

Operando TEM study of a working copper catalyst during ethylene oxidation

Corresponding Author: Professor Xing Huang

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Manuscript ID NCOMMS-24-46381

Title: Operando TEM study of a working copper catalyst during ethylene oxidation

In this contribution, Yu et al. present insights into the Cu-catalyzed ethylene oxidation via a combination of operando and in-situ TEM studies, as well as first-principles computations. They find three distinct phases: (1) low temperature – with high selectivity to partially oxidized products, (2) intermediate temperature – that favors full oxidation to CO₂ and H₂O, and (3) high temperature – which also favors full oxidation. At these three temperature phases, the authors show that the catalyst exists in different Cu and Cu₂O phases. In particular, the intermediate temperature phase exhibits oscillatory behavior between two phases – Cu₂O and metallic Cu.

This work combines several techniques to obtain a rather complete picture of Cu catalysts under ethylene oxidation conditions under various temperatures. The characterization of structure of the Cu catalysts is also carefully done. However, I have several major concerns as, despite the work being an operando study, the link between the structure and reactivity of the catalysts is not well-developed and shaky at parts:

1. While it is interesting that there are oscillatory phase transitions at intermediate temperatures, there is a lack of connection between the dynamic nature of the structure of the catalyst at these temperatures with its reactivity. As such oscillatory phase transitions have already been previously reported (Nat Commun. 11, 3554 (2020)), the next logical step would be to also show whether such oscillatory behavior has any impact on catalytic reactivity, which seems to be missing here.

2. To our understanding, and as the authors acknowledged, MS is not able to distinguish between the two possible partial oxidation products formed: EO and AcH, as they both produce $m/z=43$ amu signals. This is concerning as there could be a significant amount of AcH formed, as also discussed by the authors in the theoretical analyses section for example. Indeed, EO selectivity is a key parameter to determine the performance of the catalyst. In our view, the work would be much more relevant and informative if it were to be based on unambiguous, quantitative data that differentiates between the two products, which could be obtained using online GC-MS for example.

3. Related to the above, several places in the manuscript are also quite misleading, as they imply that the EO is the only product. For example, in the last sentence of the introduction, the authors state that: “Additionally, in a low temperature regime where Cu₂O alone is present, the catalyst favors selective products, i.e., C₂H₄O.” Moreover, Figures 3i and 3j imply that EO is the only product as only “C₂H₄O” is shown in the legend, while in fact the proportions of EO/AcH are unknown.

4. There are also some questions about the representativeness of the models used for the first-principles calculations:

High temperatures—The authors show that at high temperatures (>900 °C), the Cu catalyst exists as a Cu₂O monolayer on metallic Cu, and full oxidation of ethylene predominates. However, the DFT calculations in Figure 6 using a Cu₂O overlayer over Cu model do not seem to support this, and the authors instead show with calculations that a metallic Cu surface is more consistent with full oxidation (Figure S9). The DFT results therefore seem to contradict with the observed experimental structure. Is it possible that metallic Cu is transiently exposed on the surface of the catalyst during operation at high temperatures, and would the operando TEM experiments be able to pick this up?

Intermediate temperatures—From Figure 5, the intermediate temperature states are modelled as Cu₂O with subsurface oxygen partially removed. This does not seem to be consistent with Figures 3d and 3e, which show that the catalyst exists in a Janus-type structure with metallic Cu head connected to a Cu₂O tail. Further, the Cu₂O phase in the intermediate

temperature state (Figures 3d and 3e) has the same lattice spacing (2.43 Å) as the low temperature state (Figures 3b and 3c), which also may indicate that the Cu₂O phase should have similar levels of oxidation at both temperatures. While the authors modelled strained Cu/Cu₂O (Figure S8) to simulate the effect of the metal-oxide interface, this does not rigorously represent the catalyst: it remains unclear if the Cu phase, Cu₂O phase, or perhaps the phase boundaries between Cu/Cu₂O are the active sites at these intermediate temperatures.

5. The first-principles calculations in Figures 5 and 6 also do not explore the full mechanism for ethylene oxidation. Notably, in Figure S9, the barrier for OMC→2-oxoethyl, a key step for full oxidation, is shown. However, this is not included in Figures 5 or 6, which prevents us from obtaining a complete picture of the energetics of full oxidation versus partial ethylene oxidation.

6. All intermediate and TS structures in Figures 5 and 6 are missing. These details would be valuable to readers.

7. For the partially reduced Cu₂O surface with 1/8 ML adsorbed oxygen, it would be helpful if the authors describe how the optimal configuration of the model was obtained.

8. I wonder if the authors compared DFT and DFT+U for the Cu₂O calculations. If not, please explain why the U correction was not considered for this oxide system.

Minor points:

1. In Figure 6, the caption states that "AcH formed via state 6 with $E_a=0.7$ eV". The correct value from the figure should be 1.2 eV.

2. Page 13, "direct EO formation (not shown) is activated by 1.2 eV". I suggest the authors clarify the meaning of "not shown" and consider whether it is possible to present this data in the SI.

Reviewer #2

(Remarks to the Author)

The authors report in-situ TEM imaging of the temperature-dependent dynamics of Cu particles during ethylene oxidation, supported by mass spectroscopy, DRFIT and DFT modeling. Their findings show a quasi-static and partially reduced state of Cu at lower temperatures, oscillatory phase transitions between Cu and Cu₂O at intermediate temperatures, and a high-temperature state of metallic Cu with a monolayer of Cu₂O. These temperature-dependent states of the catalyst are associated with variations in catalytic performance and reaction product distribution. The in-situ observations provide valuable insights into the structure-property relationships of catalysts and could have broad implications for the catalysis community. However, several critical questions need to be addressed to enhance the clarity and impact of the study:

1. Mechanistic Insights: What are the mechanistic pathways and intermediates involved in the observed phase transitions of Cu particles at different temperatures? The DRIFT results appear not to show an obvious dependence of temperature on reaction intermediates. How do these transitions affect the catalytic reaction pathways and catalytic mechanisms?

2. Temperature Range Justification: Why were such large temperature ranges (up to 1000°C) chosen for the study? Are these ranges optimal for observing the phenomena discussed? How do these temperatures relate to those typically used in industrial catalytic ethylene oxidation?

3. Quantitative Analysis: Can the authors provide quantitative data on the extent of Cu reduction or oxidation at different temperatures? How does this correlate with changes in catalytic performance?

4. Monolayer Cu₂O: There is no direct evidence provided to confirm the presence of a monolayer of Cu₂O on bulk Cu. Can the authors provide evidence or detailed explanation supporting this observation?

5. DFT Modeling: The DFT modeling assumes a defect-free surface and considers strain effects in the Cu₂O overlayer. However, under realistic reaction conditions, the oxide surface is rarely perfect, and elevated temperatures may introduce significant non-stoichiometry and numerous surface defects. How might these factors impact surface adsorption and desorption properties, potentially overshadowing the strain effects?

6. Particle Mobility: In some in-situ TEM videos, smaller particles (with varying core-shell features or uniform contrast) appear less mobile compared to larger particles. This observation seems counterintuitive, as smaller particles are generally expected to migrate more easily. Can the authors provide an explanation for this behavior?

7. Support Morphology: The in-situ TEM videos suggest that the support's surface morphology, such as roughness, varies with temperature. How does the temperature affect the support's surface morphology and the mobility of Cu particles?

Reviewer #3

(Remarks to the Author)

This study employs operando TEM to investigate the structural and phase evolution of copper catalysts during ethylene oxidation across a wide temperature range (200 °C to 950 °C). The authors successfully identify three distinct structural states of the catalyst—Cu₂O, Cu/Cu₂O oscillations, and metallic Cu—and correlate these states with catalytic performance. The integration of DFT simulations provides valuable insights into the effects of interfacial strain and phase coexistence on selectivity.

