

Supplementary Information

***Operando* TEM study of a working copper catalyst during ethylene oxidation**

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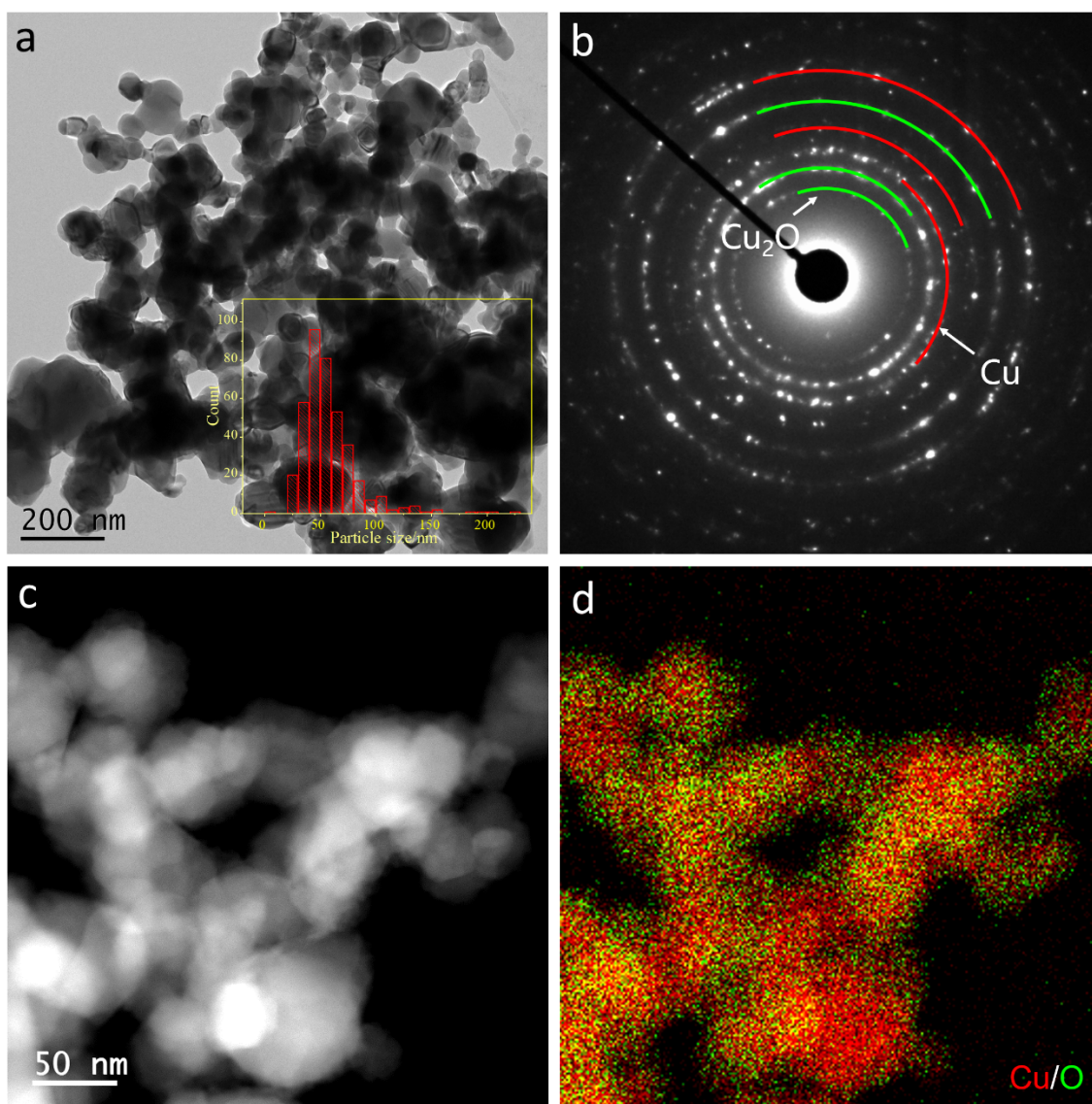


Figure S1. Characterization of the initial Cu NPs. (a) TEM image. Inset shows particle size distribution. (b) SAED pattern, showing the co-presence of both Cu and Cu_2O . (c) ADF-STEM image and (d) corresponding EDX mapping of Cu and O (overlay).

