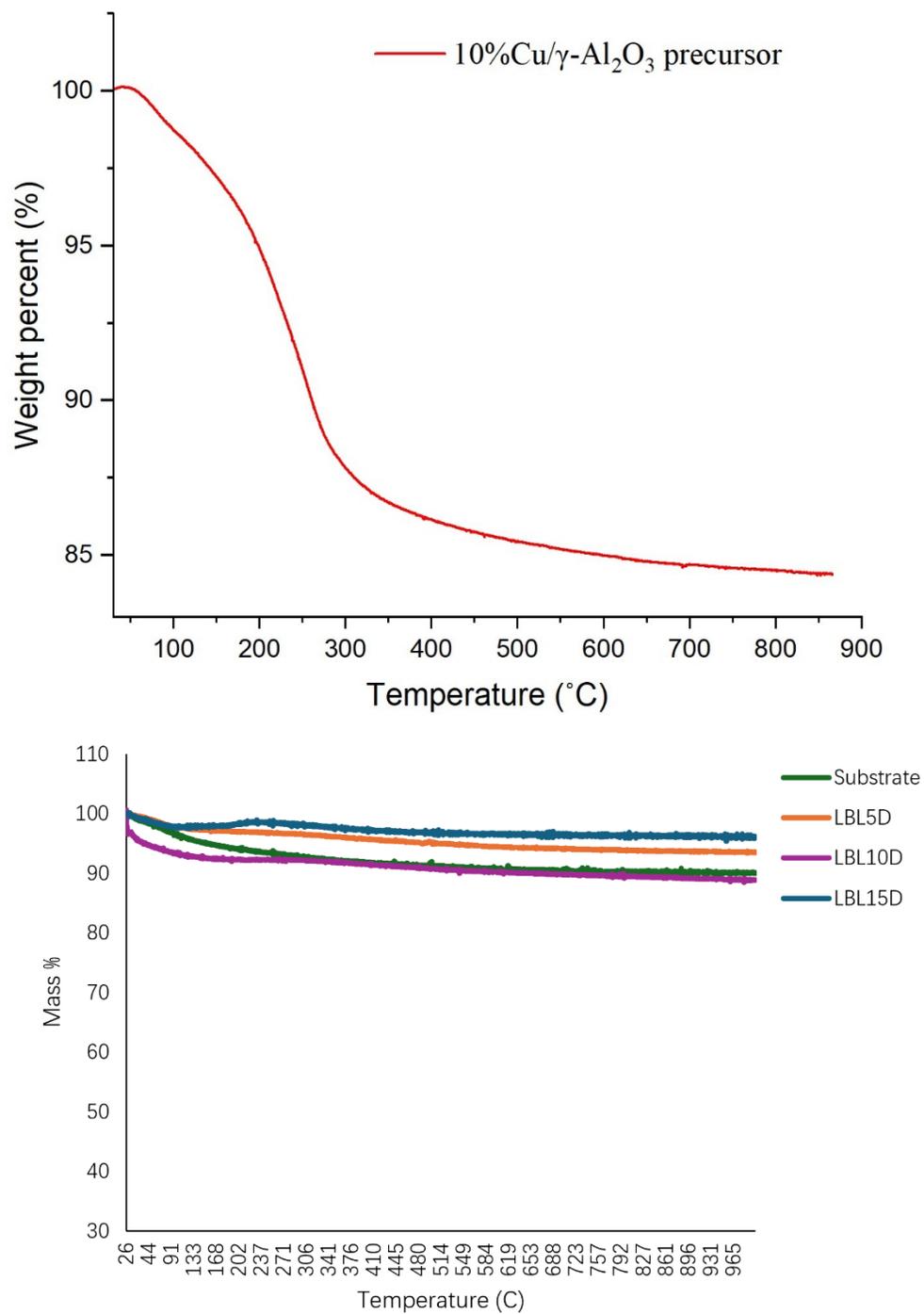
Figure S4. TGA profiles of the sol-immobilized catalyst precursor, the γ-Al$_2$O$_3$ (substrate), and LBL5D-15D.
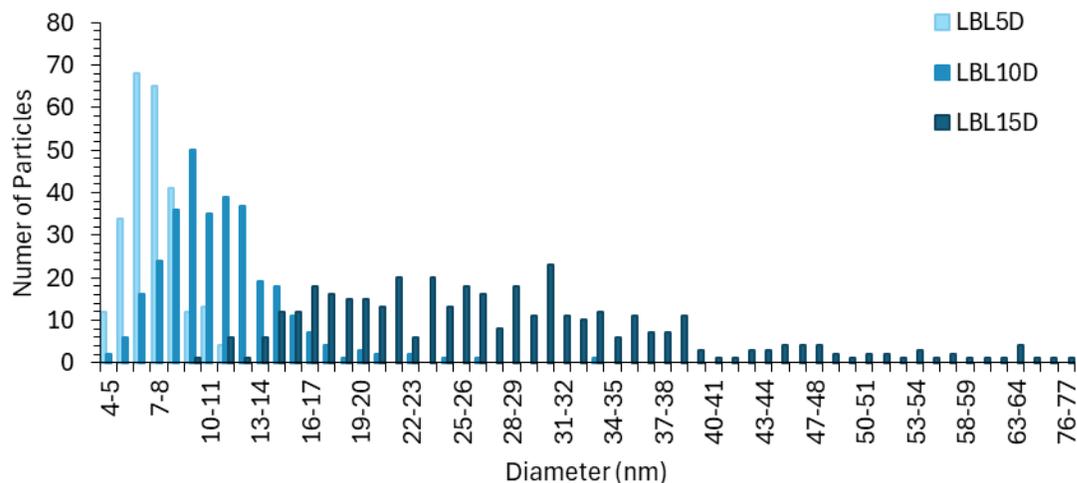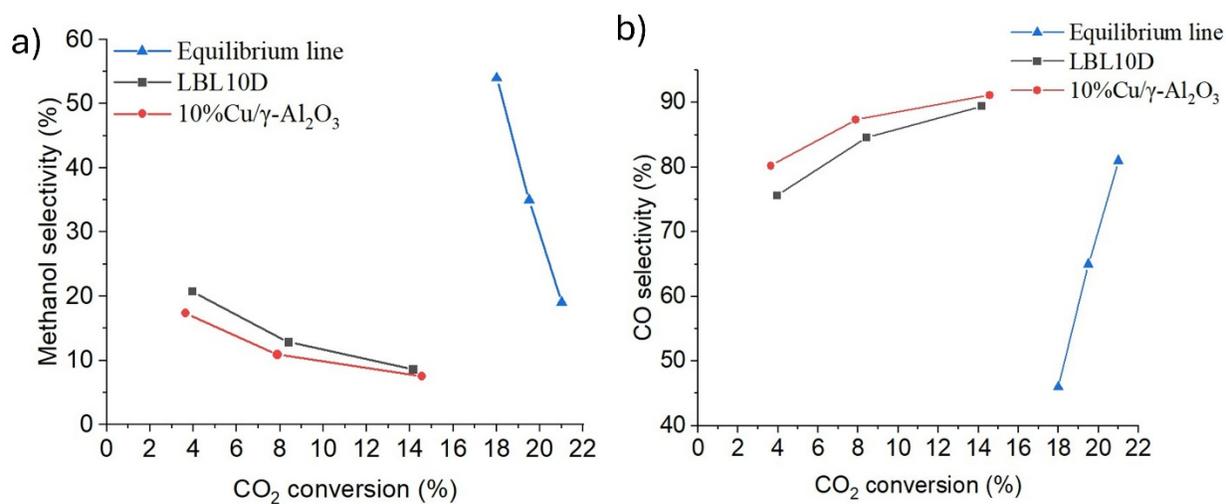
Figure S5. Particle size distribution for LBL5D-15D.

