Supplementary Information

The Cu-Al_2O_3 Interface: An Unignorable Active Site for Methanol Steam Reforming Hydrogen Production

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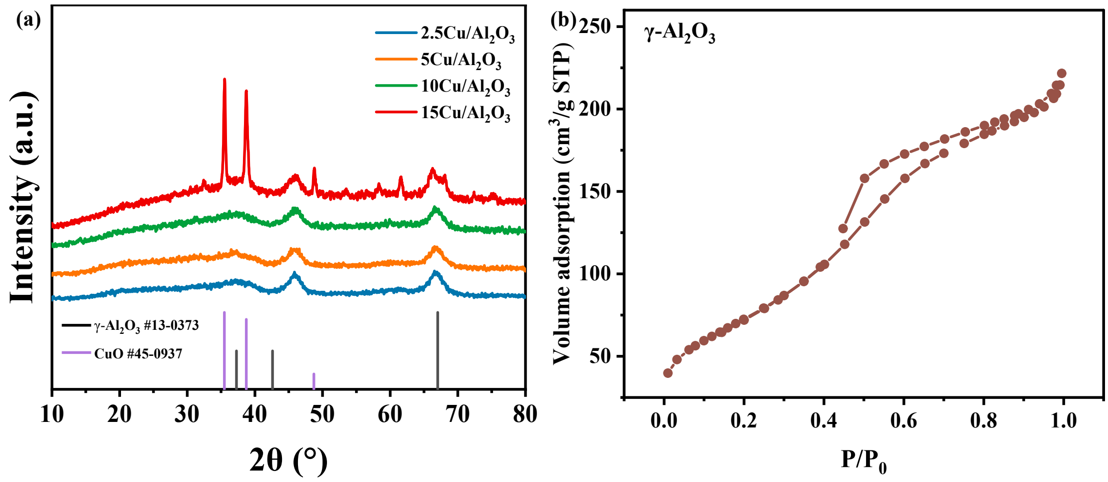

Fig. S1. (a) XRD patterns of the fresh catalysts. (b) Nitrogen physisorption isotherms of γ-Al_2O_3.

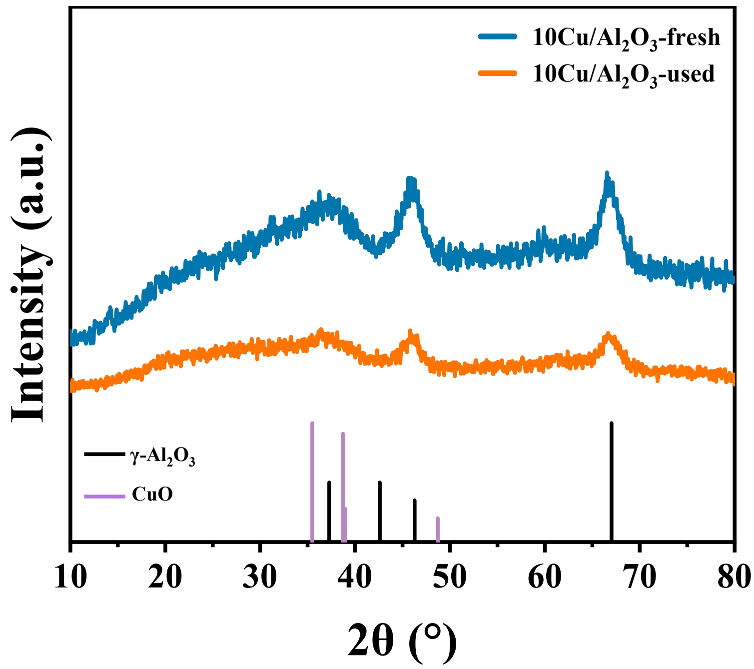

Fig. S2. XRD patterns of the fresh and used 10Cu/Al_2O_3 catalysts.