However, there are significant concerns that need to be addressed:

The authors correctly highlight the advantages of in situ microscopy for atomic-scale imaging under operando conditions. However, it is critical to emphasize that phase determination using high-resolution imaging requires careful interpretation. Relying solely on one-dimensional lattice spacing is not a robust approach for phase identification, given the variety of possible crystal orientations and lattice spacings. Furthermore, HRTEM measurements and calibrations may not achieve the precision necessary for reliable phase determination. For example, the Cu (110) plane has a lattice spacing of approximately 2.54 Å. It is problematic to assert that the 2.46 Å spacing measured and attributed to Cu₂O (111) is not actually Cu (110), as seen in Fig. 3 c-e. This ambiguity undermines the reliability of the phase identification presented.

To improve the accuracy of phase identification, it is strongly recommended that the authors use HRTEM images aligned on the zone axis. This alignment would allow for the simultaneous measurement of two lattice spacings, providing a more definitive determination of the phase and zone axis. Without such alignment, the conclusions drawn from the HRTEM images remain tentative.

The existence of intermediate phases, such as Cu_{2-x}O , cannot be ruled out based on the current data. It would greatly enhance the study if the authors could include EDX or EELS analysis and quantification to confirm the co-presence and evolution of the identified phases. Such analysis could also potentially reveal the presence of intermediate phases, offering a more comprehensive understanding of the catalyst's behavior under the experimental conditions.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors did a good job with the revisions and made the necessary changes. I believe the paper can be accepted in the current form.

Reviewer #2

(Remarks to the Author)

The authors have addressed all my concerns, and I recommend the manuscript for acceptance.

Reviewer #3

(Remarks to the Author)

This manuscript presents an operando TEM study combined with online mass spectrometry (MS) and density functional theory (DFT) calculations to investigate the dynamic behavior of copper catalysts during ethylene oxidation. The study identifies three distinct structural and reactivity regimes across different temperature ranges and explores the role of oscillatory phase transitions and surface modifications on catalytic performance.

The primary concern is the identification of Cu vs CuOx phases. For example, in Figure S7, the HRTEM image of a dynamic Cu nanoparticle recorded during C_2H_4 oxidation shows a transient CuO–Cu₂O head-tail structure, with CuO (111) parallel to Cu₂O (111). Specifically, it is stated that lattice spacings of 1.50 Å and 2.46 Å correspond to (20-2) and (111) of Cu₂O, while the 2.10 Å lattice spacing is attributed to Cu metal. However, this approach is not a sufficiently robust method to identify phases.

If the authors cannot provide EELS data, which should be highly sensitive for detecting O signals, they should instead provide XPS data to substantiate their phase identification. This is particularly relevant as the authors mentioned in their response that they have used in situ XPS for their previous PdOx work.

Other than the above concern, the authors have adequately addressed the reviewers' comments.

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Dear Reviewers,

We are very grateful for your valuable feedback and comments, which have been instrumental in enhancing the quality of our manuscript. Please find below our point-by-point response to each of the referee comments. The referees' original comments are presented in regular text, while our responses are highlighted in blue. Additionally, changes made to the main text of the manuscript are highlighted in yellow. We hope that our revised Manuscript can be accepted for publication in *Nature Communications*.

Sincerely,

Dr. Xing Huang, on behalf of all co-authors

Reviewer #1 (Remarks to the Author):

Manuscript ID NCOMMS-24-46381

Title: Operando TEM study of a working copper catalyst during ethylene oxidation

In this contribution, Yu et al. present insights into the Cu-catalyzed ethylene oxidation via a combination of operando and in-situ TEM studies, as well as first-principles computations. They find three distinct phases: (1) low temperature – with high selectivity to partially oxidized products, (2) intermediate temperature – that favors full oxidation to CO₂ and H₂O, and (3) high temperature – which also favors full oxidation. At these three temperature phases, the authors show that the catalyst exists in different Cu and Cu₂O phases. In particular, the intermediate temperature phase exhibits oscillatory behavior between two phases – Cu₂O and metallic Cu.

This work combines several techniques to obtain a rather complete picture of Cu catalysts under ethylene oxidation conditions under various temperatures. The characterization of structure of the Cu catalysts is also carefully done.

Reply: We thank Referee 1 for the generally positive evaluation of our work.

However, I have several major concerns as, despite the work being an operando study, the link between the structure and reactivity of the catalysts is not well-developed and shaky at parts:

Q1. While it is interesting that there are oscillatory phase transitions at intermediate temperatures, there is a lack of connection between the dynamic nature of the structure of the catalyst at these temperatures with its reactivity. As such oscillatory phase transitions have already been previously reported (Nat Commun. 11, 3554 (2020)), the next logical step would be to also show whether such oscillatory behavior has any impact on catalytic reactivity, which seems to be missing here.

Reply to Q1: We appreciate your valuable feedback. Following the suggestion of Referee 1, we have performed new DFT calculations and included a more detailed discussion on the impact of oscillatory behavior on catalytic reactivity. Compared to their static state (Cu₂O) at lower temperatures, the oscillatory phase transitions at the temperature range between 700 and 800 °C lead to the emergence of the metallic Cu, the formation of non-stoichiometric/partially reduced Cu₂O, the formation of the Cu⁰/Cu₂O interface, and the introduction of strain within the Cu₂O portion due to lattice mismatch between Cu⁰ and Cu₂O.

DFT calculations indicate that the emergence of Cu⁰ during these phase transitions facilitates full oxidation *via* the OMC dehydrogenation pathway. This finding helps explain the marked increase in CO₂ formation at elevated temperatures (as measured by online MS), which correlates with the increased presence of Cu⁰.

We have also investigated the selectivity of partially reduced oxide, Cu⁰/Cu₂O interface and strained Cu₂O, as well as the reaction pathways on these structures, by DFT calculations. We find that both, the strained Cu₂O and the partially reduced Cu₂O, favor the direct formation pathway for EO over AcH. The metal/oxide interface is also active in the production of partial oxidation products *via* the OMC pathway (AcH>EO), although with slightly higher barriers than these of the pristine oxide.

We have incorporated these discussions and new content into the revised manuscript. We believe that these revisions strengthen the manuscript and provide a clearer understanding of the role of Cu's oscillatory behavior in the catalytic process. We are grateful for this comment, which has enabled us to enhance the clarity and depth of our discussion.

Q2. To our understanding, and as the authors acknowledged, MS is not able to distinguish between the two possible partial oxidation products formed: EO and AcH, as they both produce $m/z=43$ amu signals. This is concerning as there could be a significant amount of AcH formed, as also discussed by the authors in the theoretical analyses section for example. Indeed, EO selectivity is a key parameter to determine the performance of the catalyst. In our view, the work would be much more relevant and informative if it were to be based on unambiguous, quantitative data that differentiates between the two products, which could be obtained using online GC-MS for example.

Reply to Q2: Thank you for your concerns regarding the differentiation between EO and AcH in this study. We understand the importance of distinguishing between these two products for a comprehensive analysis of catalyst performance. However, as Referee 1 has correctly pointed out, MS not capable of differentiating between EO and AcH using the $m/z=43$ amu signal. While GC-MS could potentially resolve this issue by providing the necessary separation and identification of these compounds, it is not compatible with *in situ* TEM studies because the amount of products generated through the *in situ* TEM cell is limited, which is a common challenge in this field.

The limitation arises from the fact that the catalysts employed in *in situ* TEM studies are often present in small quantities, resulting in a limited amount of products that fall below the detection threshold for GC analysis. MS is more sensitive than GC, which is why it is frequently utilized in *in situ* TEM studies related to catalysis.

We appreciate your feedback on this matter and regret to inform you that, given the current technology and methods available to us, there is little we can do to differentiate between EO and AcH using *operando* TEM (*in situ* TEM with online MS).

Q3. Related to the above, several places in the manuscript are also quite misleading, as they imply that the EO is the only product. For example, in the last sentence of the introduction, the authors state that: “Additionally, in a low temperature regime where Cu_2O alone is present, the catalyst favors selective products, i.e., $\text{C}_2\text{H}_4\text{O}$.” Moreover, Figures 3i and 3j imply that EO is the only product as only “ $\text{C}_2\text{H}_4\text{O}$ ” is shown in the legend, while in fact the proportions of EO/AcH are unknown.

