In situ Atomic Scale Observation of Cu$_2$O 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$_2$O, 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$_2$O reduction under methanal is crucial for understanding the active site these reactions and the underlying reaction mechanisms.

In this work, the atomic-scale dynamic reduction processes of Cu$_2$O 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$_2$O islands and Cu/Cu$_2$O interfaces, the Cu$_2$O nano-islands were grown on single crystalline Cu substrate using in-situ oxidation [3]. As shown in Figure 1, the as-grown Cu$_2$O nano-island shows cube-on-cube epitaxy with the Cu substrate, the surface of the Cu$_2$O island consists of Cu$_2$O (110) surfaces, while the Cu/Cu$_2$O interface is along Cu/Cu$_2$O(100) direction. This Cu$_2$O/Cu(110) structure serves as a model system for us to understand the stability of Cu$_2$O 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$_2$O island was observed to be reduced monolayer by monolayer along the side Cu$_2$O(110) surface of the Cu$_2$O island, while the top surface, although it’s also Cu$_2$O(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$_2$O is also observed to be reduced through interface migration along the Cu/Cu$_2$O(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$_2$O 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 Cu$_2$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$_2$O 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.