

Supplementary material

Fig S1 *In situ* XRD under H₂ of the catalysts. a) MoxC/H; b) 1CuMoxC/H; c) 3CuMoxC/H; d) CuMoxC/H; e) MoxC/H-700; f) CuMoxC/H700. XRD of spent catalyst after reaction at 230 °C: g) MoxC/H-PR; h) CuMoxC/H-PR ; i) MoxC/H700-PR j) CuMoxC/H-700-PR.

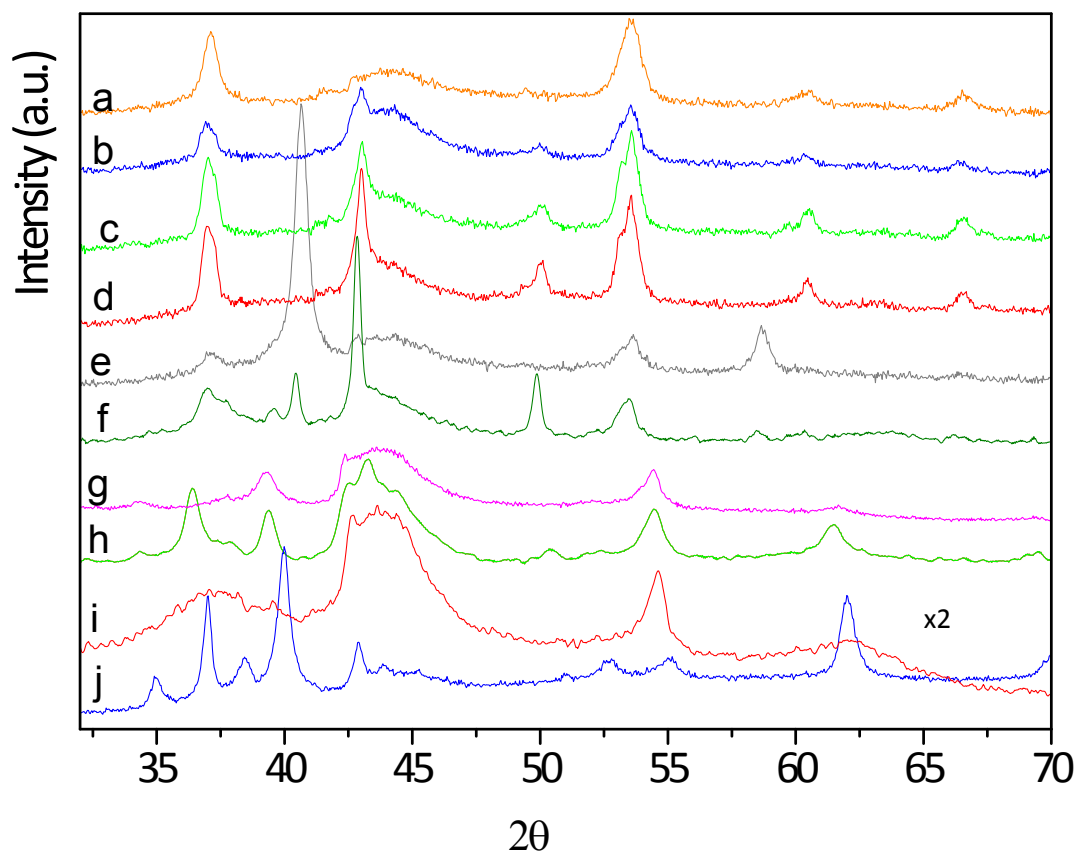
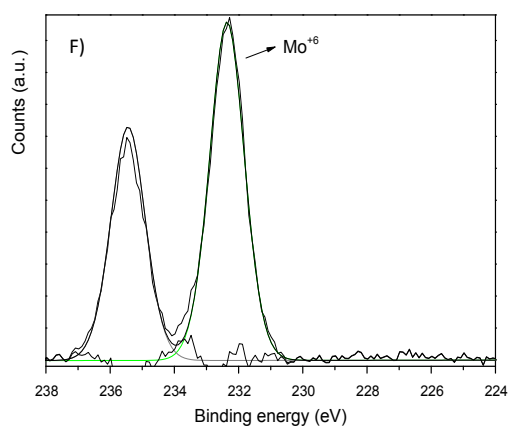
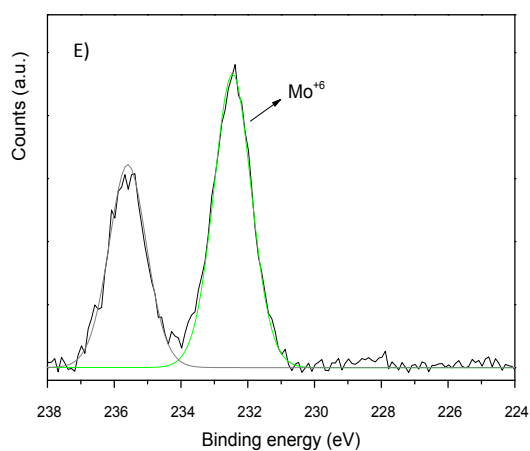
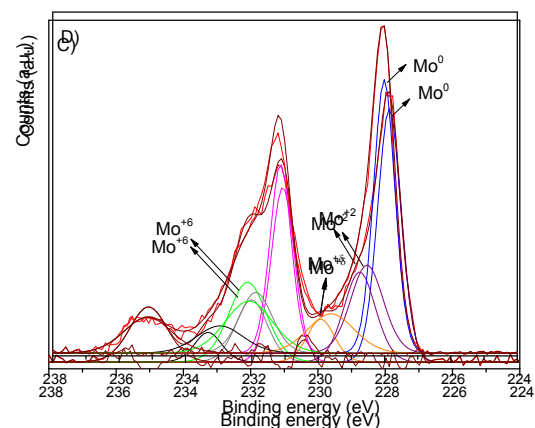
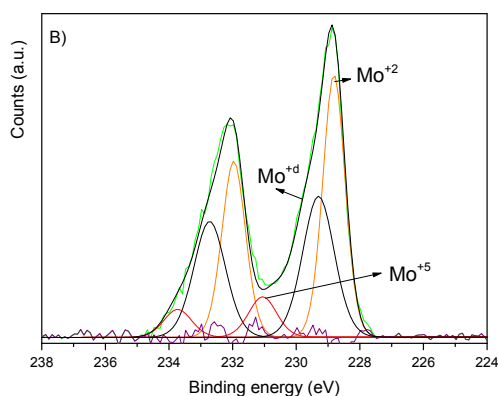
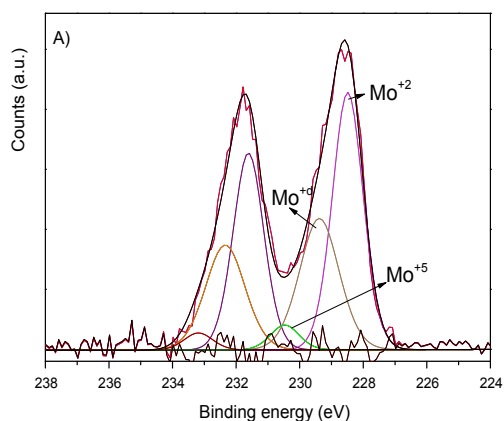