Figure S6. CO_2 conversion, methanol selectivity (a) and CO selectivity (b) over LBL10D and 10%$Cu/\gamma-Al_2O_3$. The equilibrium lines were added for comparison. Reaction conditions: 230-250-270 °C, 20 bar, 30 ml min^{-1}, $CO_2:H_2:Ar:N_2$=20:60:5:15, 0.1 g catalyst.
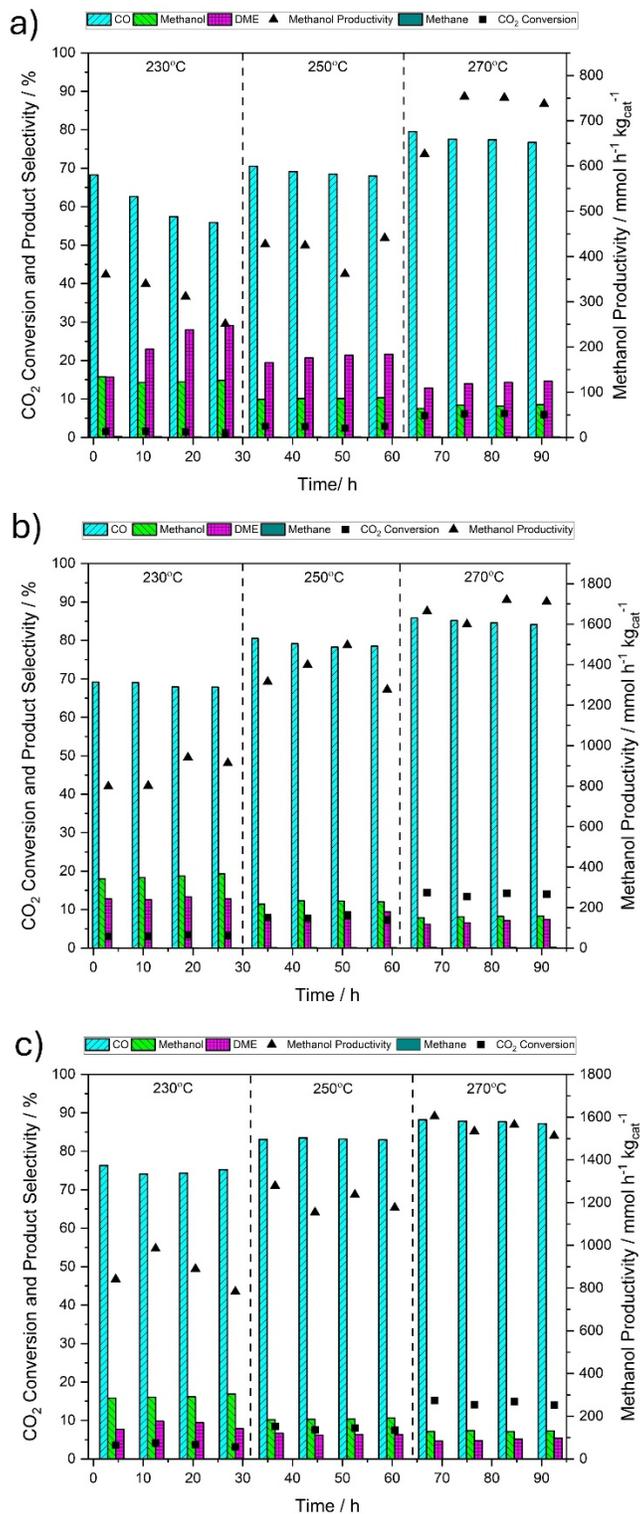