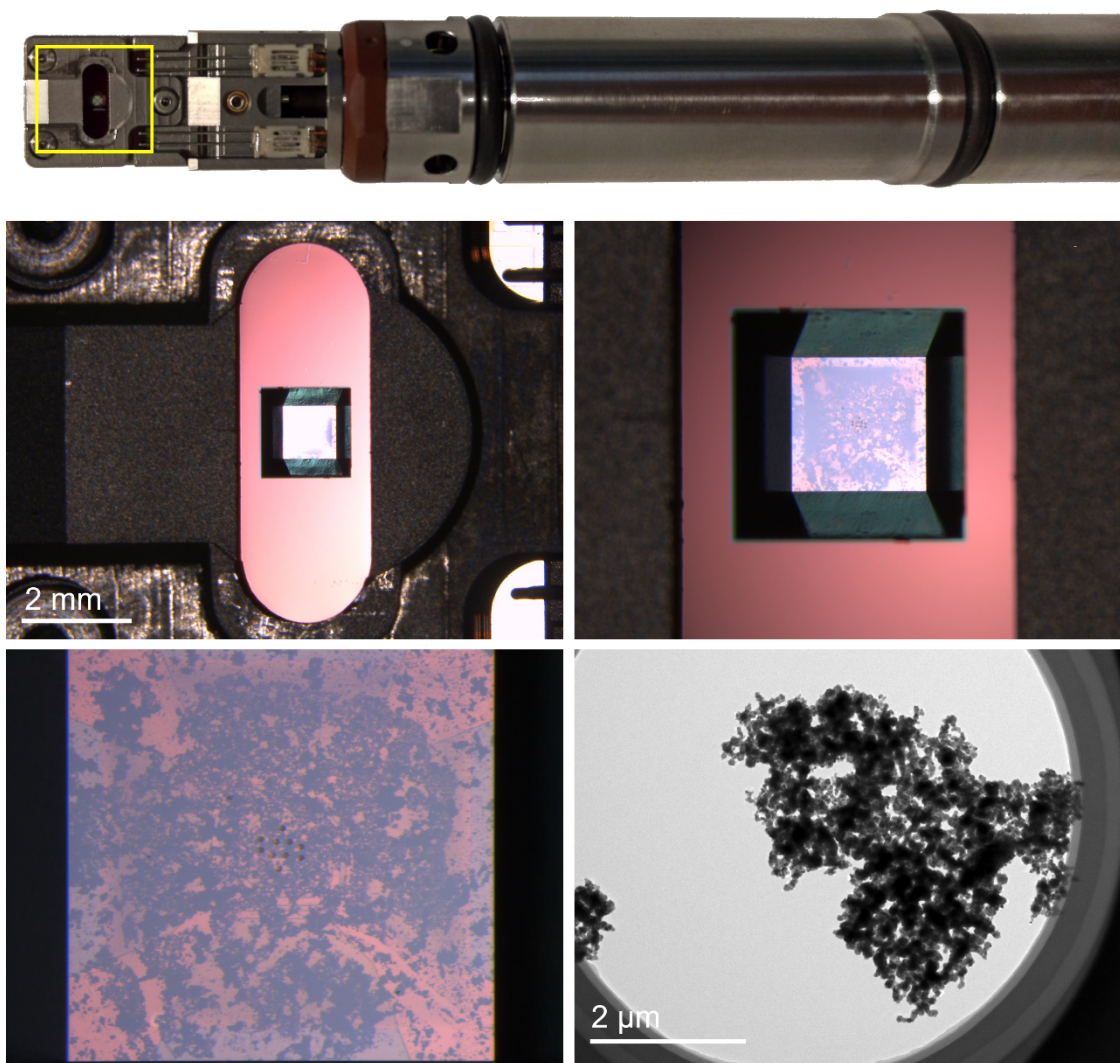


Figure S2. Optical images of a gas-flow TEM holder (DENSsolutions) assembled with a loaded MEMS chip.