Reply to Q3: We apologize for any confusion that may have arisen. In the manuscript, we used the molecular formula $\text{C}_2\text{H}_4\text{O}$ to represent both ethylene oxide (EO) and acetaldehyde (AcH), as they share the same molecular formula. To prevent any misunderstandings, we have made the necessary corrections to both the text and figures, as exemplified in Figures 4i and 4j.

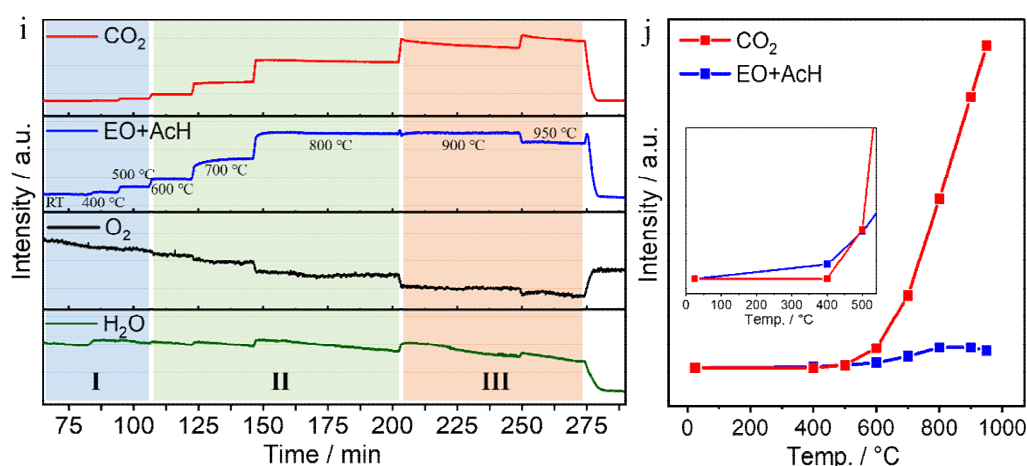


Figure 4. (i,j) Online MS study of Cu catalysts at different temperatures (from 300 to 950 °C) under conditions of the O₂-diluted C₂H₄ oxidation reaction (total pressure: 708 mbar; p_{O_2} = 4.27 mbar, $p_{\text{C}_2\text{H}_4}$ = 170.6 mbar).

There are also some questions about the representativeness of the models used for the first-principles calculations:

Q4. High temperatures—The authors show that at high temperatures (>900 °C), the Cu catalyst exists as a Cu₂O monolayer on metallic Cu, and full oxidation of ethylene predominates. However, the DFT calculations in Figure 6 using a Cu₂O overlayer over Cu model do not seem to support this, and the authors instead show with calculations that a metallic Cu surface is more consistent with full oxidation (Figure S9). The DFT results therefore seem to contradict with the observed experimental structure. Is it possible that metallic Cu is transiently exposed on the surface of the catalyst during operation at high temperatures, and would the operando TEM experiments be able to pick this up?

Reply to Q4: Thank you for the comment. At high temperatures, the surface of Cu catalysts is predominantly covered by a Cu₂O monolayer. However, at corners and specific facets of the particles, metallic Cu surfaces are revealed, as shown in Figures R1a and 1b. This observation is consistent with our previous study on Cu particle catalysts during hydrogen oxidation at 750 °C (Figures R1c-f), where Cu particles were observed to be partially covered by a Cu₂O monolayer, with metallic Cu exposed at the corners and specific facets. We have revised the manuscript to highlight this point, which reads as follow:

“Finally, at 900 °C, the particles exhibit a *quasi*-static state with metallic Cu decorated by a monolayer of Cu₂O (Figure 3g and 3h). However, the corners and some specific facets of particles are not fully covered and reveal Cu metallic surfaces (Figure 3h), demonstrating that both Cu⁰ and Cu₂O monolayer expose to the gas atmosphere at 900 °C. A similar thin oxide surface layer, along with partially exposed metallic Cu, was also observed on Cu particles during hydrogen oxidation at high temperatures.”

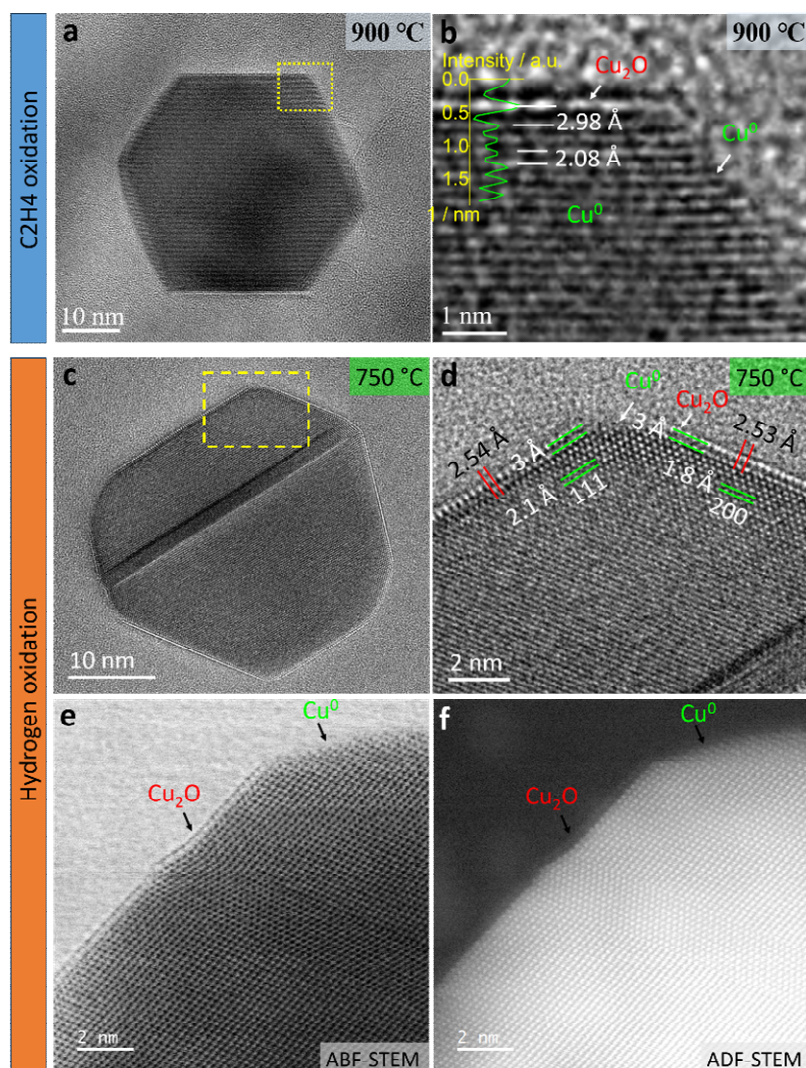


Figure R1. (a, b) TEM and HRTEM images of a Cu NP during C₂H₄ oxidation. (c, d) TEM and HRTEM images of a Cu NP during hydrogen oxidation. (e, f) High-resolution ABF-STEM and ADF-STEM images of a portion of a Cu NP at the same location during hydrogen oxidation. The Cu₂O monolayer in the ADF-STEM image appears a weaker contrast relative to the underlying metallic Cu⁰, indicating its oxidic nature.

Q5. Intermediate temperatures—From Figure 5, the intermediate temperature states are modelled as Cu₂O with subsurface oxygen partially removed. This does not seem to be consistent with Figures 3d and 3e, which show that the catalyst exists in a Janus-type structure with metallic Cu head connected to a Cu₂O tail. Further, the Cu₂O phase in the intermediate temperature state (Figures 3d and 3e) has the same lattice spacing (2.43 Å) as the low temperature state (Figures 3b and 3c), which also may indicate that the Cu₂O phase should have similar levels of oxidation at both temperatures. While the authors modelled strained Cu/Cu₂O (Figure S8) to simulate the effect of the metal-oxide interface, this does not rigorously represent the catalyst: it remains unclear if the Cu phase, Cu₂O phase, or perhaps the phase boundaries between Cu/Cu₂O are the active sites at these intermediate temperatures.

