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The Effect of Orientation on Cu_2O Reduction Under Methanol Observed by *in Situ* ETEM

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Methanol (MeOH) is an essential feedstock in chemical engineering for hydrogen production via steam reforming and partial oxidation reactions, as well as for production of chemicals such as formaldehyde and acetic acid. Cu-based catalysts are the most widely used commercial catalysts in methanol chemistry due to their low cost and high reactivity with methanol. The oxidation and reduction of Cu catalyst have been found to significantly alter the reactivity and selectivity of these reactions.[1] However, despite multiple studies on the oxidation state of Cu on methanol oxidation using experimental methods (e.g., with XPS), the effect of microstructure – such as surface orientation, interfaces and defects – on the reaction dynamics has not been extensively investigated, especially at the atomic scale. Information at this length scale is necessary for identifying the active sites for each reaction and developing accurate predictive reaction models.

In this work, we investigated and compared the atomic-scale dynamic reduction processes of Cu_2O islands grown on Cu(100), (110), and (111) substrates under MeOH using in situ Environmental TEM (ETEM). The ETEM used in this study (Hitachi H-9500 operating at 300 keV) was equipped with an in-house-designed gas delivery system that enables MeOH vapor injection in addition to O_2 and H_2 gas feeds. To obtain well-defined orientations of the Cu_2O islands and Cu/Cu_2O interfaces, the Cu_2O nano-islands were grown on single-crystal Cu substrates using in situ oxidation, in the manner described in reference [2]. Figure 1 shows the as-grown Cu_2O nano-islands on Cu(100), (110), and (111) substrates. All Cu_2O islands exhibited cube-on-cube epitaxy with their Cu substrates. These Cu_2O/Cu structures with different surface and interface orientations served as model systems for the subsequent systematic study of the impact of orientation on Cu_2O nano-island reduction. The in situ reduction was carried out at 300 °C under 1 Pa of methanol vapor. During reduction, the atomic scale dynamic processes of Cu_2O island reduction was recorded as it unfolded, revealing a distinctly different reduction behavior for each orientation. For Cu_2O islands grown on Cu(100) surfaces, as shown in Figure 2 (a-c), the height of the Cu_2O stays unchanged for the first 115 s of reduction, while the radius (half width) of the Cu_2O is shrinking. When the radius and height reach a similar value, the shrinking of the island transitions to isotropic, i.e. both height and radius decrease at similar rates. Such two-stage reduction is statistically validated through and explained by a preferential methanol reactivity on (100) surface steps of Cu_2O islands, as confirmed by DFT simulations.[3] This reaction mechanism is different from our previous work on Cu_2O islands grown on Cu(110), in which monolayer by monolayer reduction along the side $Cu_2O(110)$ surface of the Cu_2O island followed by transition caused by Cu/Cu_2O interface orientation change was observed.[4] Further analysis of $Cu_2O(111)$ islands is underway, along with correlated Density Functional Theory (DFT) simulations to verify and explain the differences in reaction mechanisms. These findings help to identify the active sites of Cu_2O during MeOH reforming reactions, which would ultimately lead to understanding and improving the properties of Cu catalysts.[5]

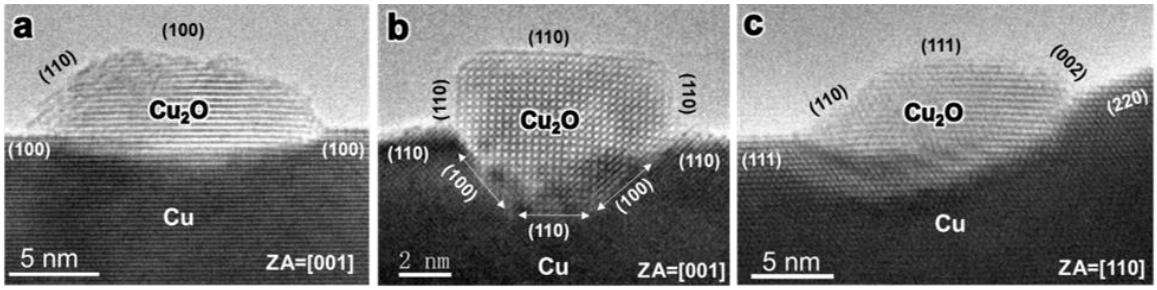

Figure 1. HRTEM images of Cu2O islands grown on different Cu substrate orientations via in situ oxidation. (a) Cu2O island grown on Cu(100) facet. (b) Cu2O island grown on Cu(110) facet. (c) Cu2O island grown on Cu(111) facet.

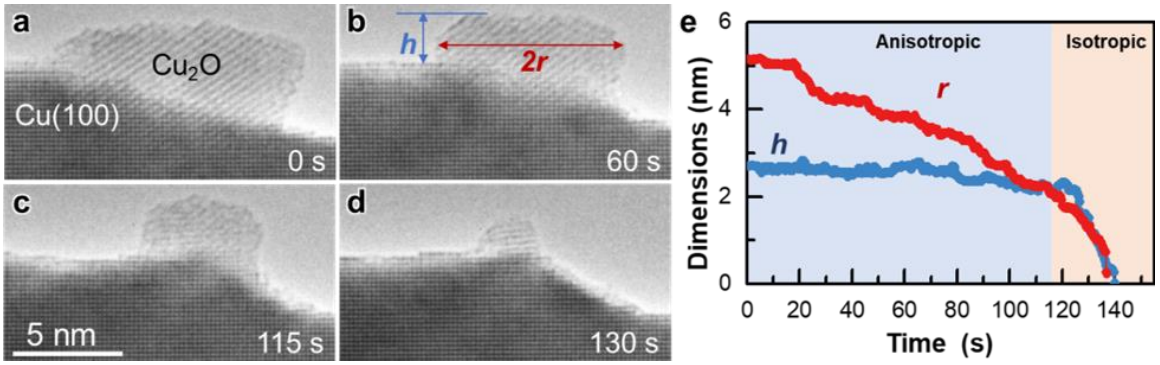

Figure 2. In situ ETEM reduction of Cu2O island grown on Cu(100) surface under 0.1 Pa MeOH at 300 °C. (a-d) Atomic resolution HRTEM images of the reduction process. (e) Plot of radius (r, red, half of the width) and height (h, blue) of the Cu2O island as a function of time, in which two-stage reduction can be observed.

References

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