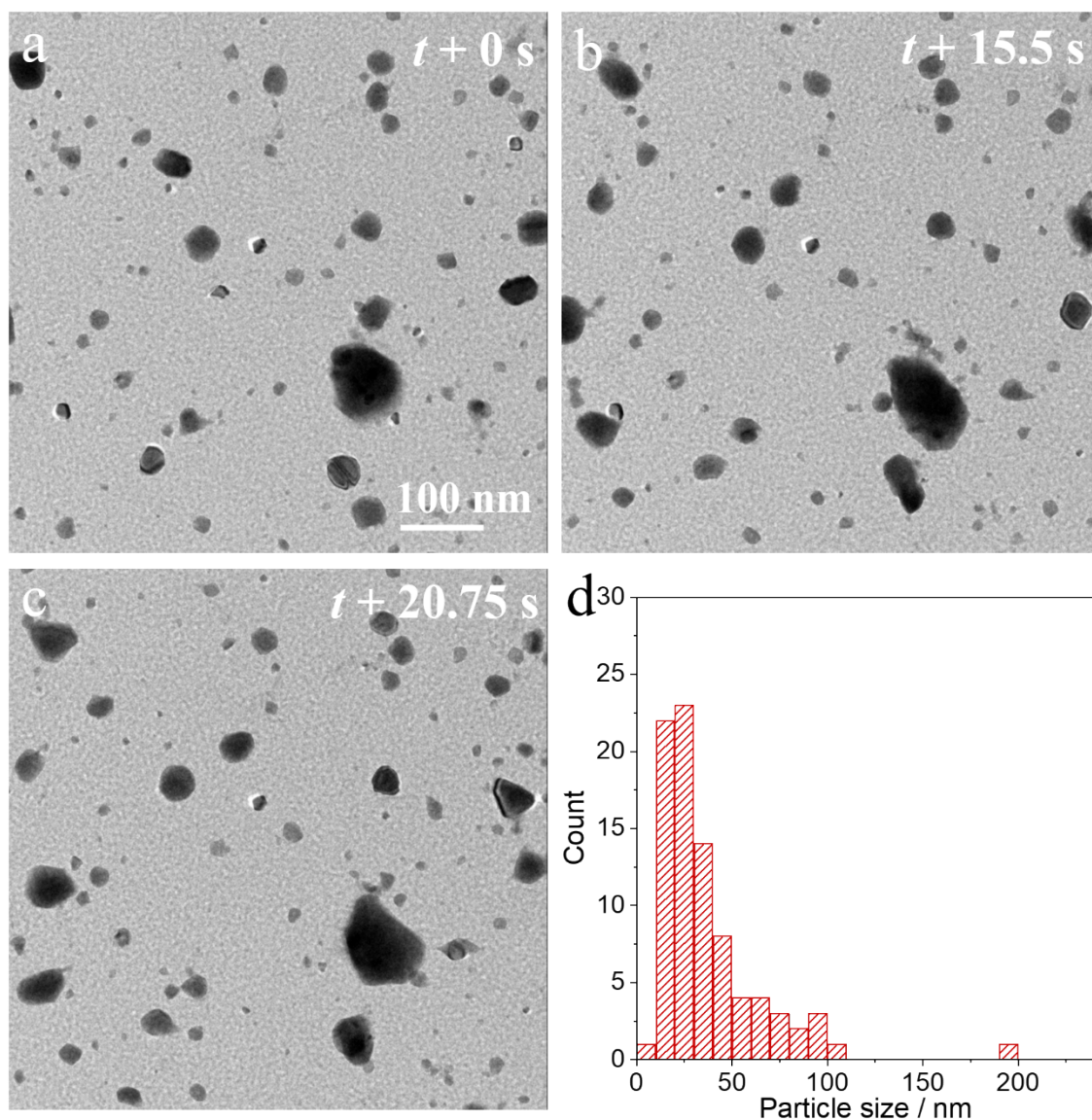


Figure S3. *In situ* TEM observations of Cu NPs at 500 °C in H₂/O₂ mixture (total pressure: 285 mbar, H₂/O₂=10:1). When exposing to the redox atmosphere at 500 °C, the Cu NPs with an initial size of 30-200 nm fragmented.

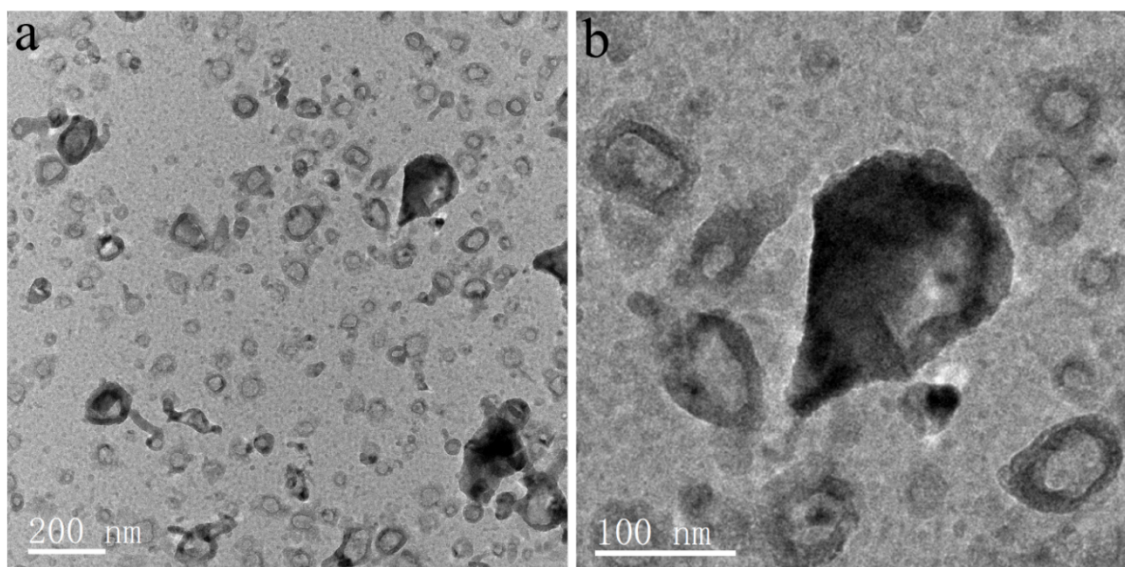


Figure S4. *In situ* TEM images of hollow Cu NPs recorded at 200 °C in C₂H₄/O₂ mixture (total pressure:708 mbar; p_{O_2} =4.27 mbar, $p_{\text{C}_2\text{H}_4}$ =170.6 mbar).

