Methanol Synthesis by Hydrogenation of Hybrid CO2−CO Feeds

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Supporting Information

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Tables

Table S1. Bulk characterization of fresh copper-containing catalysts.

Catalyst	Content (wt.%)						S_{Cu}[c] ($m^2\ g_{cat}^{-1}$)	D_{Cu}[d] (%)	$d_{CuO,XRD}$[e] (nm)
	Nominal			Measured[b]					
	Cu	Zn	*M*[a]	Cu	Zn	*M*[a]			
CuZnAl-JM	50.7	19.8	5.3	44.9	17.8	4.2	24	8	5
CuZnAl-M700	49.5	22.5	5.3	40.9	18.6	3.9	26	10	4
CuZnAl-ox	49.4	25.4	3.5	48.3	24.3	1.7	23	7	8
Cu-ZnO-ZrO_2	45.1	23.2	10.8	44.5	24.1	10.1	11	4	6

[a]*M* = Al or Zr. [b]ICP-OES. [c,d]Copper surface area and dispersion (*D*) measured by N_2O pulsed chemisorption. [e]CuO crystallite size determined using the Scherrer equation, averaging over the characteristic CuO double reflections ((002)/(11−1) and (111)/(200)) in the XRD patterns (Figure 1).

Table S2. Bulk composition of ZnO-ZrO_2 and In_2O_3-based catalysts.

Catalyst	Content (wt.%)	
	Nominal	Measured[a]
ZnO-ZrO_2	7.2[b]	7.1[b]
In_2O_3/*m*-ZrO_2	10[c]	8.58[c]

[a]ICP-OES. [b]Zn and [c]In.

Table S3. Surface composition of copper-containing catalysts.

Catalyst	Status[a]	Surface metal content[b] (at.%)		Cu/Zn (-)
		Cu	Zn	
CuZnAl-JM	Reduced	59.7	40.3	1.48
	HC	50.4	49.6	1.02
	FC	47.2	52.8	0.89
CuZnAl-M700	Reduced	59.9	40.1	1.49
	HC	57.2	42.8	1.34
	FC	51.4	48.6	1.06
CuZnAl-ox	Reduced	43.2	56.8	0.76
	HC	42.7	57.3	0.75
	FC	44.5	55.5	0.80
Cu-ZnO-ZrO_2	Reduced	47.9	52.1	0.92
	FC	59.2	40.8	1.45

[a]Data relative to catalysts in reduced form and after use in full cycles (FC) and half-cycles (HC). [b]XPS.

Table S4. Surface composition of $ZnO-ZrO_2$ and In_2O_3-based catalysts.

Catalyst	Status[a]	Oxygen relative contributions[b] (%)			Surface metal content[b] (at.%)	
		$O_{lattice}$	O_{defect}	OH	In or Zn	Zr
$ZnO-ZrO_2$	Fresh	77	14	9	1.6	53.1
	HC	69	21	10	1.8	53.3
$In_2O_3/m-ZrO_2$	Fresh	76	14	10	5.1	24.1
	HC	70	22	8	5.5	31.8
In_2O_3	Fresh	64	23	13	48.9	-
	HC	66	22	12	47.9	-

[a]Data relative to catalysts in fresh form and after use in half-cycles (HC). [b]XPS, oxygen relative contributions are determined by peak fitting.

Figures

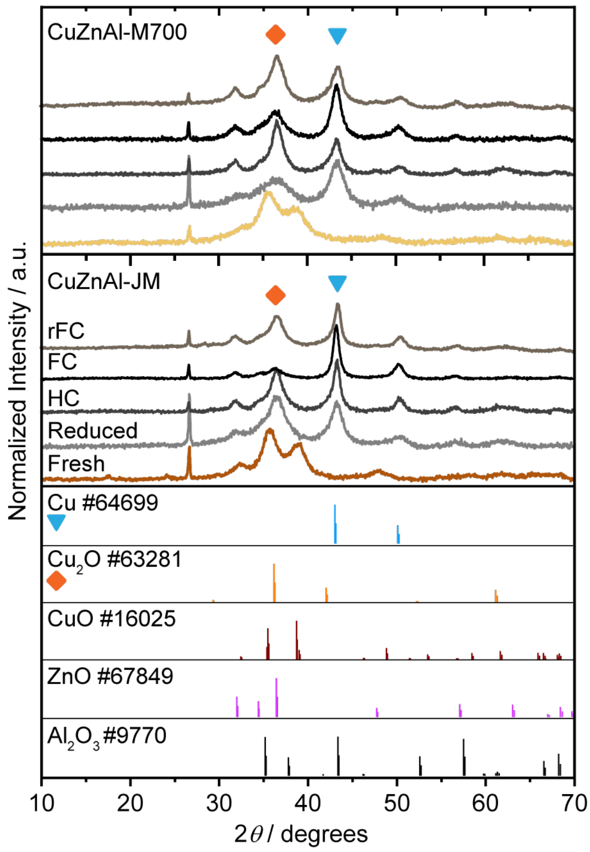

Figure S1. XRD patterns of commercial Cu-ZnO-Al_2O_3 catalysts in fresh and reduced forms and after use in full cycles (FC), half-cycles (HC), and reverse full cycles (rFC). Reference diffractograms of pure phases are shown with vertical lines. The diffractograms indicate the presence of metallic Cu and Cu_2O phases in all reduced and used samples.