Fig S2. XPS Mo 3d Region of carburised samples at 600 °C under H₂ A) Mo_xC/H; B) CuMo_xC/H; at 700 °C under H₂ C) Mo_xC/H-700, D) CuMo_xC/H-700 ,Spent catalysts: E) -Mo_xC/H-PR and F) CuMo_xC/H-PR. XPS Mo 3d Region of passivated samples G) 0.5CuMo_xC/H; H) 1CuMo_xC/H; I) 3CuMo_xC/H. XPS Cu 2p Region of the freshly carburized catalysts J) CuMo_xC/H; K) CuMo_xC/H-700



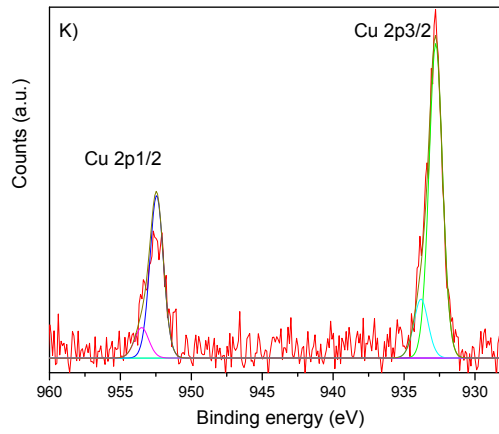
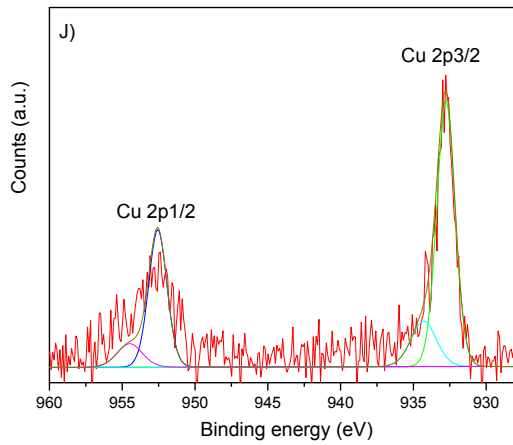
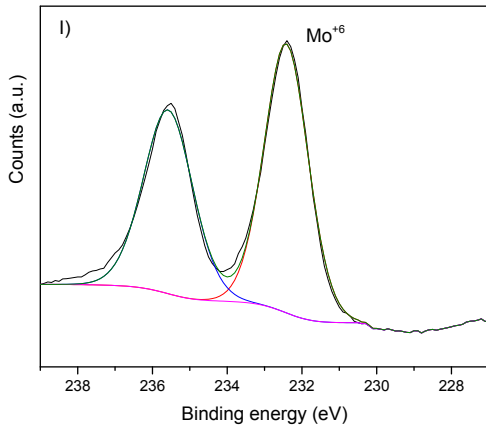
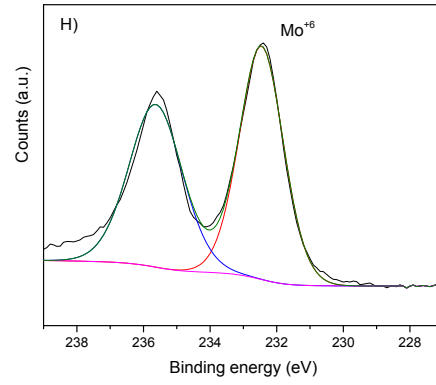
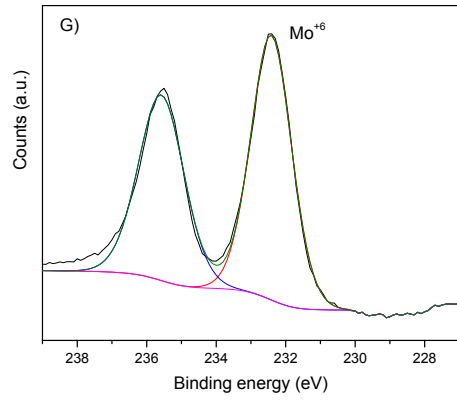
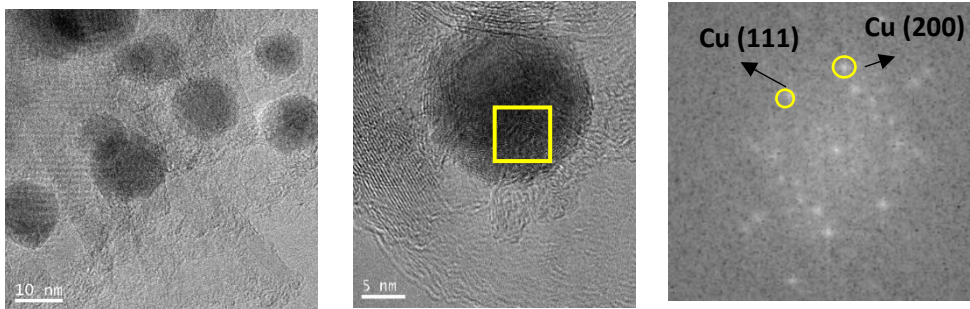
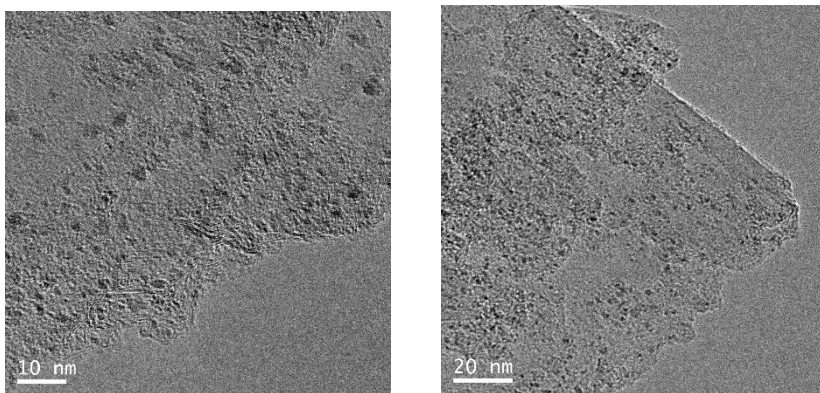


Fig S3.