Figure S7. Catalytic performance for CO_2 hydrogenation over time: a) LBL10, b) LBL10D and c) 10%Cu/γ-Al$_2$O$_3$. Reaction conditions: 230, 250, 270°C; 20 bar; 30 ml min^{-1}; CO_2:H$_2$:Ar:N$_2$=20:60:5:15; 0.1 g catalyst.
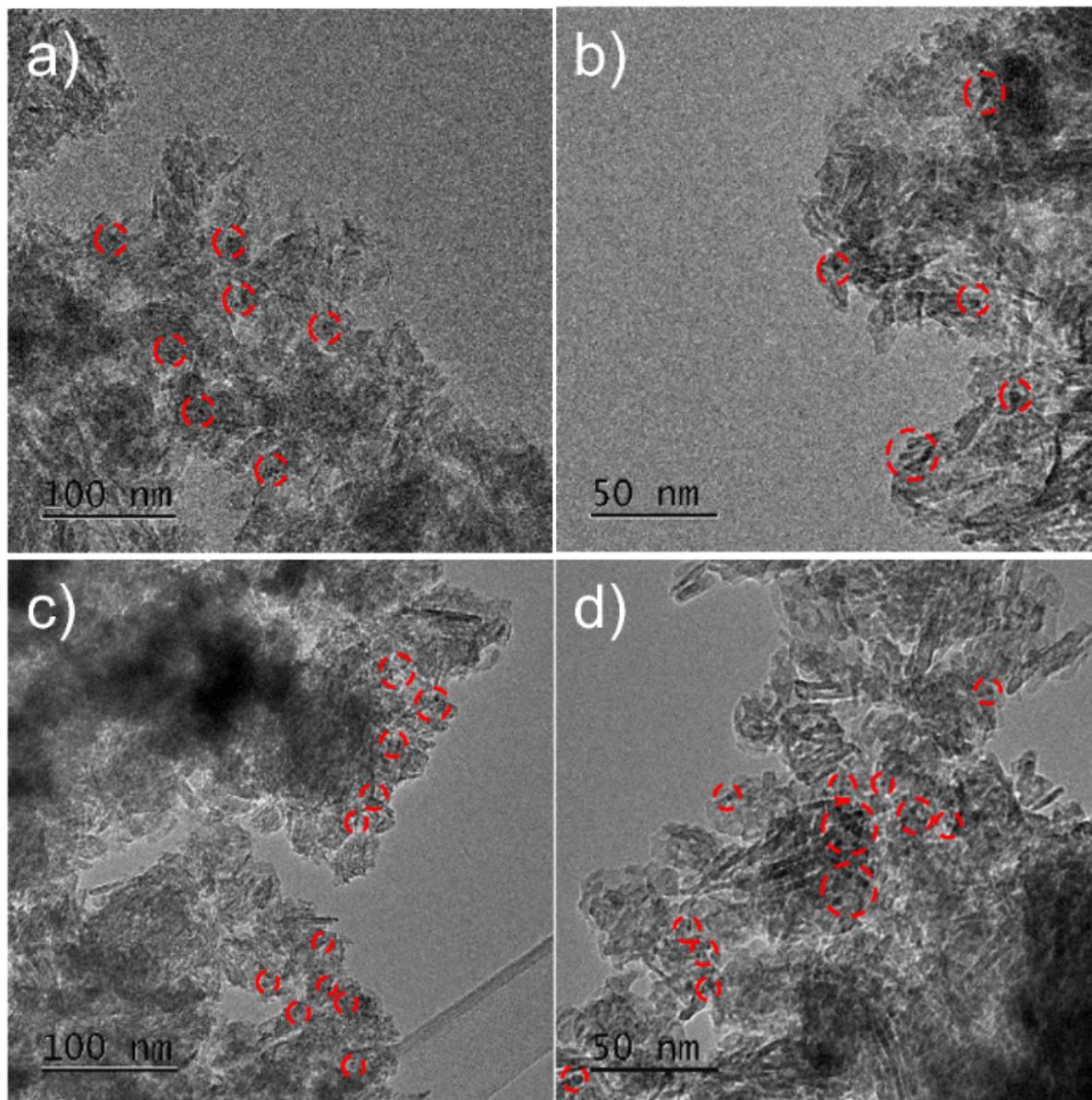
Figure S8. Representative post-reaction TEM images of LBL10D (a and b) and 10%Cu/γ-Al$_2$O$_3$ (c and d).