Reply to Q5: We thank the referee for the comment. This is an excellent point, and to gain an understanding of the behavior of the metal/oxide interface we have computed the activation energies for AcH and EO formation at a Cu₂O(110)/Cu(110) interface. These results are now included as Figure S9. We have made corresponding revisions to the text, which reads as follows:

“The metal/oxide interface shows similar, albeit slightly higher, barriers for partial oxidation (Figure S9). These results suggest that the oxide surface can remain active in the production of partial oxidation products even as it becomes non-stoichiometric and with the appearance of metal/oxide interfaces. Notably, the activity of direct EO formation increases with (sub)surface reduction, potentially making the non-stoichiometric/partially reduced oxide more selective in EO production than the pristine oxide or the metal/oxide interface.”

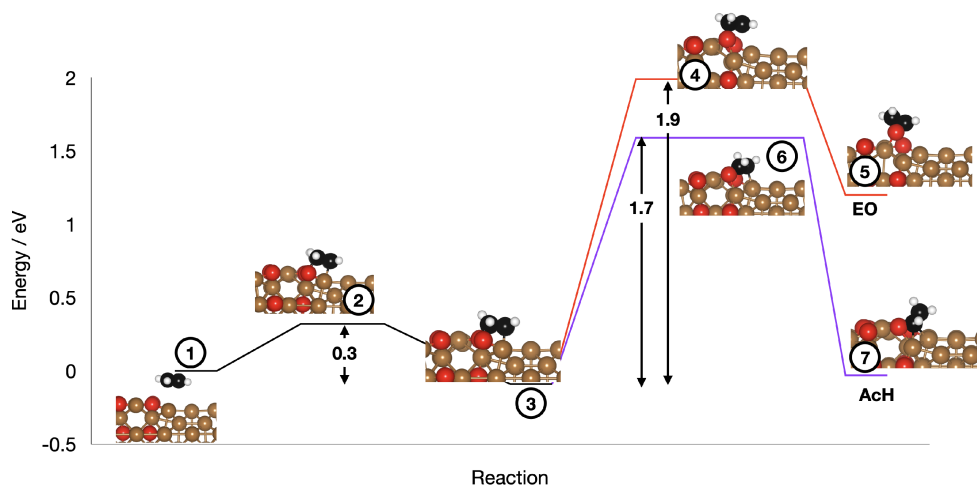


Figure S9. Reaction energetics for ethylene partial oxidation *via* an OMC on Cu₂O(110)/Cu(110). The adsorbed ethylene (state 1) forms an OMC (state 3) *via* the transition state shown in state 2. This process has an activation energy of 0.3 eV, as compared to 0.6 eV on the pure oxide. Once the OMC is formed it can decompose into EO *via* state 4 with an activation energy of $E_a=1.9$ eV, this value is larger than that found on the pure oxide, see Figure S10. The OMC can also decompose into AcH *via* state 6 with $E_a=1.7$ eV. This value too is higher than the barrier on the pure oxide, Figure S10.

Q6. The first-principles calculations in Figures 5 and 6 also do not explore the full mechanism for ethylene oxidation. Notably, in Figure S9, the barrier for OMC→2-oxoethyl, a key step for full oxidation, is shown. However, this is not included in Figures 5 or 6, which prevents us from obtaining a complete picture of the energetics of full oxidation versus partial ethylene oxidation.

Reply to Q6: We thank Referee 1 for the comment and have now included 2-oxoethyl formation on the oxide overlayer in Figure S12. We find its formation is highly activated, see below. We note that catalytic formation of 2-oxoethyl is not the only combustion route. At high temperatures AcH can be expected to undergo combustion since its autoignition temperature is ~200 °C, therefore gas-phase AcH will not be observed at temperature significantly above ~200 °C. Gas-phase EO, however, has an autoignition temperature of ~400 °C. Thus, we expect EO to survive in the gas-phase to higher temperatures than AcH. Because the metallic surface is predicted to have higher selectivity to EO relative to AcH, and EO may not undergo complete autoignition, we also considered partial oxidation to 2-

oxoethyl on the metallic surface (Figure S12). Like AcH, this partial oxidation product will under rapid oxidation to CO_2 and H_2O . When AcH is favored we did not consider the 2-oxoethyl species since the system already has a route to CO_2 .

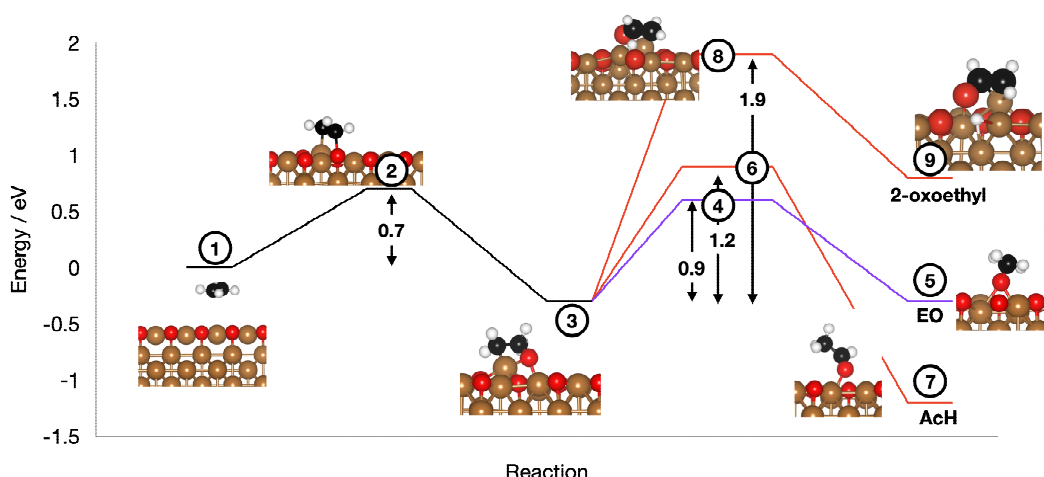


Figure S12. Reaction energetics for 2-oxoethyl formation on a single layer of Cu_2O on Cu metal plotted together with the OMC pathway. The corresponding OMC pathway is shown in Figure 6. Unlike on the metallic surface, partial oxidation to 2-oxoethyl *via* state 8 is highly activated ($E_a = 1.9$ eV) compared to EO and AcH formation.

Q7. All intermediate and TS structures in Figures 5 and 6 are missing. These details would be valuable to readers.

Reply to Q7: We thank the referee for the comment and have included the missing structures in Figure 6 in the revised manuscript.

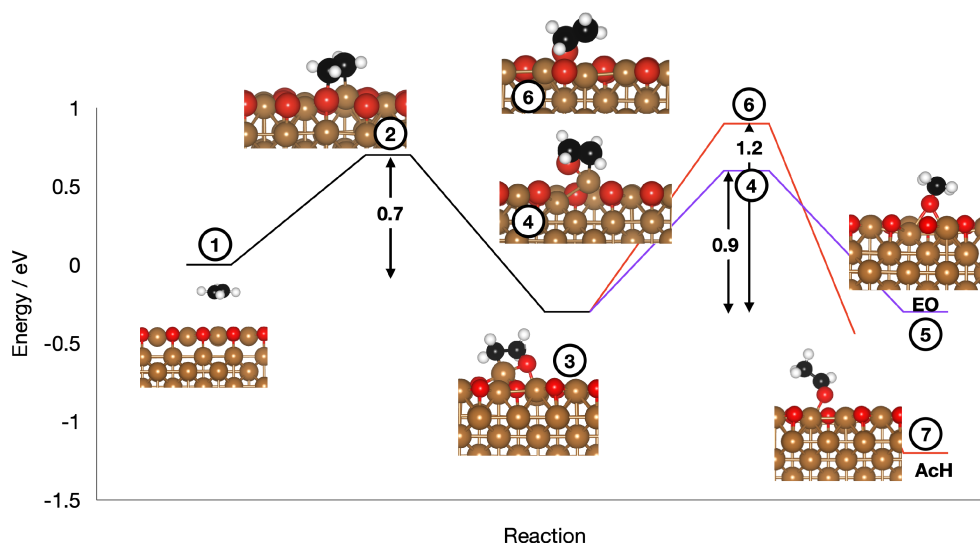


Figure 6. Computed ethylene (partial) oxidation pathways on a single layer of Cu_2O on Cu metal. State 1 shows adsorbed ethylene. State 3 is the OMC formed *via* state 2 with $E_a = 0.7$ eV. State 5 is EO formed *via* state 4 with $E_a = 0.9$ eV, and state 7 is AcH formed *via* state 6 with $E_a = 1.2$ eV.

