doi:10.1017/S1431927619010067
Microsc. Microanal. 25 (Suppl 2), 2019

In situ Atomic Scale Observation of Cu_2O 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 (Cu_2O, 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 Cu_2O reduction under methonal is crucial for undertanding the active site these reactions and the underlying reaction mechanisms.

In this work, the atomic-scale dynamic reduction processes of Cu_2O 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 Cu_2O islands and Cu/Cu_2O interfaces, the Cu_2O nano-islands were grown on single crystalline Cu substrate using *in-situ* oxidation [3]. As shown in Figure 1, the as-grown Cu_2O nano-island shows cube-on-cube epitaxy with the Cu substrate, the surface of the Cu_2O island consists of Cu_2O (110) surfaces, while the Cu/Cu_2O interface is along Cu/Cu_2O(100) direction. This Cu_2O/Cu(110) structure serves as a model system for us to understand the stability of Cu_2O 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 Cu_2O island was observed to be reduced monolayer by monolayer along the side Cu_2O(110) surface of the Cu_2O island, while the top surface, although it's also Cu_2O(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 Cu_2O is also observed to be reduced through interface migration along the Cu/Cu_2O(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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[4] The authors acknowledge funding from National Science Foundation (NSF) grants DMR-1410055, CBET-1264637, DMR-1508417, DMR-1410335, and DMREF CHE-1534630, as well as support from Hitachi-High-Tech and technical assistance from the Nanoscale Fabrication and Characterization Facility (NFCF) in the Petersen Institute of Nano Science and Engineering (PINSE) at University of Pittsburgh. The ECC is funded through U. Pitt and Hitachi High Technologies.

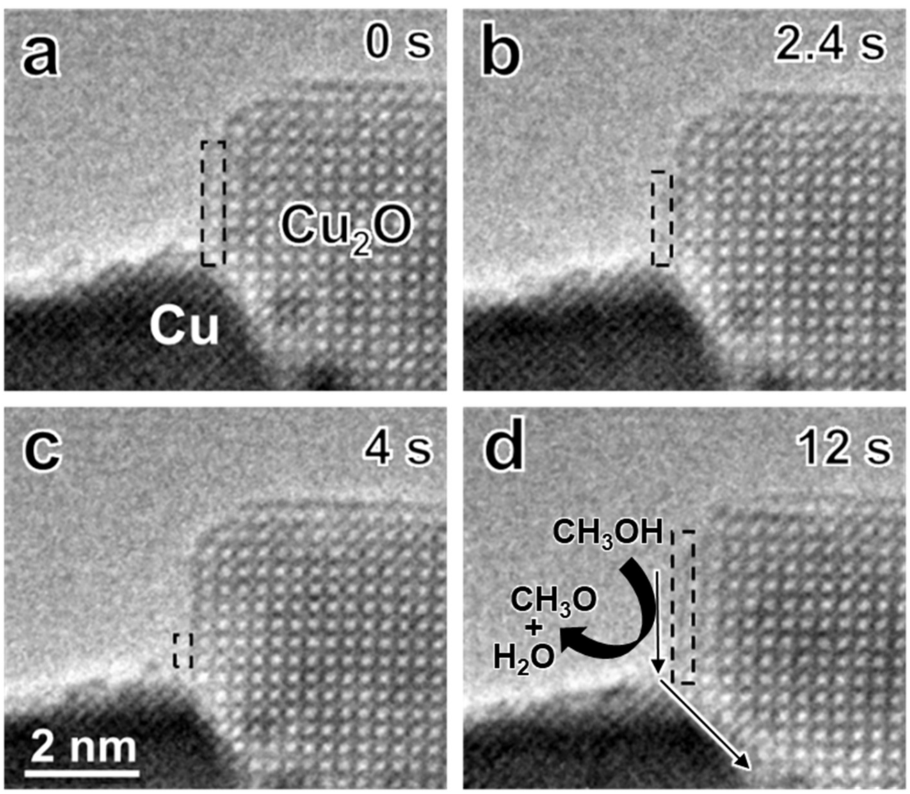

Figure 1. *In situ* observation of layer-by-layer reduction of $Cu_2O(110)$ under 1 Pa MeOH vapor at 300°C. The black dashed boxes in (a)-(c) marks the vertical atomic side layer of Cu_2O island that is being reduced, the box in (d) marks a new layer that is being reduced. Note the top side of the island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

https://doi.org/10.1017/S1431927619010067 Published online by Cambridge University Press