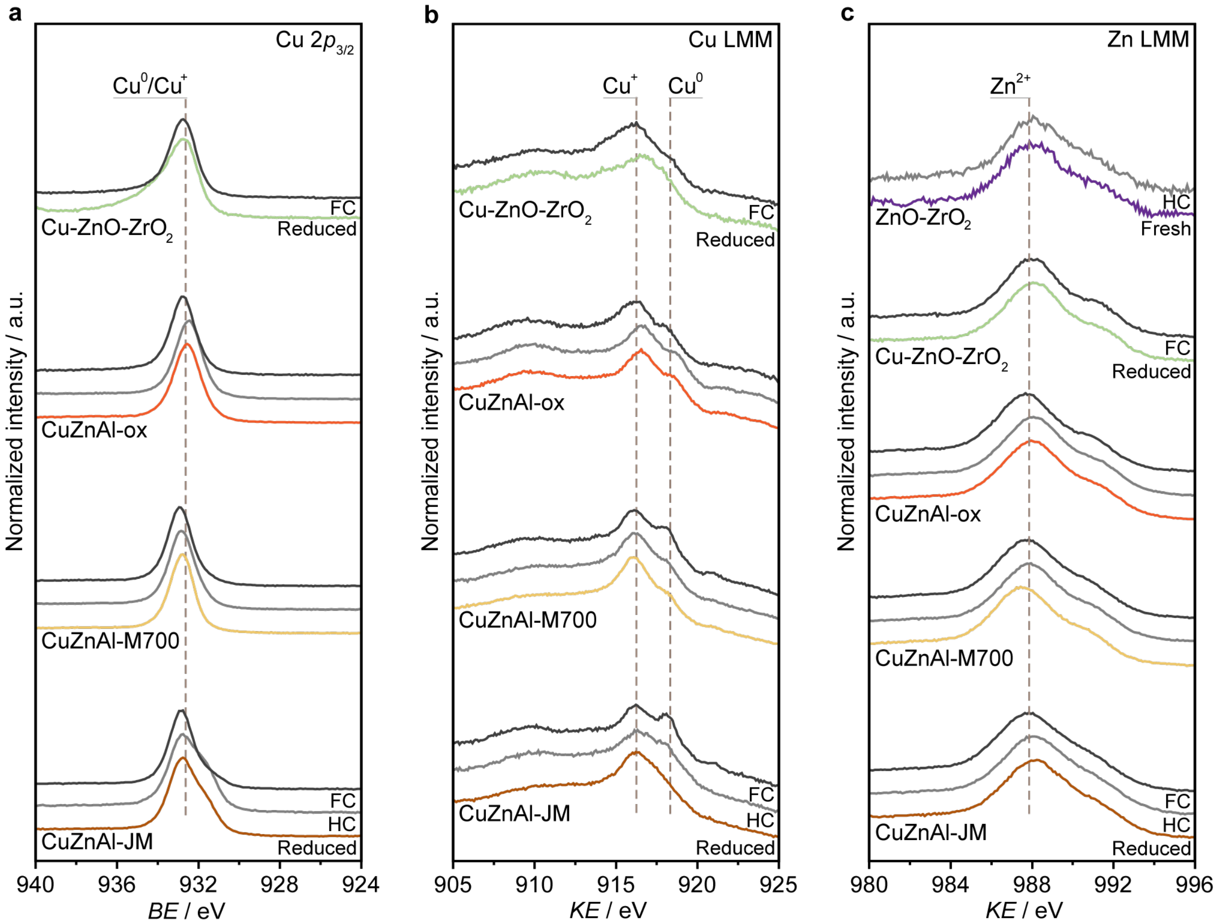

Figure S2. (a) Cu 2*p* core-level XPS (b) Cu LMM, and (c) Zn LMM Auger spectra of Cu-ZnO-Al_2O_3 catalysts, Cu-ZnO-ZrO_2, and ZnO-ZrO_2 in reduced or fresh, and used forms. Spectra in (a) and (b) indicate the presence of metallic Cu and Cu^+ and the absence of Cu^{2+} species, while those in (c) evidence zinc solely as Zn^{2+} cations.

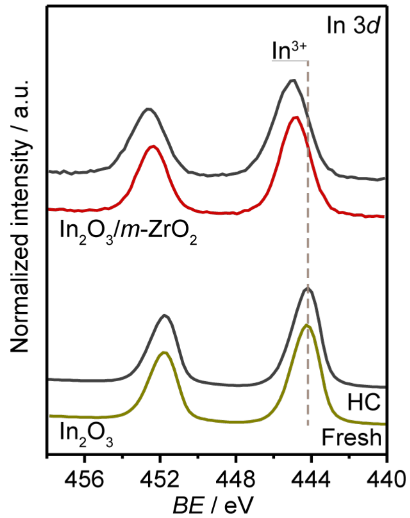

Figure S3. In 3*d* core-level XPS spectra of bulk In_2O_3 and In_2O_3/*m*-ZrO_2 in fresh from and used in half-cycles (HC). The shift of the signal for In_2O_3/*m*-ZrO_2 towards higher binding energies indicates a more oxidic character of indium species due to their interaction with the support.