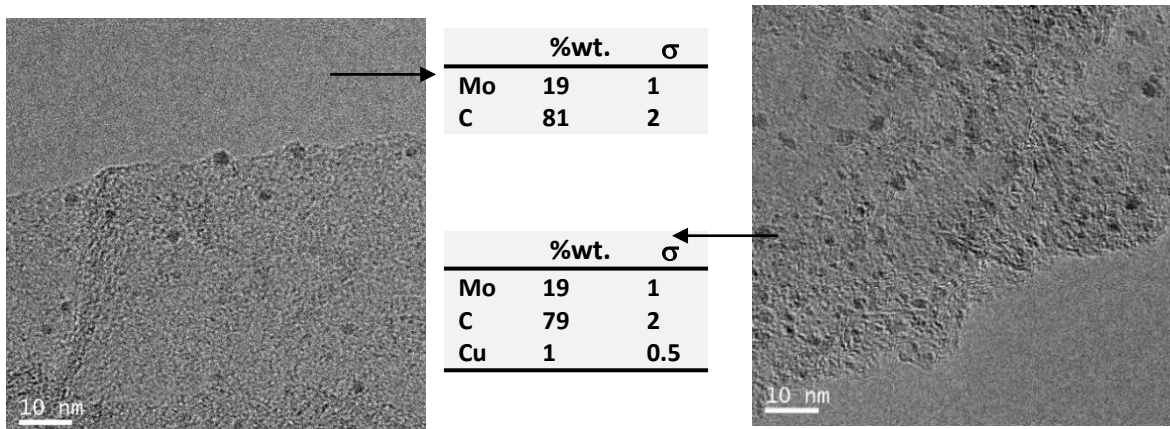
a) TEM Cu/H and the corresponding Fast-Fourier transform (FFT) pattern



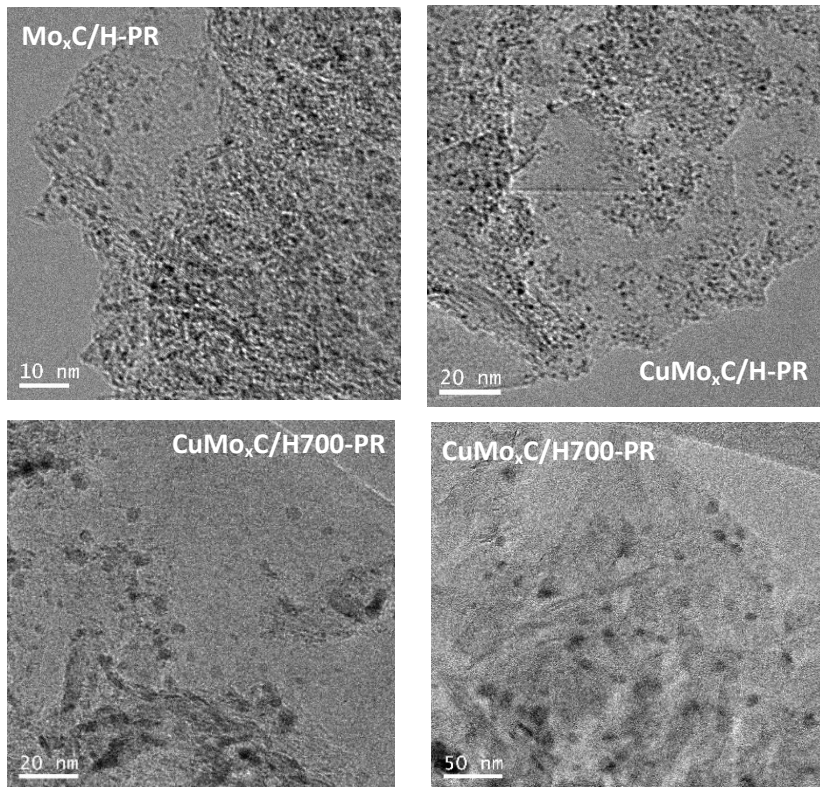
b) TEM images of Mo_xC/H



c) TEM images of CuMo_xC/H showing areas with small Mo phases



d) TEM images of spent catalysts.



e) $\text{CuMo}_x\text{C}/\text{H}$ HAADF-STEM images showing individual large Cu particles where no Mo was identified.