Q8. For the partially reduced Cu_2O surface with 1/8 ML adsorbed oxygen, it would be helpful if the authors describe how the optimal configuration of the model was obtained.

Reply to Q8: We thank the referee for pointing out this oversight and have included the requested description, which reads as follows:

“Partially reduced structures were obtained by reducing the surface oxygen coverage to 1/8 ML; the effect of removing subsurface oxygen was also studied by removing the first, and then the second subsurface oxygen layer while maintaining 1/8 ML adsorbed oxygen.”

Q9. I wonder if the authors compared DFT and DFT+U for the Cu₂O calculations. If not, please explain why the U correction was not considered for this oxide system.

Reply to Q9: We thank the referee for the question. We did not include a Hubbard U term for Cu₂O since Cu is formally d¹⁰ and the Hubbard correlation energy vanishes for a filled band. We also note PBE has been used successfully in the past to model Cu₂O and including a U on Cu₂O (for instance, 10.1103/PhysRevB.75.125420) would add ambiguity to simulations with both metal and oxidized copper.

Minor points:

Q10. In Figure 6, the caption states that “AcH formed via state 6 with Ea=0.7 eV”. The correct value from the figure should be 1.2 eV.

Reply to Q10: We have fixed this error. Thank you for pointing this out. Please refer to the figure caption of Figure 6 in our reply to Q6.

Q11. Page 13, “direct EO formation (not shown) is activated by 1.2 eV”. I suggest the authors clarify the meaning of “not shown” and consider whether it is possible to present this data in the SI.

Reply to Q11: We have added Figure S11 to show this pathway (see below). Thank you for the comment.

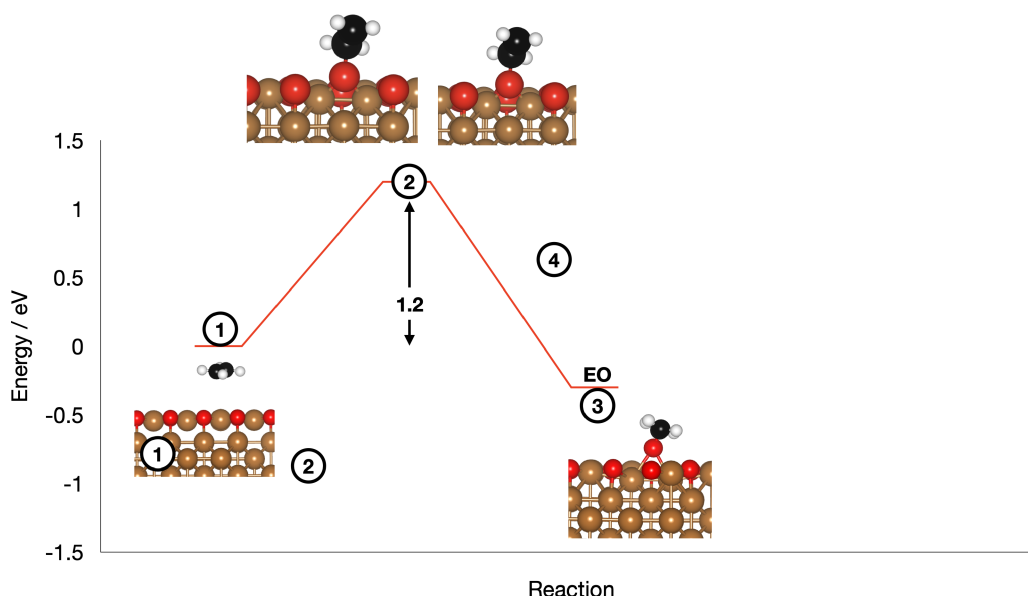


Figure S11. Reaction energetics for direct EO formation on a single layer of Cu₂O on Cu metal. The corresponding OMC pathway is shown in Figure 6.

Reviewer #2 (Remarks to the Author):

The authors report in-situ TEM imaging of the temperature-dependent dynamics of Cu particles during ethylene oxidation, supported by mass spectroscopy, DRFIT and DFT modeling. Their findings show a quasi-static and partially reduced state of Cu at lower temperatures, oscillatory phase transitions between Cu and Cu₂O at intermediate temperatures, and a high-temperature state of metallic Cu with a monolayer of Cu₂O. These temperature-dependent states of the catalyst are associated with variations in catalytic performance and reaction product distribution. The in-situ observations provide valuable insights into the structure-property relationships of catalysts and could have broad implications for the catalysis community.

Reply: We thank Reviewer 2 for the positive feedback of our work.

However, several critical questions need to be addressed to enhance the clarity and impact of the study:

Q12. Mechanistic Insights: What are the mechanistic pathways and intermediates involved in the observed phase

transitions of Cu particles at different temperatures? The DRIFT results appear not to show an obvious dependence of temperature on reaction intermediates. How do these transitions affect the catalytic reaction pathways and catalytic mechanisms?

Reply to Q12: Thank you for your comments. We admit that our previous manuscript lacked clarity regarding the mechanistic pathways and intermediates involved in the observed phase transitions at different temperatures. To gain a better understanding, we conducted new DFT results, which, in combination with our previous DFT results, now provide a more complete picture about the reaction mechanisms involved in the (partial) oxidation of ethylene on Cu.

In summary, at low temperature ranges (200 to 500 °C), where the Cu₂O phase predominates, the reaction tends to produce selective products (AcH and EO) *via* the OMC mechanism.

At elevated temperatures (600 to 800 °C), the catalyst features a highly dynamic state characterized by oscillatory phase transitions between Cu and Cu₂O. Consequently, multiple structures and phases emerge, including metallic Cu, Cu₂O, partially reduced Cu₂O, and strained Cu₂O at the metal-oxide interface. The reaction mechanisms associated with these structures are discussed in our response to Q1 and in the discussion section of our revised manuscript. Please refer to these sections for further details.

At high temperatures (900 °C and above), the catalyst is composed of metallic Cu partially covered by a monolayer Cu₂O. While metallic Cu favors CO₂ formation *via* the OMC dehydrogenation pathway, the monolayer Cu₂O favors the formation of EO over AcH through the OMC mechanism.

We have revised our manuscript to further elucidate the catalytic reaction mechanisms across different structures and phase transitions at varying temperatures (please refer to both green highlights (original text) and yellow highlights (revised text)).

Q13. Temperature Range Justification: Why were such large temperature ranges (up to 1000°C) chosen for the study? Are these ranges optimal for observing the phenomena discussed? How do these temperatures relate to those typically used in industrial catalytic ethylene oxidation?

Reply to Q13: We conducted investigations across a temperature range of 200 to 950 °C in order to explore the various possible states and structures of copper, as well as their correlations with catalytic performance and mechanisms. Under atmospheric conditions of C₂H₄:O₂ = 40:1 within this temperature range, we successfully transitioned the structure of copper catalysts from Cu₂O to Cu⁰/Cu₂O, ultimately achieving a predominant presence of Cu⁰, accompanied by a monolayer of Cu₂O. This transition enabled us to examine how these phases and structures influence catalytic functions through a combination of *in situ* TEM and online mass spectrometry.

While industrial catalytic ethylene oxidation is typically conducted at temperatures between 200 and 400 °C, our research is fundamentally focused on exploring the phase/structure-reactivity relationships of copper catalysts. As such, the reaction temperature in our experiments was not limited by industrial constraints but was chosen to provide a comprehensive understanding of the catalyst's behavior.

In response to this feedback, we have revised our manuscript to provide a clear justification for the use of the 200-950 °C temperature range (see below). Thank you for your comment.

“A broad temperature range (from 200 to 900 °C) is chosen for investigation in order to fully explore the various possible states/structures of Cu and their correlations with catalytic reactivity.”