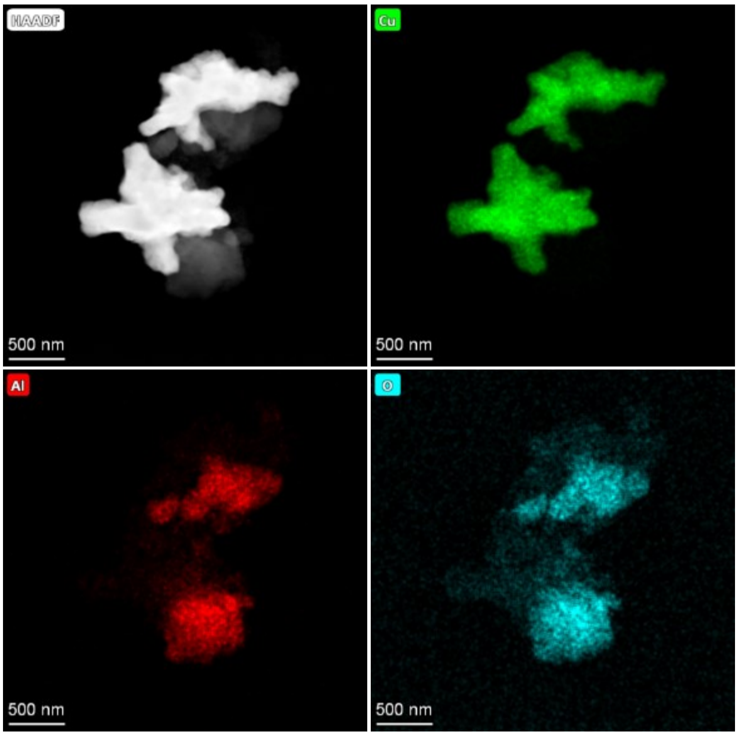

Fig. S3. High-angle annular dark-field STEM images of 15Cu/Al_2O_3, corresponding EDS elemental maps.

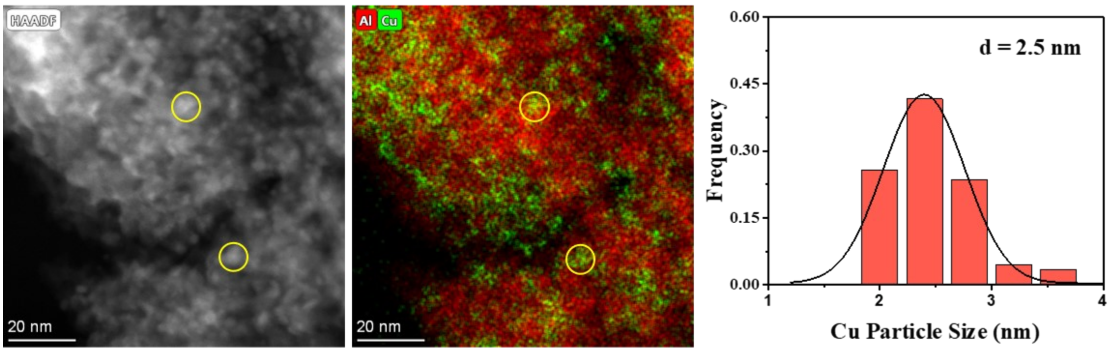

Fig. S4. High-angle annular dark-field STEM images of 10Cu/Al_2O_3-used, corresponding EDS elemental maps and size distribution.