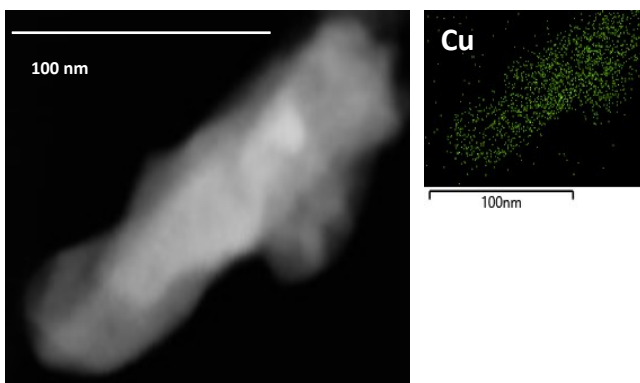
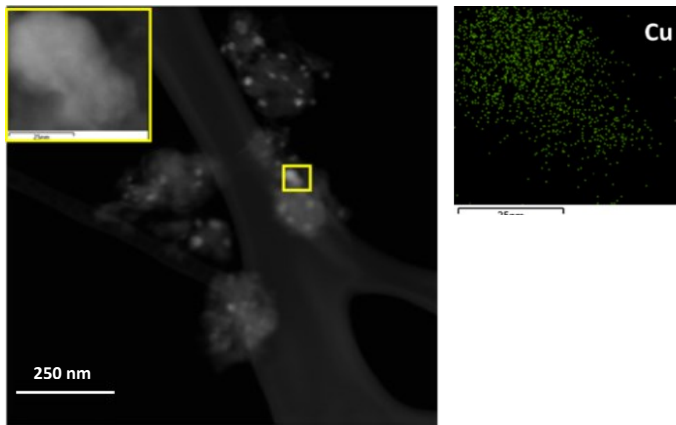
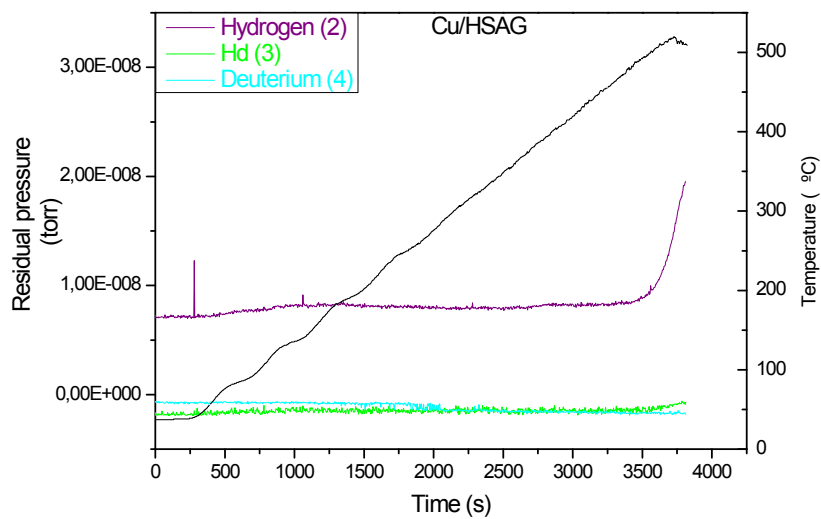
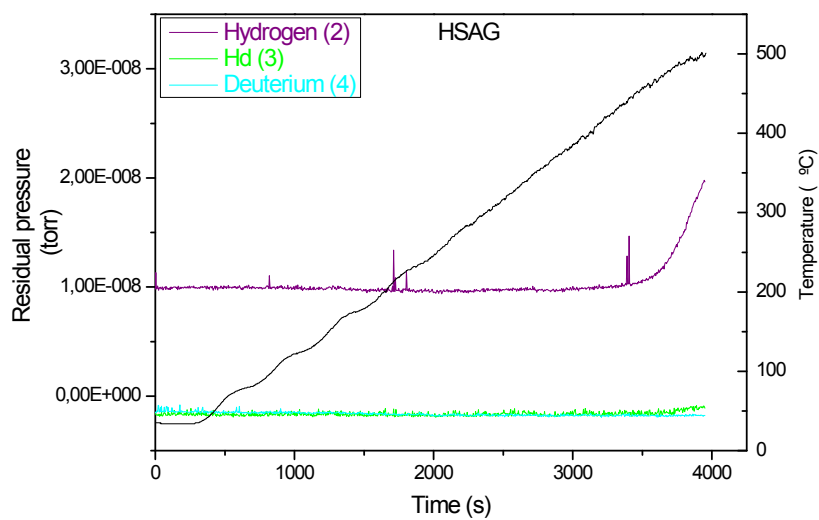


Fig S4 TPD experiments with detection of hydrogen evolved.