References

S1.   X. Ma, S. Peng, W. Li, H. Liu and Y. Chen, *CrystEngComm*, 2018, **20**, 407–411.

S2.   (H. Ren, C.-H. Xu, H.-Y. Zhao, Y.-X. Wang, J. Liu and J.-Y. Liu, *Journal of Industrial and Engineering Chemistry*, 2015, **28**, 261–267.

S3.   Y. Zhang, J. Fei, Y. Yu and X. Zheng, *Energy Conversion and Management*, 2006, **47**, 3360–3367.

S4.   R. Ismail, M. A. H. Saad, M. J. Al-Marri, A. Sardar, A. T. Mohamed, M. El-Naas, A. M. Soliman and A. Benamor, *Journal of Environmental Chemical Engineering*, 2024, **12**, 112325.

S5.   N. Kanjanasoontorn, T. Permsirivanich, T. Numpilai, T. Witoon, N. Chanlek, M. Niamlaem, C. Warakulwit and J. Limtrakul, *Catalysis Letters*, 2016, **146**, 1943–1955.

S6.   S. Li, Y. Wang, B. Yang and L. Guo, *Applied Catalysis A: General*, 2019, **571**, 51–60.

S7.   T. Witoon, S. Bumrungsalee, M. Chareonpanich and J. Limtrakul, *Energy Conversion and Management*, 2015, **103**, 886–894.

S8.   X. Song, C. Yang, X. Li, Z. Wang, C. Pei, Z.-J. Zhao and J. Gong, *ACS Catalysis*, 2022, **12**, 14162–14172.

S9.   V. D. Dasireddy and B. Likozar, *Renewable Energy*, 2019, **140**, 452–460.

S10.   C. Zhang, H. Yang, P. Gao, H. Zhu, L. Zhong, H. Wang, W. Wei and Y. Sun, *Journal of CO2 Utilization*, 2017, **17**, 263–272.