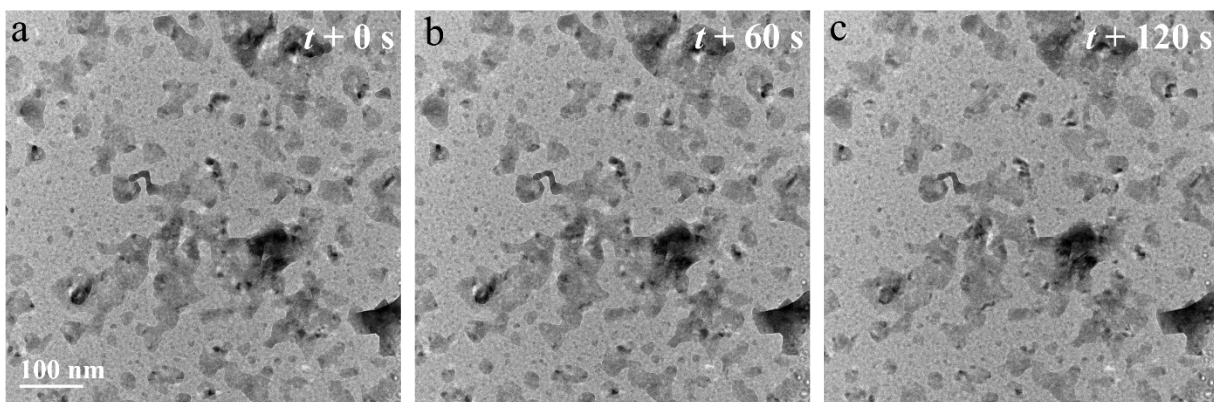


Figure S5. *In situ* TEM images of Cu NPs recorded at 500 °C in C₂H₄/O₂ mixture (total pressure:708 mbar; p_{O_2} =4.27 mbar, $p_{\text{C}_2\text{H}_4}$ =170.6 mbar). No further changes in morphology are observed for 2 mins.

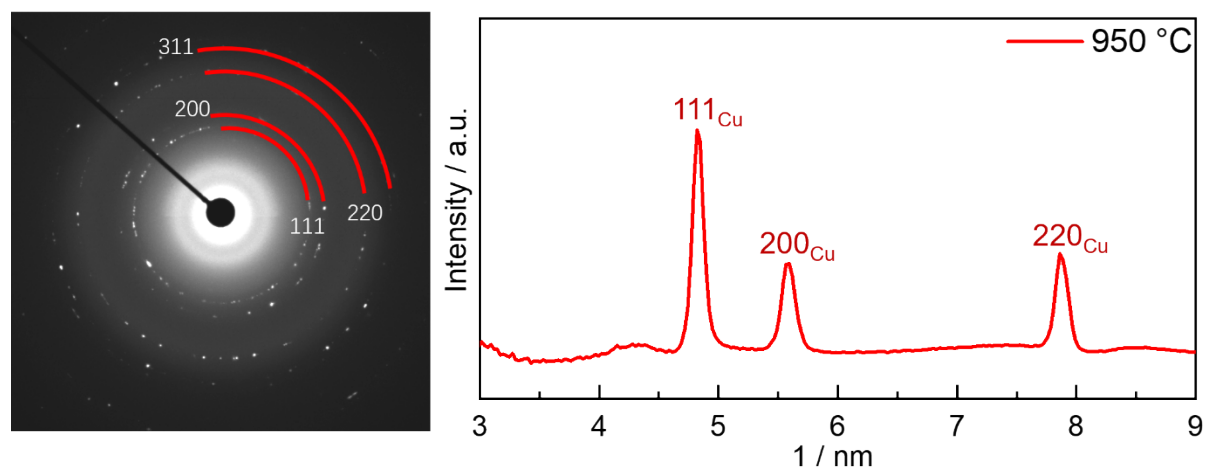


Figure S6. *In situ* electron diffraction of Cu NPs recorded at 950 °C in $\text{C}_2\text{H}_4/\text{O}_2$ mixture (total pressure: 708 mbar; p_{O_2} = 4.27 mbar, $p_{\text{C}_2\text{H}_4}$ = 170.6 mbar). Phase analysis reveals the predominant presence of metallic Cu at this high temperature.