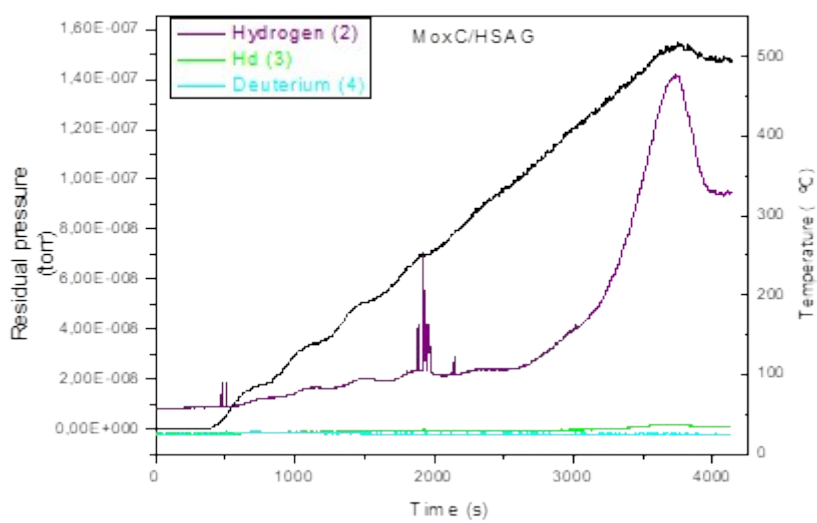
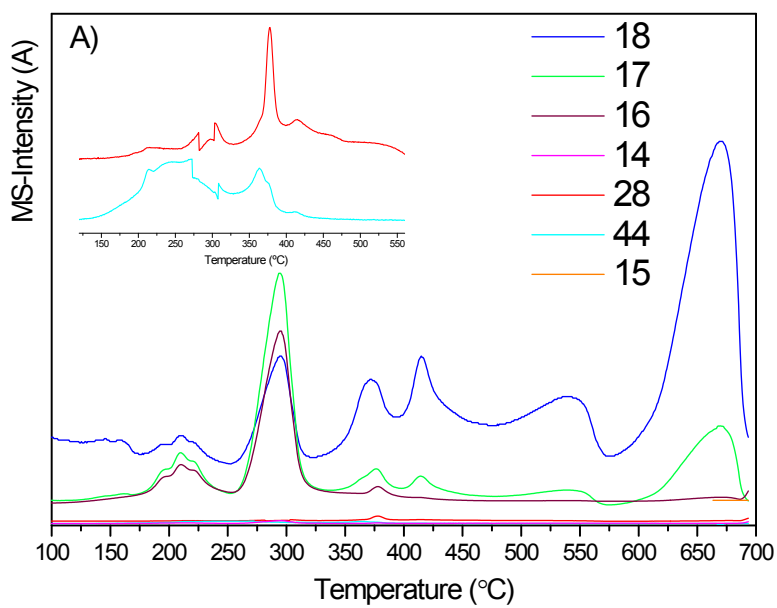


Fig S5 MS profiles during H₂-TPR of impregnated samples. A) MoxC/H, B) CuMoxC/H and C) Cu/H.