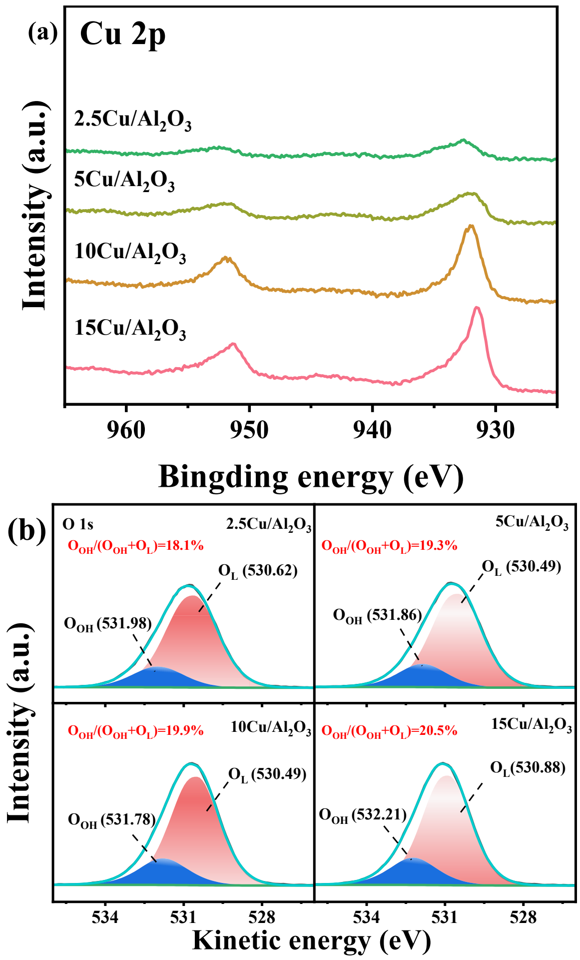

Fig. S5. Quasi *in-situ* X-ray photoelectron spectroscopy spectra of (**a**) Cu 2p and (**b**) O 1s.

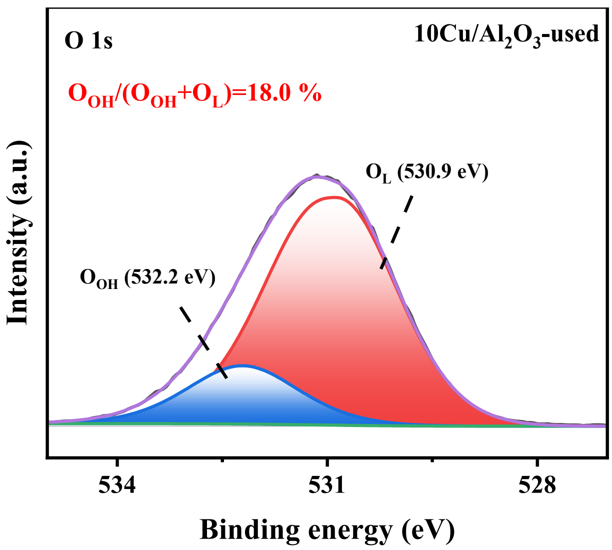

Fig. S6. Quasi *in-situ* O 1s XPS spectra of 10Cu/Al_2O_3-used.

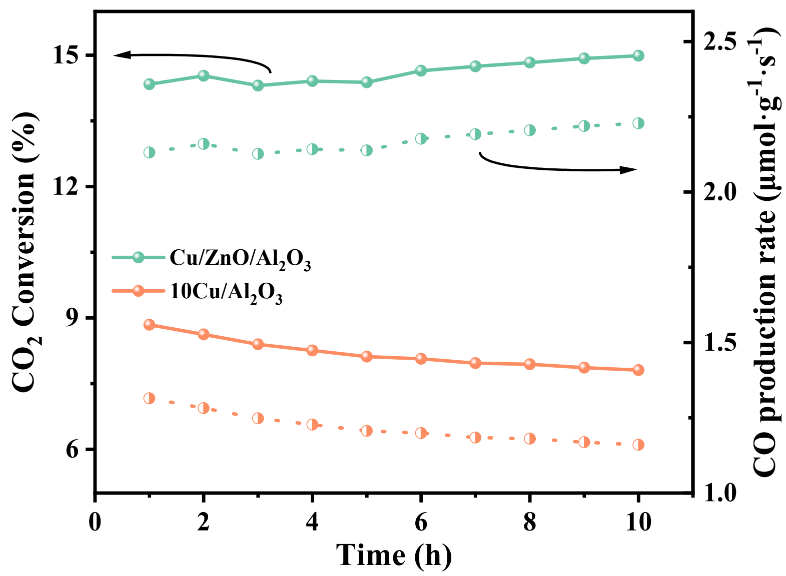

Fig. S7. Catalytic performance of $10Cu/Al_2O_3$ and commercial $Cu/ZnO/Al_2O_3$ catalysts for reverse water-gas shift at 250 °C. Reaction conditions: 0.1 Mpa, gas flow rate 20 $mL\cdot min^{-1}$ for $10\%CO_2/30\%H_2/60\%N_2$, 0.1 g catalyst, WHSV = 12000 $mL\cdot g^{-1}\cdot h^{-1}$.