Q14. Quantitative Analysis: Can the authors provide quantitative data on the extent of Cu reduction or oxidation at different temperatures? How does this correlate with changes in catalytic performance?

Reply to Q14: Thank you for the comment. It is not straightforward to get quantitative information on the extent of Cu reduction or oxidation as a function of temperature with the available data. This is particularly true for the high temperature conditions (900 °C and above), where a Cu₂O monolayer forms on the metallic Cu particles. We have been unable to identify a method to quantify the relative amount of this oxide monolayer (in relation to Cu⁰). *In situ* XPS may be a potential option; however, this method is surface-sensitive, lacking bulk information, and is generally limited to relatively low and medium temperatures.

Nevertheless, the analysis of our SAED data (shown here as Figure R2) can provide qualitative information about the phase composition of the catalyst (Cu_2O monolayer is not included). Our analysis indicates a clear phase transition of catalyst and changes in phase composition with temperature. Below 500 °C, the catalyst is predominantly in the form of Cu_2O . As the temperature increases, a gradual reduction in the Cu_2O phase is observed. This is accompanied by the increased presence of metallic Cu, particularly noticeable from 600 °C to 800 °C. At and above 900 °C, metallic Cu becomes the predominant phase. A monolayer of Cu_2O is present, partially covering the metallic Cu as a minor phase. In combination with online MS and DFT calculations, we have established correlations between the structures and catalytic performance, which have been detailed further in our revised manuscript. Please refer to relevant part of the manuscript for these details.

In all, we appreciate Referee 2 for highlighting this important point, which indeed merits further consideration. Methods such as image segmentation might be able to provide quantitative information on the extent of metal reduction or oxidation with temperature, as well as the relationship between phase composition, rate of change and catalytic activity/selectivity. However, such studies require considerable effort and experimentation, which we prefer to address in a dedicated publication in the future (contingent upon obtaining reasonable results).

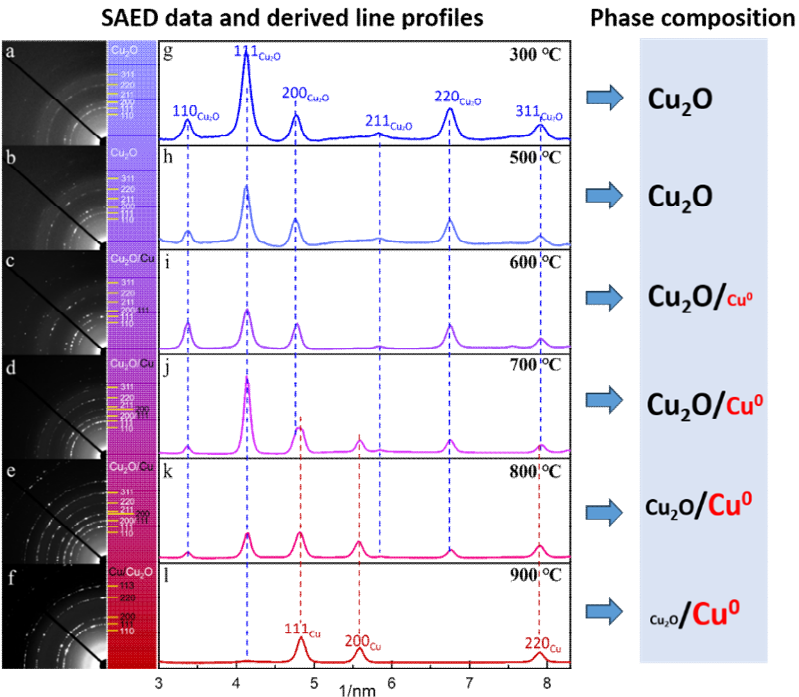


Figure R2. Phase composition analysis based on *in situ* SAED.

Q15. Monolayer Cu_2O : There is no direct evidence provided to confirm the presence of a monolayer of Cu_2O on bulk Cu. Can the authors provide evidence or detailed explanation supporting this observation?

Reply to Q15: The presence of a monolayer Cu_2O is validated by the identification of a lattice fringe exhibiting a larger *d*-spacing than that of the underlying Cu (111) on the surface of Cu NPs. Technically, the oxide layer may not be stoichiometric Cu_2O , considering its monolayer nature. This observation is consistent with our previous work, where we detected a similar oxide layer on Cu^0 surface under hydrogen oxidation reaction conditions. The clarity of the oxide layer visualization in our prior study was enhanced by the fortunate alignment of the observed Cu NPs along the zone axis, a condition not met in the present study (see above Figures R1c,d and e,f).

We have also observed the presence of a monolayer oxide on Pd metal during methane oxidation in our recent research (Nat. Commun., 2024, 15, 4678), suggesting that this phenomenon might be a common phenomenon for catalytically active transition metals under redox reactions. Regarding the HRTEM imaging recorded at 900 °C in the present work, we acknowledge the lack of alignment of the particle along the zone axis, and the presence of SiN membranes (60 nm) further complicates a clear view of this layer. Nonetheless, the imaging remains adequate to detect the difference in *d*-spacing between the Cu metal and the oxide layer (see Figure R1a,b), which is pivotal for

our analysis and serves as the primary method for identifying this oxide layer. We have expanded our discussion in the revised manuscript to offer a more detailed explanation the presence of an oxide layer on metallic Cu NPs.

Q16. DFT Modeling: The DFT modeling assumes a defect-free surface and considers strain effects in the Cu₂O overlayer. However, under realistic reaction conditions, the oxide surface is rarely perfect, and elevated temperatures may introduce significant non-stoichiometry and numerous surface defects. How might these factors impact surface adsorption and desorption properties, potentially overshadowing the strain effects?

Reply to Q16: We thank the referee for the comment and fully agree with the importance of strain. This is why we included models with varying non-stoichiometry. We have attempted to make this clearer in the revised manuscript and have also included simulations on the metal/oxide interface in Figure S9 (see below).

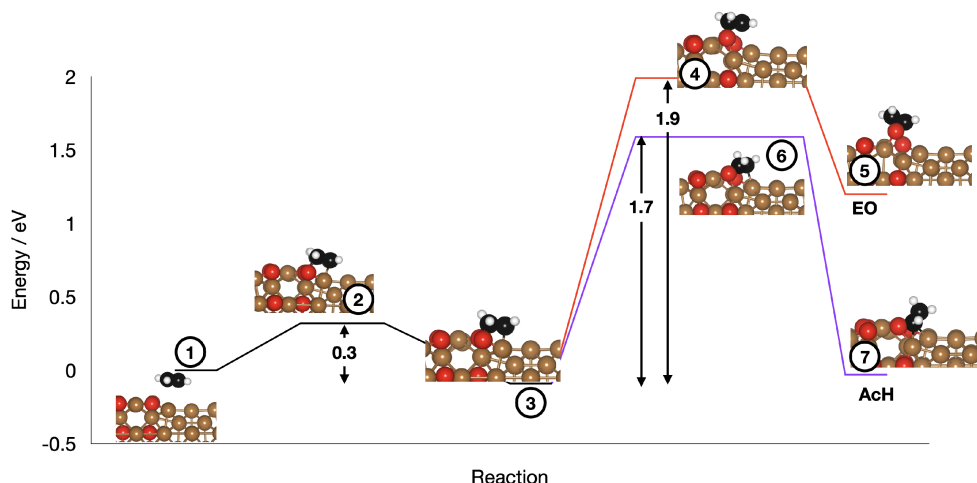


Figure S9. Reaction energetics for ethylene partial oxidation *via* an OMC on Cu₂O(110)/Cu(110). The adsorbed ethylene (state 1) forms an OMC (state 3) *via* the transition state shown in state 2. This process has an activation energy of 0.3 eV, as compared to 0.6 eV on the pure oxide. Once the OMC is formed it can decompose into EO *via* state 4 with an activation energy of $E_a=1.9$ eV, this value is larger than that found on the pure oxide, see Figure S10. The OMC can also decompose into AcH *via* state 6 with $E_a=1.7$ eV. This value too is higher than the barrier on the pure oxide, Figure S10.