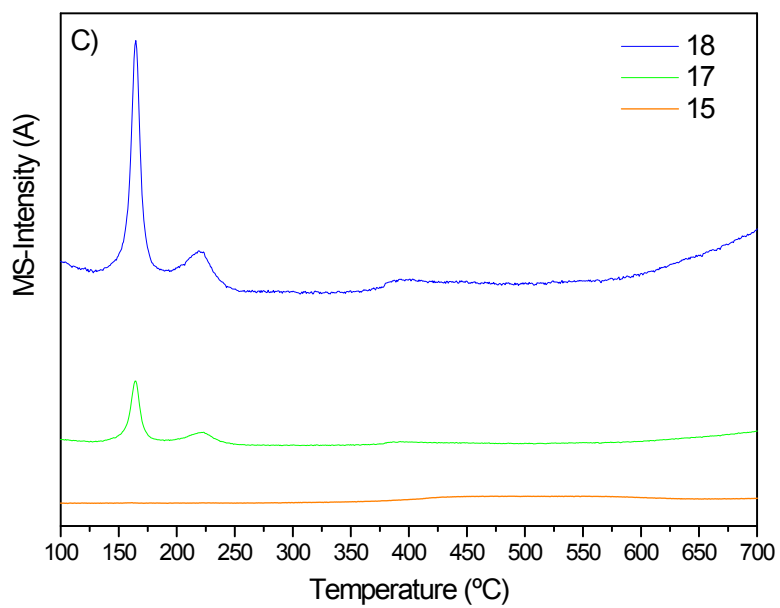
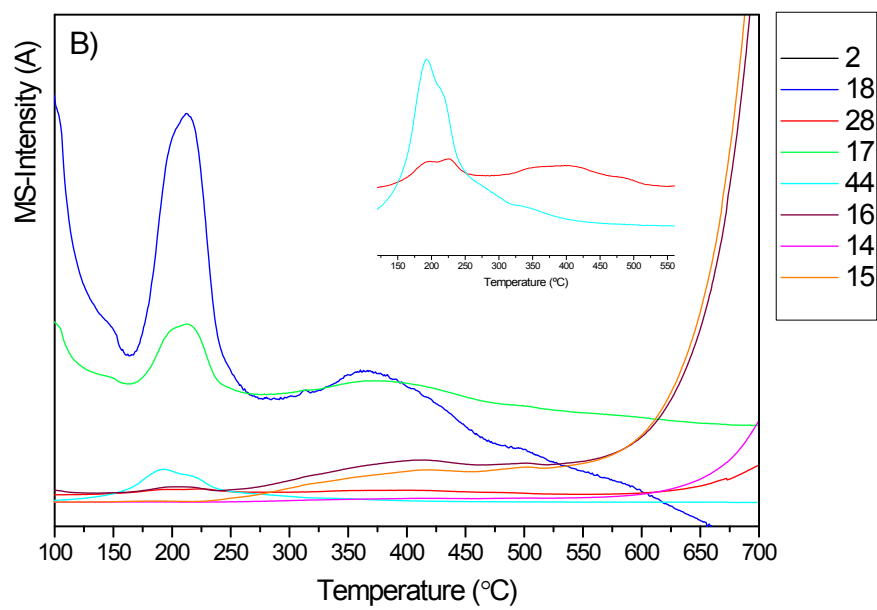


Fig. S6 Rates of CH₄ and CO formation at 20 bar, WHSV=3600 h⁻¹ and CO₂:H₂:He (1:3:6)

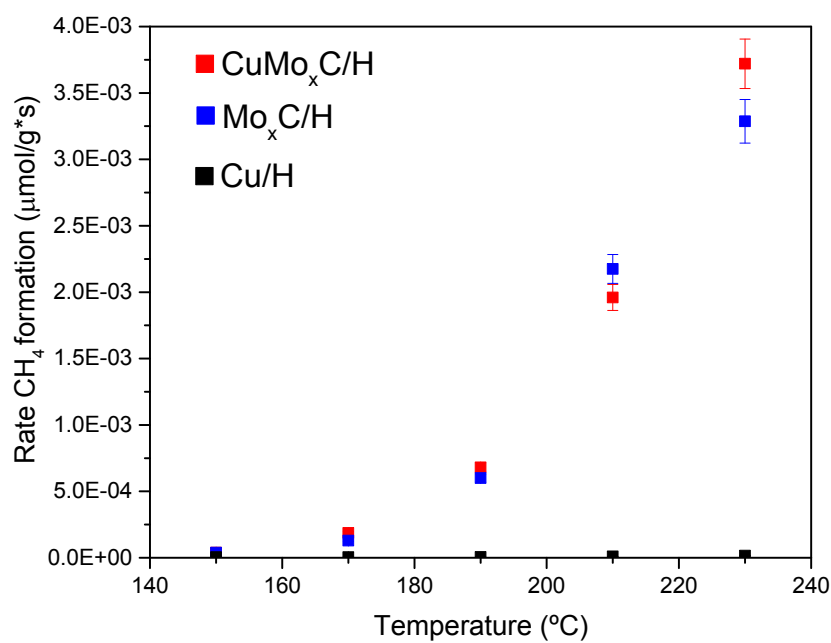
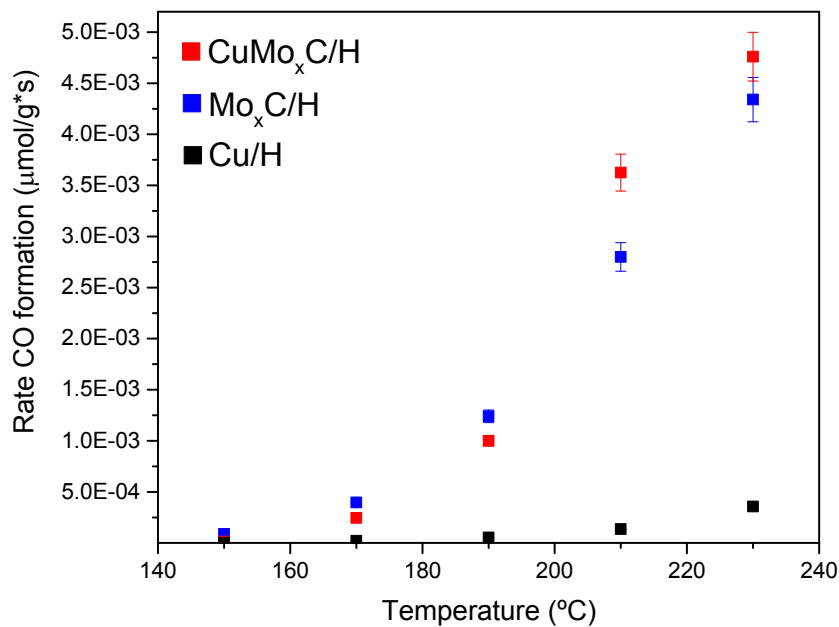