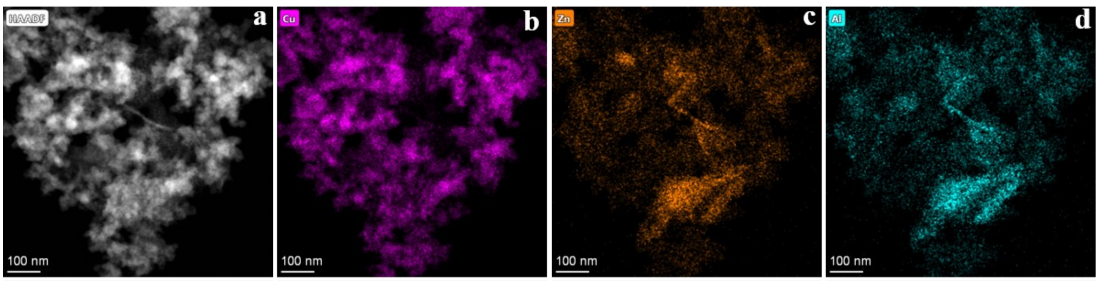

Fig. S8. (a) High-angle annular dark-field STEM images, corresponding (b, c, d) EDS elemental maps of reduced $Cu/ZnO/Al_2O_3$.

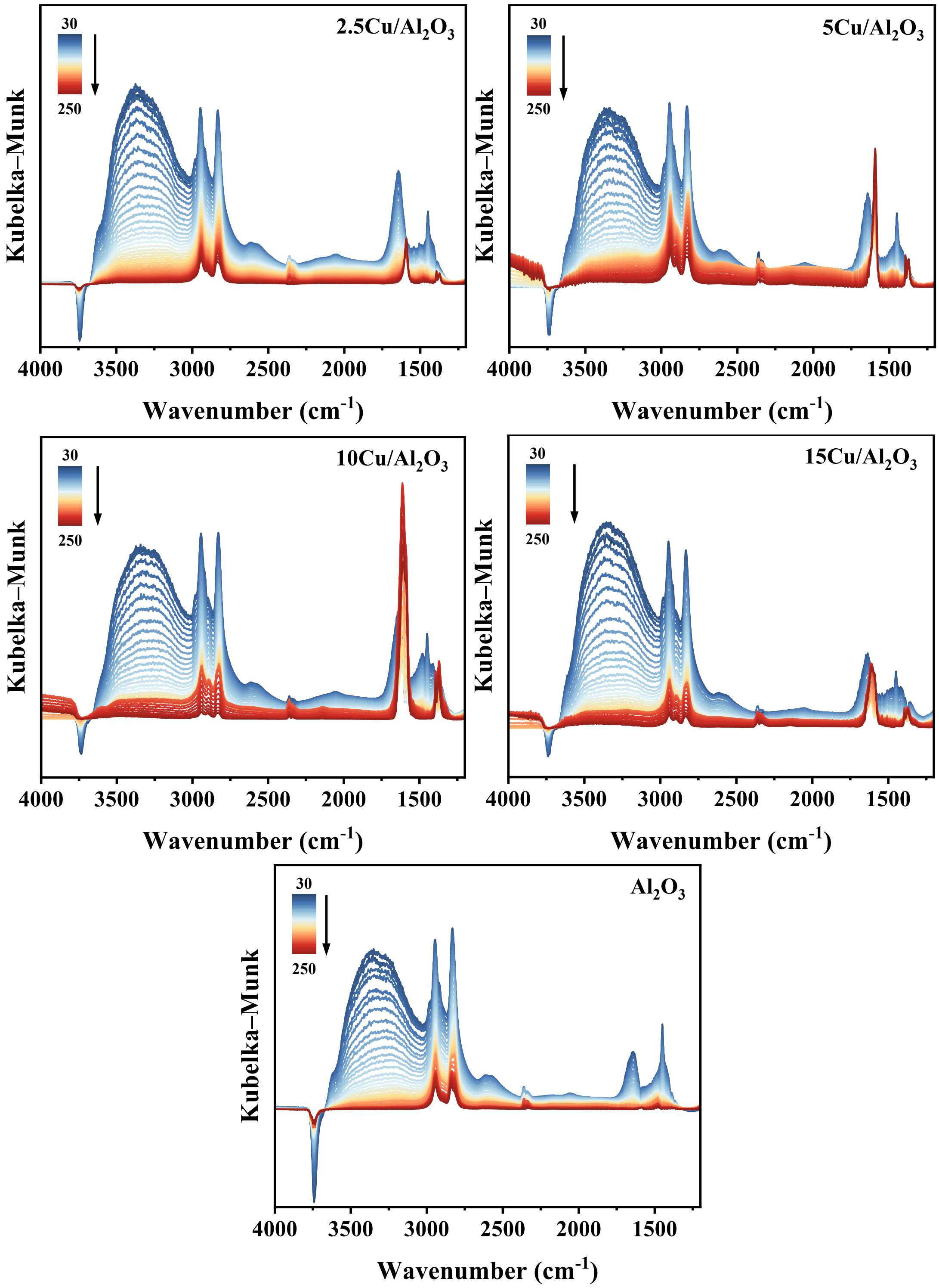

Fig. S9. *In-situ* temperature-programmed DRIFTS of mCu/Al_2O_3 with the spectra collected with an increasing temperature to 250 °C in Ar after preadsorption of methanol and water at 30 °C.

