

***In situ* Atomic Scale Observation of Cu₂O Reduction under Methanol**

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Cu-based catalysts are widely used in methanol related reactions, such as partial oxidation of methanol, water-gas shift and methanol synthesis. Reduction of Cu oxides under methanol (MeOH) is also applied in the pretreatment or regeneration of a catalyst. The reduction process of Cu oxides (Cu₂O, CuO) plays an important role in controlling the reaction mechanism of catalytic reactions. Phase transformations between Cu and Cu oxides under oxidizing or reducing (redox) conditions are often found to alter the reactivity and selectivity of these reactions.[1] Although Cu-based catalytic reactions have been studied in much detail in terms of active phases of Cu using both experimental methods such as XPS and theoretical methods such as DFT, in terms of active sites, the dynamic microstructure transformations among different Cu phases under catalytic conditions is less investigated, especially at atomic scale, due to lack of experimental approaches.

In situ TEM techniques, especially environmental TEM(ETEM) has been proven to be a very powerful tool to study dynamic processes of gas-solid reactions. However, very few studies are focused on the reduction of Cu oxides, especially under methanol. Understanding the atomic scale microstructure evolution of Cu₂O reduction under methanol is crucial for understanding the active site these reactions and the underlying reaction mechanisms.

In this work, the atomic-scale dynamic reduction processes of Cu₂O island grown on Cu(110) facets under MeOH were investigated using *in situ* ETEM. The ETEM we used (Hitachi H-9500 operating at 300 keV) is equipped with a home-made gas delivery system that enables MeOH vapor injection[2]. In order to have controllable orientations of the Cu₂O islands and Cu/Cu₂O interfaces, the Cu₂O nano-islands were grown on single crystalline Cu substrate using *in-situ* oxidation [3]. As shown in Figure 1, the as-grown Cu₂O nano-island shows cube-on-cube epitaxy with the Cu substrate, the surface of the Cu₂O island consists of Cu₂O (110) surfaces, while the Cu/Cu₂O interface is along Cu/Cu₂O(100) direction. This Cu₂O/Cu(110) structure serves as a model system for us to understand the stability of Cu₂O nano-island and its interface, as well as crystallography dependent reactivity under MeOH reducing environment. The *in situ* reduction was carried out at 300 °C under 1 Pa methanol vapor. During reduction, the Cu₂O island was observed to be reduced monolayer by monolayer along the side Cu₂O(110) surface of the Cu₂O island, while the top surface, although it's also Cu₂O(110) plane, remains unchanged, as shown in Figure 1, indicating the perimeter site of the island might be the preferential reaction site of MeOH. Besides, the buried part of the Cu₂O is also observed to be reduced through interface migration along the Cu/Cu₂O(100) interface. Further quantitative analysis of the reduction dynamics was carried out using a homemade *in situ* movie processing approach followed by data analysis using statistical approaches. Correlated Density Functional Theory (DFT) simulations are

underway out to verify and better understand the reaction mechanisms. Our results would help determining the atomic level active sites of Cu_2O during MeOH reforming reactions, which would ultimately lead to understanding and improving the properties of Cu catalysts.[4]

References:

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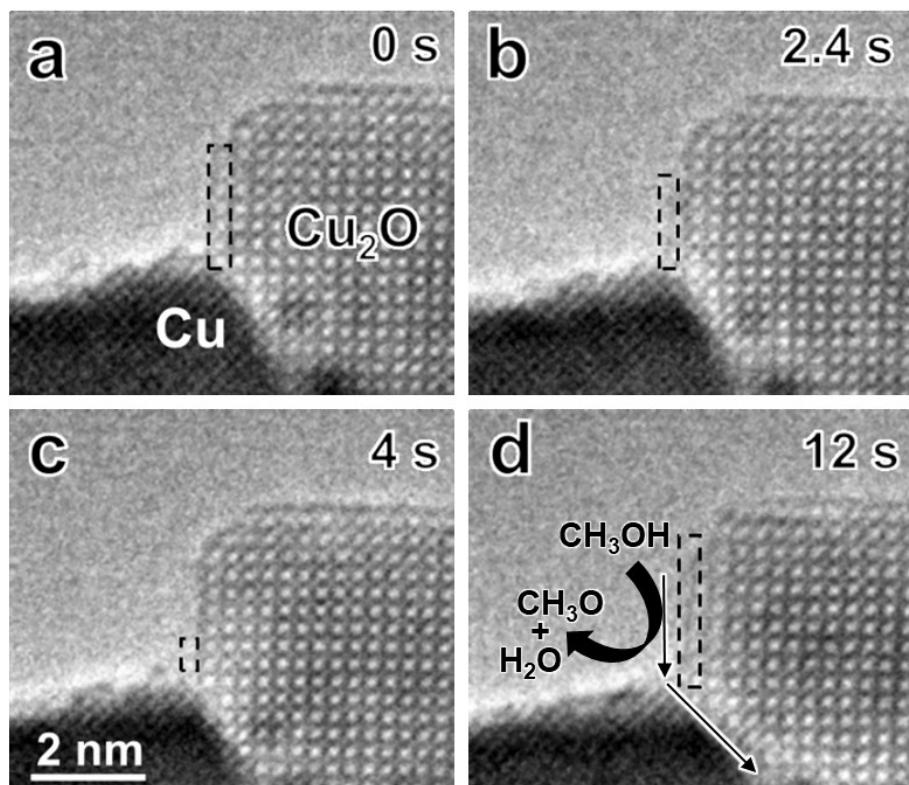


Figure 1. *In situ* observation of layer-by-layer reduction of $\text{Cu}_2\text{O}(110)$ under 1 Pa MeOH vapor at 300°C. The black dashed boxes in (a)-(c) marks the vertical atomic side layer of Cu_2O island that is being reduced, the box in (d) marks a new layer that is being reduced. Note the top side of the island remains unchanged throughout this process.