Fig S7. Cu/Mo XPS atomic ratio vs theoretical value.

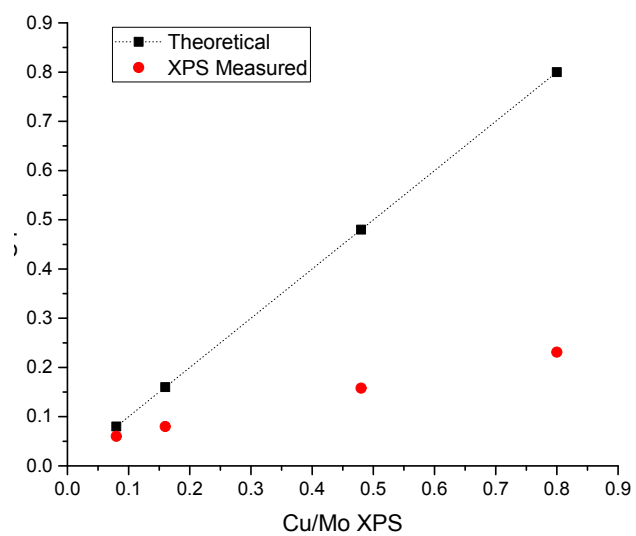


Table S1. Conversion (%) and selectivity (%) at 20 bar, WHSV=3600 h⁻¹ and CO₂:H₂:He (1:3:6)

Catalyst	T(°C)	Conversion	S-CH ₃ OH	S-CH ₄	S- CO
MoxC/H	150	2.5	85.4	4.0	9.2
	170	7.2	74.0	7.9	17.1
	190	11.8	48.1	17.0	31.2
	210	21.1	25.7	28.1	40.1
	230	31.3	16.0	35.8	41.9
CuMoxC/H	150	4.8	96.0	2.4	0.9
	170	9.2	85.0	4.2	8.1
	190	15.0	65.0	12	20
	210	29.0	36.0	22.5	37.5
	230	34.0	25.0	29	42
Cu/H	150	0.2	88.0	7.0	3.0
	170	0.3	67.3	6.2	25.1
	190	0.4	55.2	4.0	39.8
	210	0.7	40.2	3.9	55.2
	230	1.5	27.1	3.1	70.1
Cu/H600	150	0.3	87.1	7.2	2.9
MoxC/H-700	150	2.2	70.3	6.8	22.4
CuMoxC/H-700	150	3.8	89.3	2.9	7.1
MoxC/H-700	230	20.1	12.2	37.3	46.4
CuMoxC/H-700	230	22.1	22.2	24.4	48.1
0.5CuMoxC/H	150	3.1	90.2	2.9	6.8
1 CuMoxC/H	150	3.3	90.6	2.4	6.4
3 CuMoxC/H	150	3.5	90.2	1.9	6.2