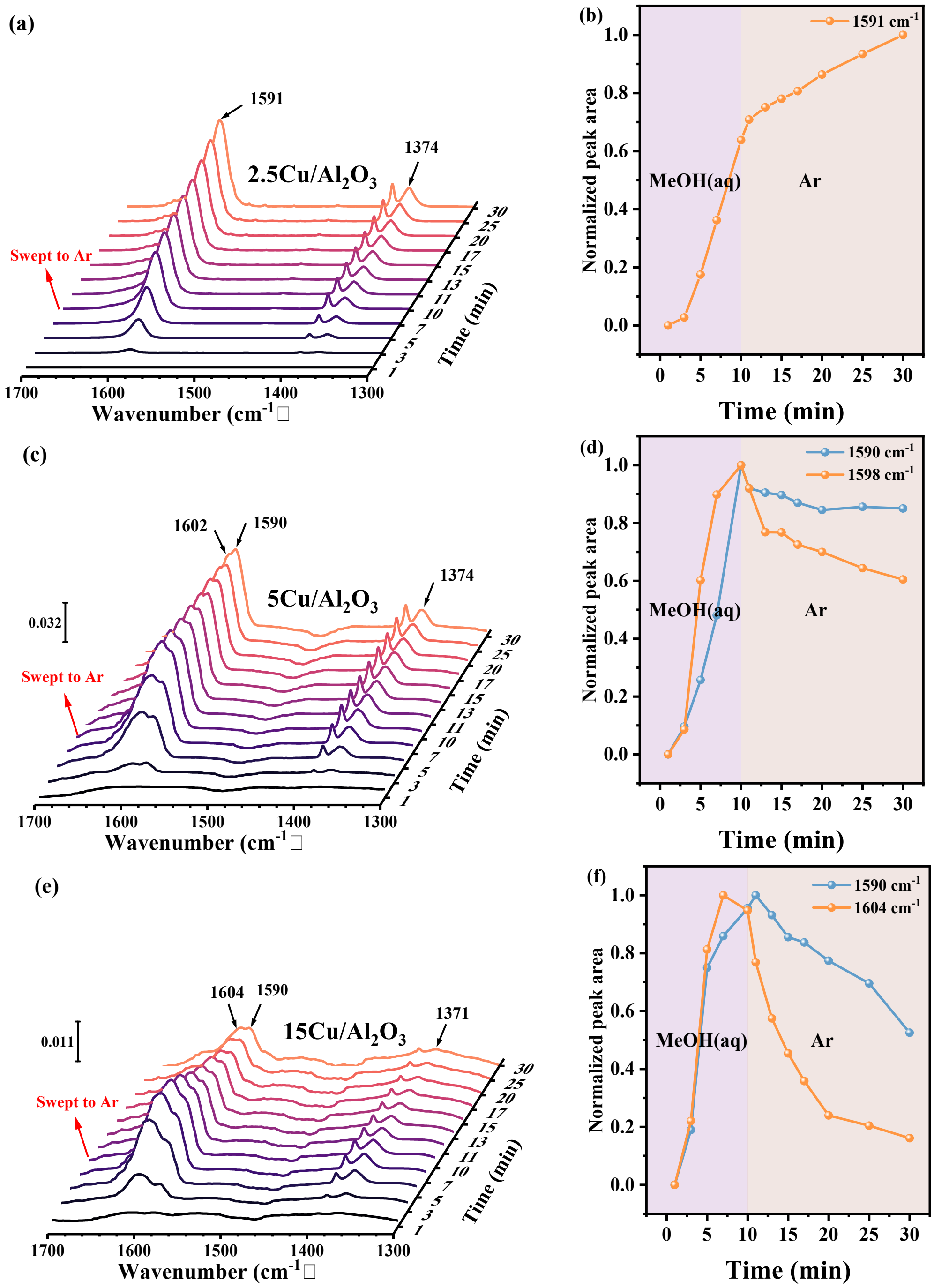

Fig. S10. *In-situ* DRIFTS of MSR on **(a)** 2.5Cu/Al_2O_3, **(c)** 5Cu/Al_2O_3, and **(e)** 15Cu/Al_2O_3 exposed to the mixture of CH_3OH/H_2O for 10 min and followed Ar flushing for another 20 min at 250 °C; variations in the peak areas of two different surface formates (1590 cm^{-1}) and (1602 cm^{-1}) on **(b)** 2.5Cu/Al_2O_3, **(d)** 5Cu/Al_2O_3, and **(f)** 15Cu/Al_2O_3, respectively.