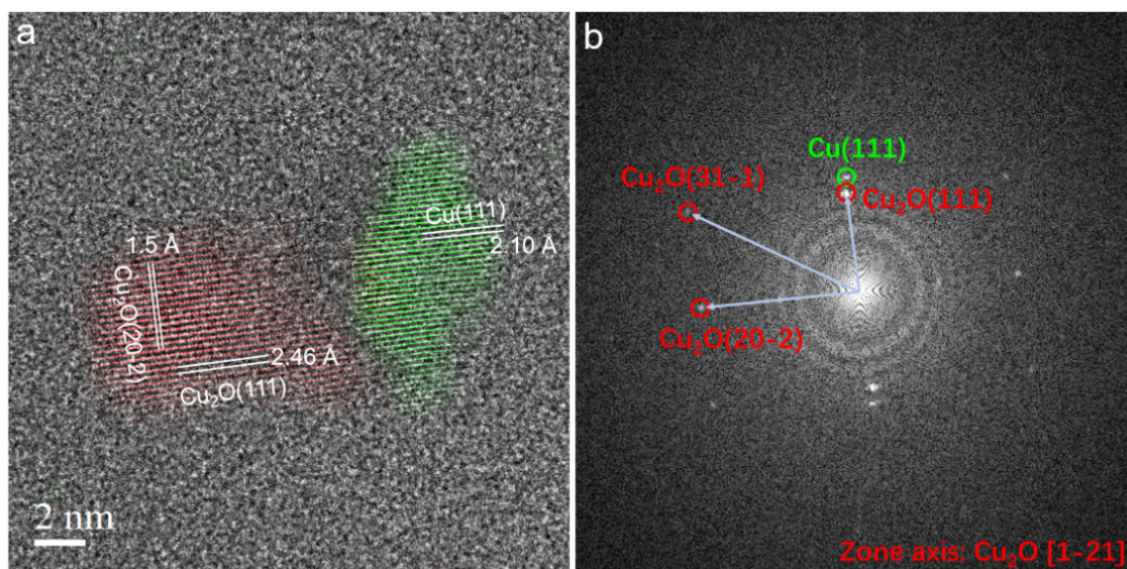


Figure S7. HRTEM image of a dynamic Cu nanoparticle recorded during C₂H₄ oxidation, showing a transient Cu⁰-Cu₂O head tail structure with Cu⁰ (111) parallel to Cu₂O (111). The Cu₂O is viewed along the [1-21] zone axis, and the diffraction spots fit well to Cu₂O (111), Cu₂O (20-2), and Cu₂O (31-1), with measured *d*-spacings of 2.46 Å, 1.5 Å, and 1.28 Å.

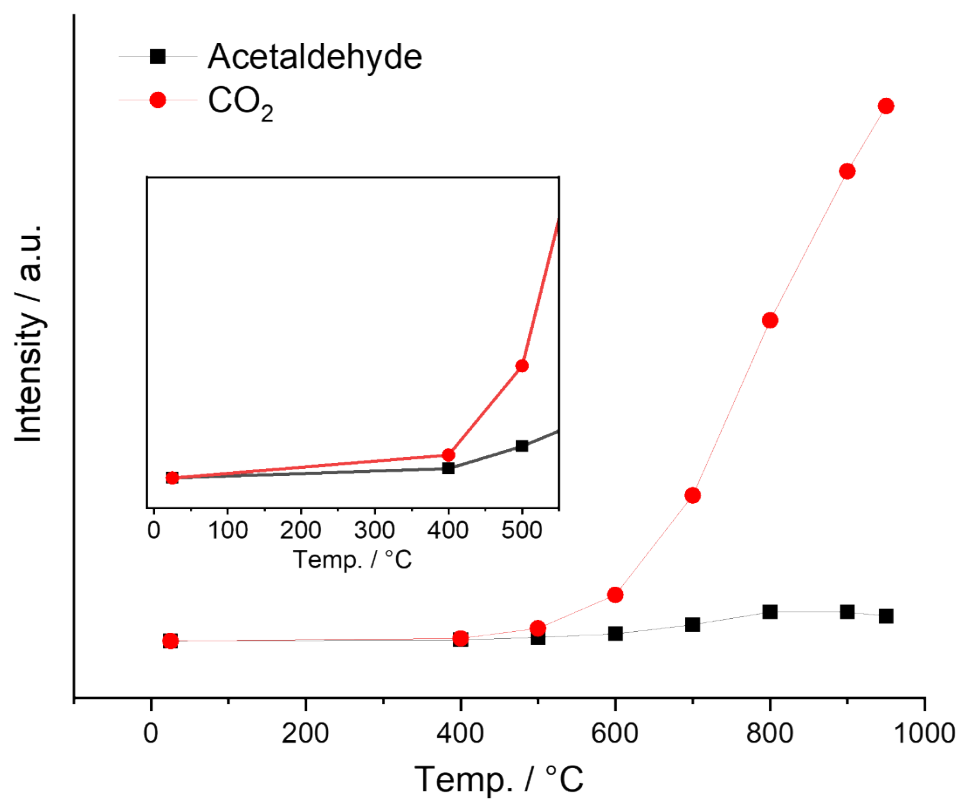


Figure S8. MS signals of AcH and CO₂ with increasing temperature, assuming that the measured signal of 43 m/z is solely attributed to the EO formation.