Q17. Particle Mobility: In some in-situ TEM videos, smaller particles (with varying core-shell features or uniform contrast) appear less mobile compared to larger particles. This observation seems counterintuitive, as smaller particles are generally expected to migrate more easily. Can the authors provide an explanation for this behavior?

Reply to Q17: We appreciate your attention to this detail.

Indeed, some small particles in Supplementary Video S3 exhibit reduced mobility compared to the larger particles. This phenomenon may be attributed to surface carbon contamination of these particles and/or the entanglement and capture of the smaller particles by carbon materials formed during ethylene cracking, which is shown in Supplementary Video 4 recorded in a higher magnification. In response to your comments, we have revised our manuscript to include a description of this behavior. The updated section now reads as follows:

“Additionally, it is noted that as the temperature increases, the roughness of the SiN membrane support also increases. This rise in surface roughness is correlated with the increased instability of the support at higher temperatures and the formation of carbonaceous materials resulting from the decomposition of C₂H₄. Particularly in the latter case, some smaller particles get trapped within the framework of the carbonaceous materials, thereby restricting their mobility (Supplementary Video S4). Moreover, some of these particles may be contaminated by carbon species, resulting in deactivation.”

Q18. Support Morphology: The in-situ TEM videos suggest that the support's surface morphology, such as roughness, varies with temperature. How does the temperature affect the support's surface morphology and the mobility of Cu

particles?

Reply to Q18: Our observations indicate that at elevated temperatures, some carbon materials are formed, considerably due to the cracking of C_2H_4 on Cu catalysts. The formation of carbon increases the roughness of the support's surface. Some Cu particles become even trapped within these carbon materials or contaminated by carbon species, which hinders their migration and possibly lead to the deactivation of the Cu particles. Additionally, the elevated temperatures may also cause instability in the SiN membrane support, further contributing to the roughness of the support. We are grateful to Referee 2 for drawing attention to this phenomenon. We have included following text in the revised manuscript to emphasize this aspect:

“Additionally, it is noted that as the temperature increases, the roughness of the SiN membrane support also increases. This rise in surface roughness is correlated with the increased instability of the support at higher temperatures and the formation of carbonaceous materials resulting from the decomposition of C_2H_4 . Particularly in the latter case, some smaller particles get trapped within the framework of the carbonaceous materials, thereby restricting their mobility (Supplementary Video S4). Moreover, some of these particles may be contaminated by carbon species, resulting in deactivation.”

Reviewer #3 (Remarks to the Author):

This study employs operando TEM to investigate the structural and phase evolution of copper catalysts during ethylene oxidation across a wide temperature range (200 °C to 950 °C). The authors successfully identify three distinct structural states of the catalyst— Cu_2O , Cu/ Cu_2O oscillations, and metallic Cu—and correlate these states with catalytic performance. The integration of DFT simulations provides valuable insights into the effects of interfacial strain and phase coexistence on selectivity.

Reply: We appreciate the supportive and encouraging feedback by Referee 3.

However, there are significant concerns that need to be addressed:

Q19. The authors correctly highlight the advantages of in situ microscopy for atomic-scale imaging under operando conditions. However, it is critical to emphasize that phase determination using high-resolution imaging requires careful interpretation. Relying solely on one-dimensional lattice spacing is not a robust approach for phase identification, given the variety of possible crystal orientations and lattice spacings. Furthermore, HRTEM measurements and calibrations may not achieve the precision necessary for reliable phase determination. For example, the Cu (110) plane has a lattice spacing of approximately 2.54 Å. It is problematic to assert that the 2.46 Å spacing measured and attributed to Cu_2O (111) is not actually Cu (110), as seen in Fig. 3 c-e. This ambiguity undermines the reliability of the phase identification presented. To improve the accuracy of phase identification, it is strongly recommended that the authors use HRTEM images aligned on the zone axis. This alignment would allow for the simultaneous measurement of two lattice spacings, providing a more definitive determination of the phase and zone axis. Without such alignment, the conclusions drawn from the HRTEM images remain tentative.

Reply to Q19: We agree with Referee 3 that phase determination must be conducted with great care. Ideally, the particles should be oriented along a specific zone axis to facilitate precise determination. However, as the authors have noted, the particles exhibit significant dynamics and rapid movement on the surface of the SiN membrane, rendering it impractical to align them along the zone axis. Consequently, we must continuously capture movies in hopes of recording a temporarily aligned state. Frequently, we observe either a lack of lattice fringes due to rapid migration and surface diffusion, or only one-dimensional (1D) lattice spacings.

In cases where only 1D lattice fingers are observed, we have used Cu^0 (111) as a reference, performing careful calibration of the images and measuring the spots of the fast Fourier Transform (FFT) to minimize potential measurement errors. We acknowledge that Cu^0 (110) has a d -spacing of 2.56 Å, which is twice that of Cu^0 (220). If Cu^0 (110) planes were present, we would expect to see lattice fringes of Cu^0 (220) planes as well, given their equivalence. However, this was not observed in our study, allowing us to rule out the d -spacing of 2.46 Å fitting Cu^0 (110).

Moreover, we fortunately captured 2D lattice fingers of a dynamic copper particle with the Cu_2O portion precisely on

the zone axis. As shown in the figure below, the Cu_2O is viewed along the $[1-21]$ zone axis, and the diffraction spots fit well to Cu_2O (111), Cu_2O (20-2), and Cu_2O (31-1), with measured d -spacings of 2.46 Å, 1.5 Å, and 1.28 Å. In particular, the Cu_2O (111) is parallel to Cu^0 (111). This observation is consistent with our previous finding on Cu during hydrogen oxidation. We have included this data (as Figure S7) into the SI to support the validity of our claim on the phase determination.

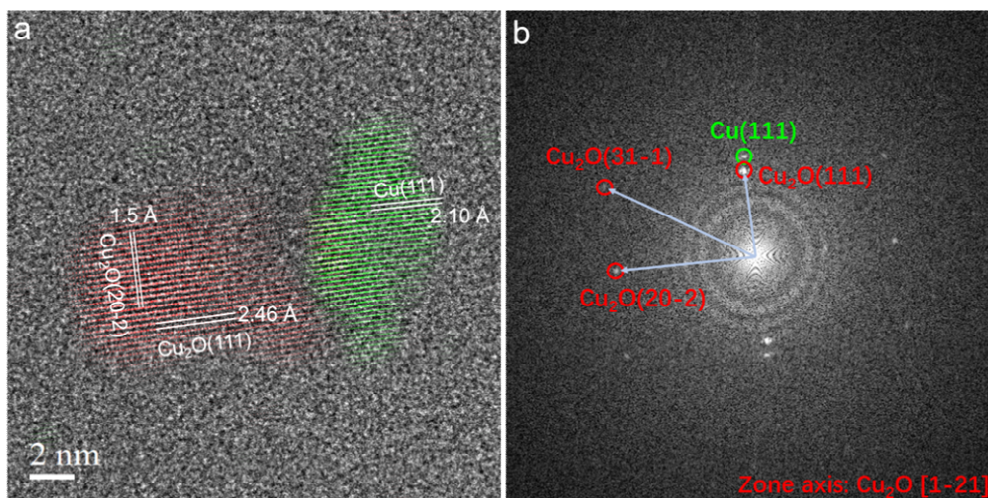


Figure S7. HRTEM image of a dynamic Cu nanoparticle recorded during C_2H_4 oxidation, showing a transient Cu^0 - Cu_2O head tail structure with Cu^0 (111) parallel to Cu_2O (111).

Q20. The existence of intermediate phases, such as Cu_{2-x}O , cannot be ruled out based on the current data. It would greatly enhance the study if the authors could include EDX or EELS analysis and quantification to confirm the co-presence and evolution of the identified phases. Such analysis could also potentially reveal the presence of intermediate phases, offering a more comprehensive understanding of the catalyst's behavior under the experimental conditions.