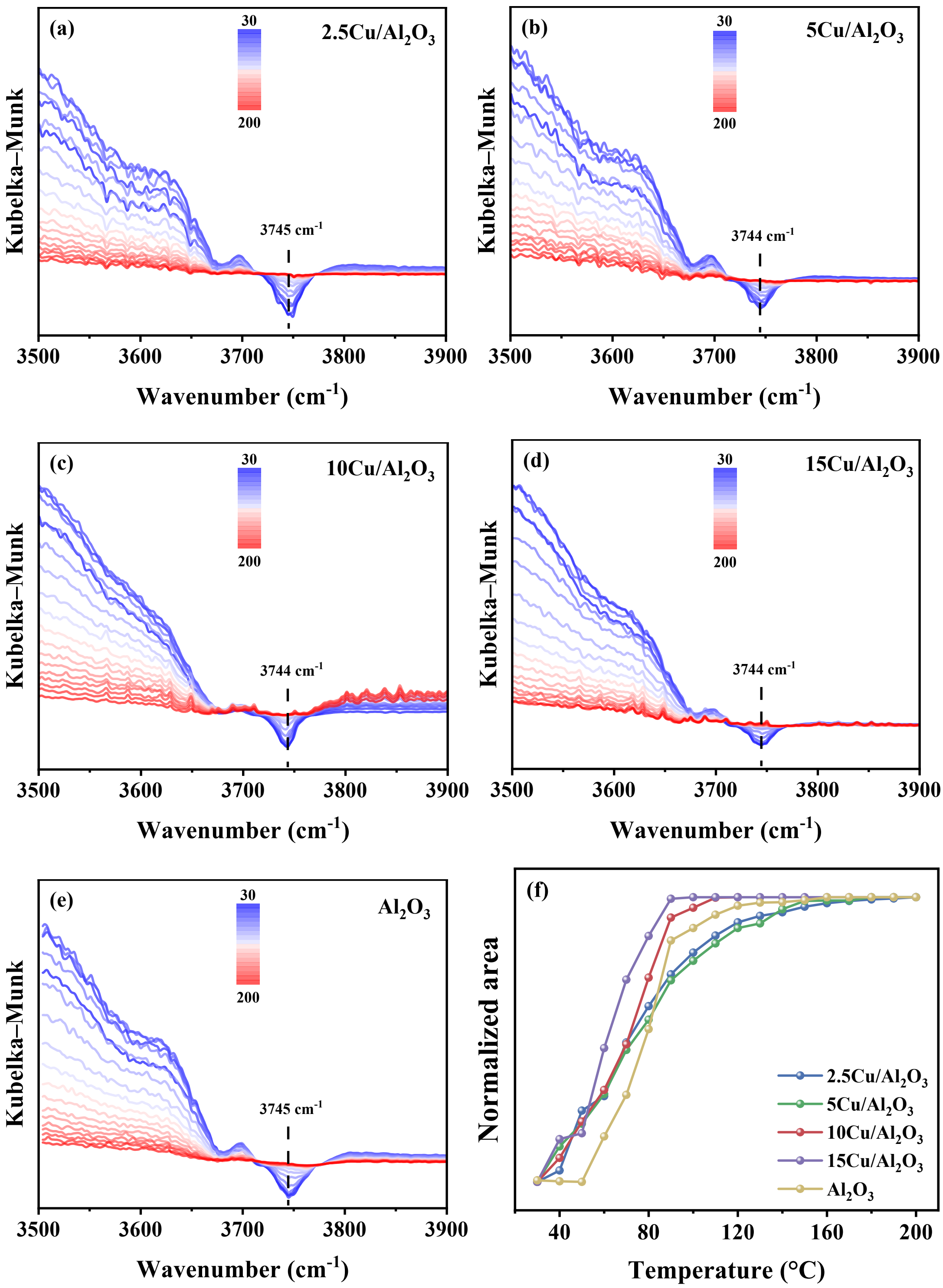

Fig. S11. (a-e) *In-situ* temperature-programmed DRIFTS of mCu/Al_2O_3 with the spectra collected with an increasing temperature to 200 °C in Ar after preadsorption of water at 30 °C. (f) The