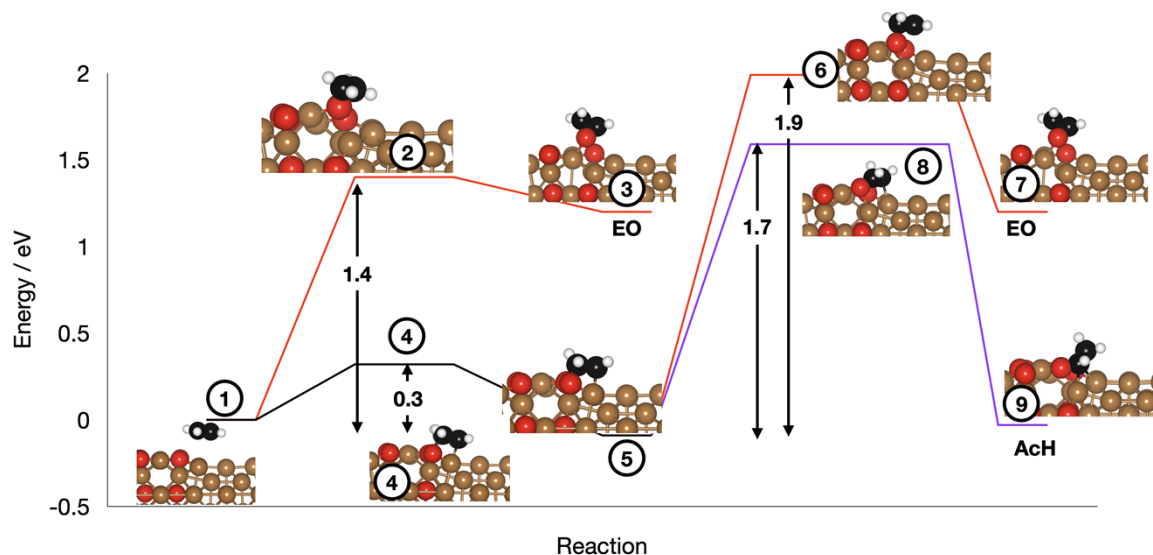


Figure S9. Reaction energetics for ethylene partial oxidation via an OMC on Cu₂O(110)/Cu(110). The adsorbed ethylene (state 1) forms EO directly via state 2 with a 1.4 eV barrier, which competes with OMC formation *via* state 4 with a 0.3 eV barrier. Both direct EO formation and OMC formation have lower barriers than on the pristine oxide, see Figure S10. Once the OMC is formed (state 5) it can decompose into EO via state 6 with an activation energy of $E_a=1.9$ eV, this value is larger than that found on the pure oxide, see Figure S8. The OMC can also decompose into AcH via state 8 with $E_a=1.7$ eV. This value too is higher than the barrier on the pure oxide, Figure S10.

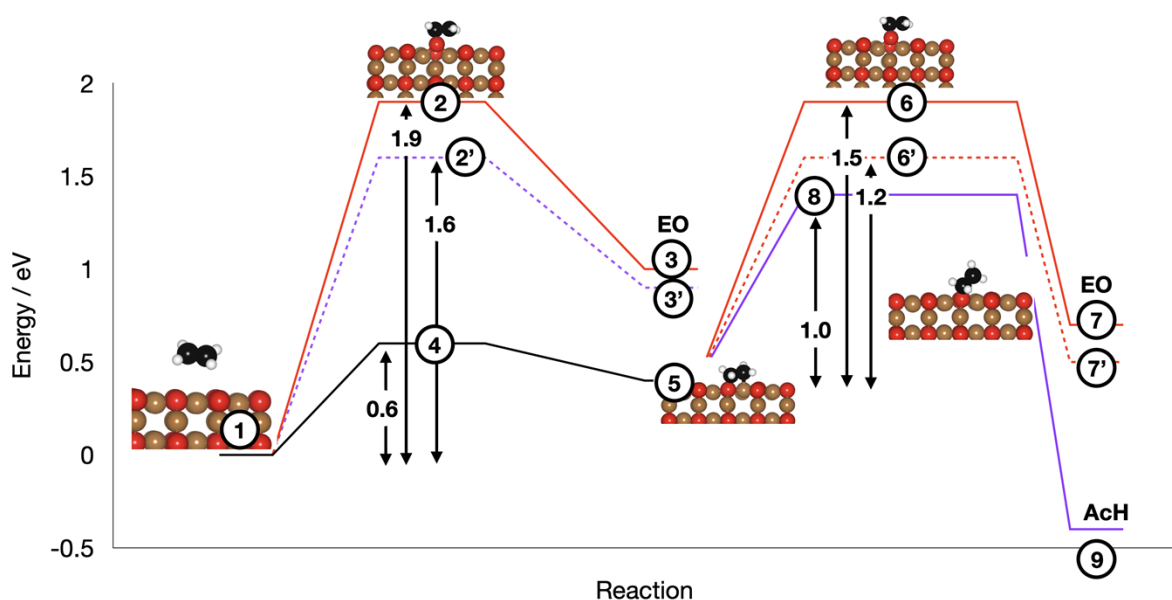


Figure S10. Effect of strain on the partial oxidation energetics of ethylene on Cu_2O . State 1 corresponds to adsorbed ethylene. State 2 is the direct transition state to EO on the pristine surface. State 2' is the direct transition state to EO on the surface with 5% compressive strain. States 3 and 3' are the correspond EO products. State 4 is the transition state to an OMC, the energy of which is nearly independent of strain. State 5 is the OMC. State 6 is the transition state from the OMC to EO; state 6' is the transition state to EO on the strained surface. States 7 and 7' are the product EO states. State 8 is the transition state from the OMC to AcH, which is independent of strain; state 9 is the product AcH.