Reply to Q20: We thank Referee 3 for this valuable suggestion. During the oscillatory phase transition between Cu and Cu_2O , it is highly likely and logical to consider that a transient partially reduced Cu_2O (with oxygen vacancies) exists during the phase transitions from Cu to Cu_2O and from Cu_2O back to Cu. However, as demonstrated in Supplementary Video S2 and S3, the particles are in a highly dynamic state, characterized by constant reconstruction and migration. Consequently, it is not feasible to record EDX or EELS to verify the existence of intermediate oxides in such dynamic particles. Plus, the oscillatory phase transitions occur at temperatures of 700-800 °C, which is too high for EDX measurement (saturating the detector). Dropping temperatures to lower temperatures is not a good option, since this would change the structure and state of Cu catalysts.

It is worth mentioning that, in our previous research on methane oxidation over Pd particle catalysts, a transient PdO_x state was identified during the oscillatory phase transition between Pd^0 and PdO using *in situ* XPS. In principle, a similar approach could be applied to study Cu during ethylene oxidation. However, we currently lack access to the *in situ* XPS facility at the beamline within the allotted revision timeframe.

Given these constraints, we prefer to reference our prior work on Pd to infer the potential existence of partially reduced Cu_2O phases or species during C_2H_4 oxidation, especially within the 700-800 °C range, where oscillatory phase transitions are observed. We have added the following text into the revised manuscript:

“Moreover, due to the constant oscillatory phase transitions between Cu^0 and Cu_2O , non-stoichiometric/partially Cu_2O (with oxygen vacancies), may transiently exist. This hypothesis is further strengthened by our previous study, where partially reduced PdO_x was detected *via in situ* XPS during oscillatory phase transitions between Pd^0 and PdO, albeit in a different system.”

Response to reviewers

Reviewer #1 (Remarks to the Author):

The authors did a good job with the revisions and made the necessary changes. I believe the paper can be accepted in the current form.

Reply: We extend our gratitude to Reviewer 1 for re-evaluating our revised manuscript and for the recommendation of acceptance.

Reviewer #2 (Remarks to the Author):

The authors have addressed all my concerns, and I recommend the manuscript for acceptance.

Reply: We thank Reviewer 2 for re-evaluating our revised manuscript and for the recommendation of acceptance.

Reviewer #3 (Remarks to the Author):

This manuscript presents an operando TEM study combined with online mass spectrometry (MS) and density functional theory (DFT) calculations to investigate the dynamic behavior of copper catalysts during ethylene oxidation. The study identifies three distinct structural and reactivity regimes across different temperature ranges and explores the role of oscillatory phase transitions and surface modifications on catalytic performance.

Q1. The primary concern is the identification of Cu vs CuO_x phases. For example, in Figure S7, the HRTEM image of a dynamic Cu nanoparticle recorded during C₂H₄ oxidation shows a transient CuO–Cu₂O head-tail structure, with CuO (111) parallel to Cu₂O (111). Specifically, it is stated that lattice spacings of 1.50 Å and 2.46 Å correspond to (20-2) and (111) of Cu₂O, while the 2.10 Å lattice spacing is attributed to Cu metal. However, this approach is not a sufficiently robust method to identify phases.

Reply to Q1: We thank Reviewer 3 for the additional comment, which raises concerns regarding the accuracy of our phase determination.

In the HRTEM image shown in Figure S7, the moving particle is temporarily oriented along a zone axis, revealing two-dimensional lattice fringes on the left side of the particle (red region). This oriented state allows for an accurate determination of the phases within the particle. For the observed two sets of lattice fringes, we measured their *d* spacings to be 2.46 Å and 1.50 Å, respectively, with an angle of 90°. These measurements correspond well to the (111) and (20-2) planes of the Cu₂O phase (zone axis: [1-21]), exhibiting an error margin of less than 1%, as determined by "CaRine Crystallography," a professional software commonly employed for structural analysis and phase determination. The red region of the particle cannot be metallic, as it exhibits a *d* spacing of 2.46 Å, which exceeds the maximum *d* spacing of 2.10 Å associated with the (111) plane of metallic Cu. Reviewer 3 expressed concerns regarding the ability to distinguish between Cu(111) and Cu₂O(200) based on *d* spacing measurements, given the small differences in their *d* spacings (2.10 Å vs 2.13 Å). However, with a properly calibrated microscope, these differences can be effectively discerned. Moreover, the well-characterized Cu₂O phase can aid in further calibrating the HRTEM images for precise measurements of lattice *d* spacings. Therefore, we are confident in the accuracy of our measurements and

results.

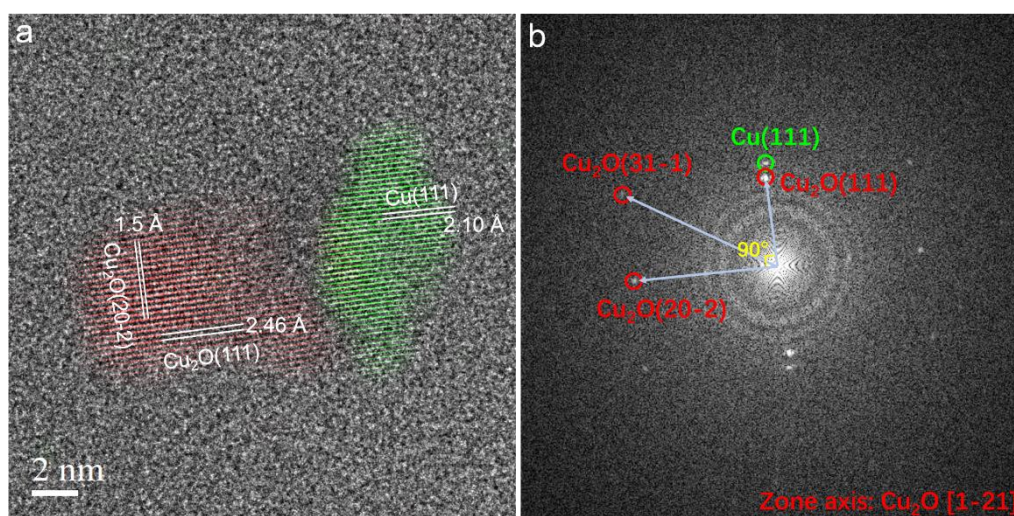


Figure S7. HRTEM image of a dynamic Cu nanoparticle recorded during C₂H₄ oxidation, showing a transient Cu⁰-Cu₂O head tail structure with Cu⁰ (111) parallel to Cu₂O (111).

Q2: If the authors cannot provide EELS data, which should be highly sensitive for detecting O signals, they should instead provide XPS data to substantiate their phase identification. This is particularly relevant as the authors mentioned in their response that they have used *in situ* XPS for their previous PdO_x work. Other than the above concern, the authors have adequately addressed the reviewers' comments.

Reply to Q2: Thank you for your comment.

Under the reaction conditions, an O₂ atmosphere is present, which can lead to signal overlap between the oxygen from copper oxide and that from the O₂ atmosphere when recording the O K edge EELS, thus challenging post-analysis. Furthermore, as demonstrated in this study, the particles exhibit high mobility, which prevents us from recording EELS maps or point EELS on these particles to ascertain their oxidation states (and gain further insights into their phases).

Instead, we employed SAED and HRTEM imaging for phase identification, which is sufficient to determine the structural configuration of the migrating particle—a head-tail structure comprising a Cu⁰ head and an oxide tail (Cu₂O). These particles undergo constant oscillatory phase transitions between Cu₂O and Cu⁰, suggesting the potential transient presence of intermediate phases of Cu₂O_{1-x} (where x ranges from 0 to 1).

Synchrotron based *in situ* XPS would certainly be beneficial to gain further insights into chemical state of the catalyst. However, as mentioned in our previous response to the reviewers, we currently lack access to a suitable beamline and must submit an application, a process that may take several months. Furthermore, based on our previous experience, we are uncertain about the feasibility of conducting experiments at temperatures up to 850 and 950 °C while obtaining reliable data. In light of these considerations, we respectfully request that the discussion remains at its current level in this work.

Nonetheless, we are very interested in acquiring *in situ* XPS data for this system and intend to

conduct further studies on the state of the copper catalyst under redox-active conditions (likely in hydrogen oxidation to begin) in our future research, focusing particularly on the origins of particle mobility and the splitting associated with oscillatory phase transitions.