integrated peak area of surface hydroxyl (3744 cm^{-1}) versus temperature during temperature ramping.

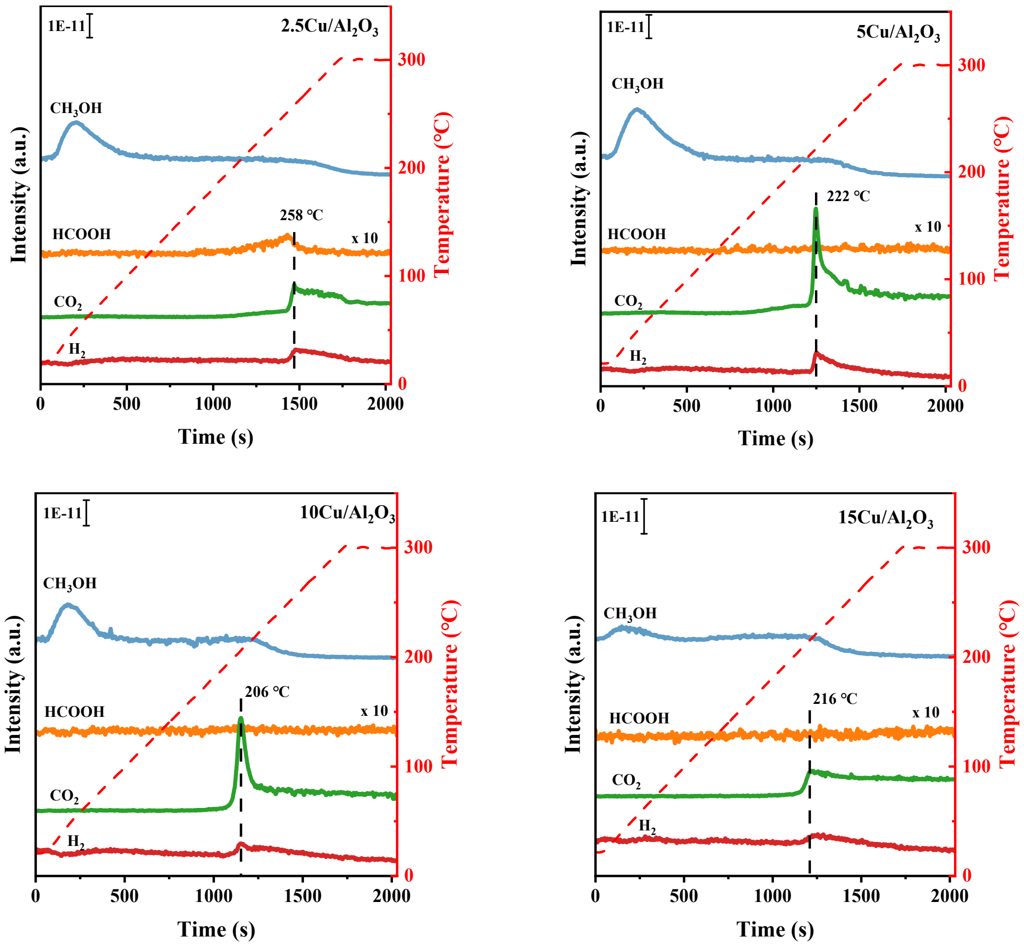

Fig. S12. Temperature-programmed surface reaction (TPSR) of MSR on mCu/Al_2O_3 catalysts.