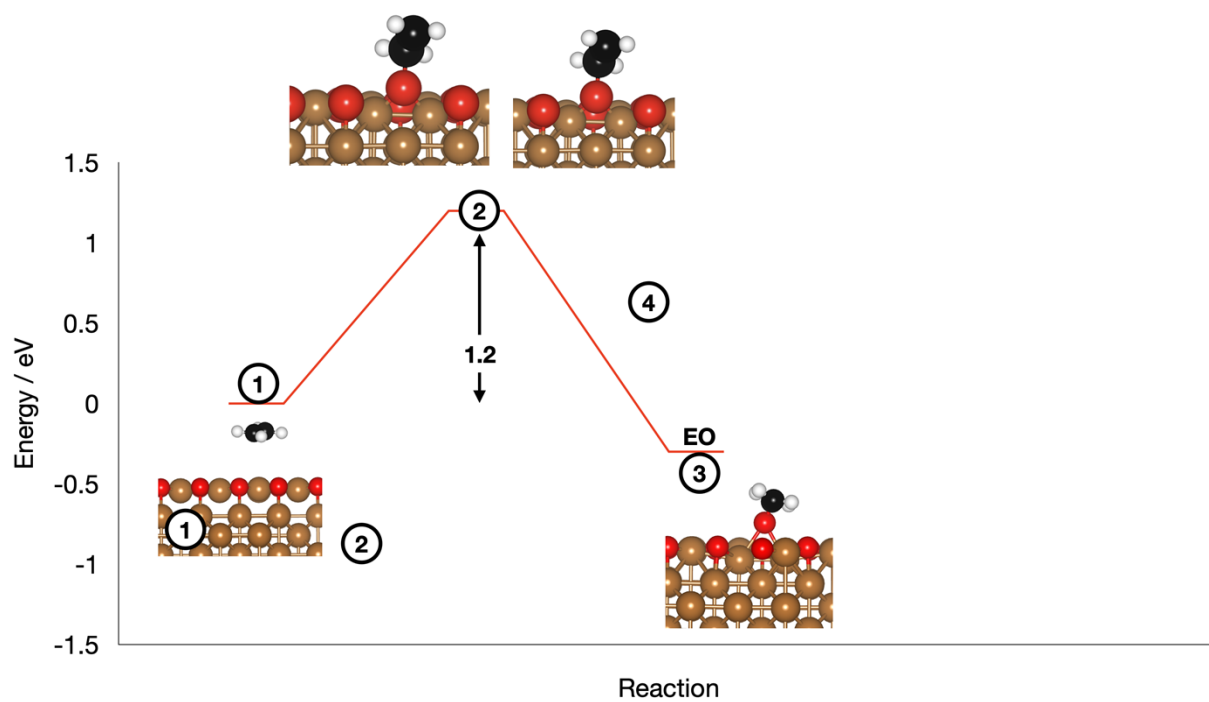


Figure S11. Reaction energetics for direct EO formation on a single layer of Cu_2O on Cu metal. The corresponding OMC pathway is shown in Figure 6 and Figure S13.

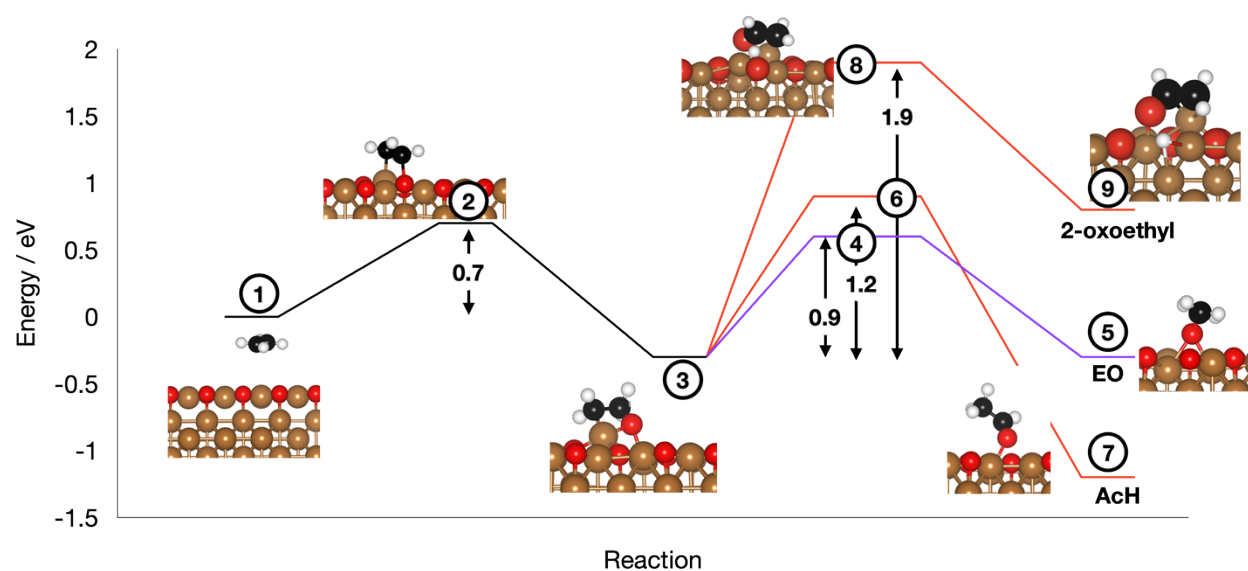


Figure S12. Reaction energetics for 2-oxoethyl formation on a single layer of Cu₂O on Cu metal plotted together with the OMC pathway. The corresponding OMC pathway is shown in Figure 6. Unlike on the metallic surface, partial oxidation to 2-oxoethyl via state 8 is highly activated ($E_a = 1.9$ eV) compared to EO and AcH formation.

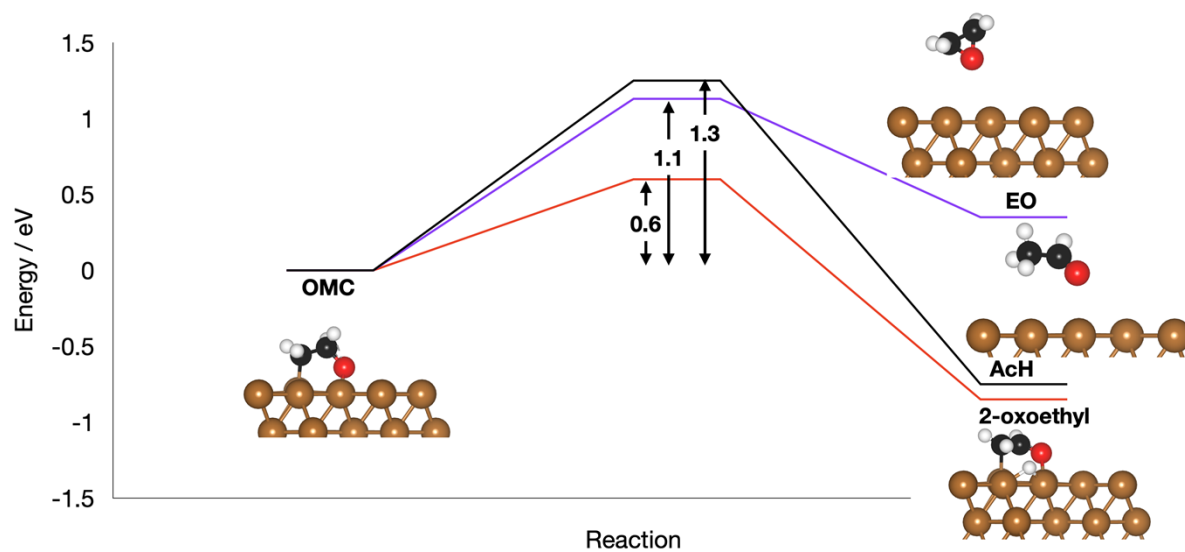


Figure S13. Reaction energetics for OMC decomposition on Cu(111). The OMC decomposes selectively into 2-oxoethyl by transferring an H atom to the Cu(111) surface, $E_a=0.6$ eV. The competing formation of EO ($E_a=1.1$ eV) and AcH ($E_a=1.3$ eV) would be minor pathways.

Table S1. The mass intensities of 44 m/z and 43 m/z measured during online MS and calculated intensity of CO₂, under assumption that the measured intensity of 43 m/z is solely attributed to the EO formation.

	RT	400 °C	500 °C	600 °C	700 °C	800 °C	900 °C	950 °C	
44	0	387	1653	5107	15231	32487	45582	50712	Measured
43/EO	0	93	315	623	1430	2534	2538	2179	Measured
44/EO	0	390.6	1323	2616.6	6006	10642.8	10659.6	9151.8	Calculated
44/CO ₂	0	-3.6	330	2490.4	9225	21844.2	34922.4	41560.2	Calculated

If we assume that the intensity of 43 m/z measured by MS is exclusively attributed to EO formation, the intensity of 44 m/z corresponding to EO should be 4.2 times that of the intensity of 43 m/z, based on the MS data for EO provided by NIST. Consequently, we can deduce the intensity of 44 m/z due to EO from the measured intensity of 44 m/z to calculate the intensity of 44 m/z resulting from CO₂ formation.

Table S2. The mass intensities of 44 m/z and 43 m/z measured during online MS and calculated intensity of CO₂, under assumption that the measured intensity of 43 m/z is solely attributed to the AcH formation.

	RT	400 °C	500 °C	600 °C	700 °C	800 °C	900 °C	950 °C	
44	0	387	1653	5107	15231	32487	45582	50712	Measured
43/AcH	0	93	315	623	1430	2534	2538	2179	Measured
44/AcH	0	158.1	535.5	1059.1	2431	4307.8	4314.6	3704.3	Calculated
44/CO ₂	0	228.9	1117.5	4047.9	12800	28179.2	41267.4	47007.7	Calculated

If we assume that the intensity of 43 m/z measured by MS is exclusively attributed to AcH formation, the intensity of 44 m/z corresponding to AcH should be 1.7 times that of the intensity of 43 m/z, based on the MS data for AcH provided by NIST. Consequently, we can deduce the intensity of 44 m/z due to AcH from the measured intensity of 44 m/z to calculate the intensity of 44 m/z resulting from CO₂ formation.