Table S1. Physicochemical properties of catalysts

Samples	BET ($m^2 \cdot g^{-1}$)[a]	Average pore diameter (nm)[b]	Content of Cu (%)[c]	D_{Cu} (%)[d]	d_{Cu} (nm)[e]
2.5Cu/Al_2O_3	239.3	4.6	2.5	95.8	1.6
5Cu/Al_2O_3	250.6	4.5	5.0	54.2	1.9
10Cu/Al_2O_3	227.2	4.7	9.2	26.9	2.1
15Cu/Al_2O_3	242.4	4.5	15.0	12.4	2.5
10Al_2O_3/Cu	37.9	20.9	68.0	1.3	-
Cu/ZnO/Al_2O_3	85.1	18.8	57.7	6.4	23.2
Al_2O_3	266.6	4.2	-	-	-
CuO	10.6	28.1	79.9	-	-

[a] BET surface area was calculated by the BET method.

[b] Average pore diameter from BJH method.

[c] Content of copper was determined by ICP-AES.

[d] Dispersion of copper was calculated with N_2O-RFC.

[e] Size of copper particles was collected from HAADF images.

Table S2. Catalytic performance of Cu-Al catalysts towards MSR reaction.

Catalyst	Methanol Conversion (%)	CO Selectivity (%)	Production rate (μmol·g^{-1}·s^{-1})			TOF[a] (h^{-1})
			CO	CO_2	H_2	
2.5Cu/Al_2O_3	23.2	0.8	0.11	13.5	44.1	252.2
5Cu/Al_2O_3	49.2	0.8	0.22	28.7	93.8	584.9
10Cu/Al_2O_3	89.7	0.9	0.46	52.2	147.6	1080.2
15Cu/Al_2O_3	49.7	0.9	0.13	14.4	93.6	787.2
Cu/ZnO/Al_2O_3	89.0	6.3	3.28	48.9	137.8	1051.2

[a] TOF was evaluated with methanol conversion below 10%. (High WHSV was used to control the methanol conversion. The WHSV was 67.58 h^{-1} for 2.5Cu/Al_2O_3, 124.8 h^{-1} for 5Cu/Al_2O_3, 10Cu/Al_2O_3 and 5Cu/Al_2O_3, 168.96 h^{-1} for Cu/ZnO/Al_2O_3)

Table S3. Catalytic performance towards reverse water-gas shift reaction.

Catalyst	CO_2 Conversion (%)	CO production rate (μmol·g^{-1}·s^{-1})
10Cu/Al_2O_3	15.0	2.2
Cu/ZnO/Al_2O_3	7.8	1.2

Reaction conditions: 0.1 Mpa, gas flow rate 20 mL·min^{-1} for 10%CO_2/30%H_2/60%N_2, 0.1 g catalyst, WHSV = 12000 mL·g^{-1}·h^{-1}.

Table S4. Catalytic performance of copper-based catalysts towards MSR reaction.

Samples	T(°C)	X_{MeOH} (%)	Acitivity ($\mu mol_{H2}\cdot g_{cat}^{-1}\cdot s^{-1}$)	S_{CO}(%)
10Cu/Al_2O_3	**250**	**80.8**	**147.6**	**0.9**
4.25Cu/Cu(Al)O_x[1]	240	>99	110.8	1
Cu/ZnO[2]	250	94.2	105	0.4
Cu/ZnO[3]	260	67	99	0.9
Cu/CeO_2[3]	260	91	135	2.3
Cu/CeO_2[4]	270	-	162.9	0.5
Cu/Al_2O_3[3]	260	22	32	0.4
Cu/ZrO_2[5]	260	100	90	-
Cu-Mn spinel[6]	260	92.9	79	0.7
Cu/Cr_2O_3[7]	240	-	28	5
Cu/CoO[7]	240	-	17	14
Cu/Y_2O_3[8]	300	75	100	-

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