Introduction

Higher alcohols (C<sub>n</sub>OH), commonly referred to alcohols higher than methanol, has drawn considerable interest as value-added chemicals, oxygenates fuels or fuel additives. Adding higher alcohols to fossil oil benefits the fuel to combust more completely because of presence of oxygen, which increases the combustion efficiency and reduces air pollution. One promising method of higher alcohols production, is catalytic conversion of mixtures of carbon monoxide and hydrogen (syngas) derived from coal, biomass, natural gas, or shale gas. Although rhodium-based catalysts offer high selectivity (C<sub>n</sub>OH), their prohibitive cost has urged research on comparable and less expensive copper-based alternatives, mainly modified Fischer-Tropsch (FT) catalysts, such as Cu-Co and Cu-Fe based catalysts. Compared with Cu-Co based catalysts, Cu-Fe based catalysts exhibit higher intrinsic activity and selectivity. Higher alcohols synthesis (HAS) via modified FT catalysts shares some common reactions with methanol synthesis and FT synthesis (FTS). Methanol synthesis only requires oxygenation, in which an associative C=O bond introduces oxygen into carbon chain. FTS only requires chain propagation, which needs C=O breaking and then hydrogenation into alkenes and alkanes. However, HAS requires a dual site, involving both oxygenation and chain propagation.

To date, Cu active site for methanol synthesis and Fe active site for FTS were deliberately investigated. However, detailed insights into the active Cu-Fe dual site is rare. Thus, it is essentially desirable to unravel the Cu-Fe dual sites, in order to gain a fundamental understanding of the intrinsic activity. Since increasing the dual site surface area and balancing oxygenation and chain propagation reactions on the dual site would be the two key factors to rationally maximize the synergism for HAS, three-dimensionally ordered macroporous (3DOM) catalysts can be one of such promising candidates.

Objective

Design a catalyst to produce higher alcohol with high intrinsic activity and high Cu:OH selectivity.

Investigate the active sites of the catalyst for higher alcohols synthesis from syngas.

Experimental

Table 1. Physicochemical Properties and Catalytic Performance*

Table 2. GC-MS analysis of higher alcohols in hydrocarbon phase

Conclusions

The self-supported 3DOM Cu-Fe catalysts were applied in higher alcohols synthesis for the first time, having high intrinsic activity and higher alcohols (C<sub>n</sub>OH) selectivity (up to ca. 83% of total alcohols). The unique structure not only eliminates the need for frame support from the third party materials, but also prevents the agglomeration and segregation of both active components to the great extent.

The homogeneous distribution of defective Cu and Hägg (χ<sub>Fe</sub>C<sub>3</sub>) nanoparticles help to provide abundant dual sites, resulting in a synergetic effect between Cu<sup>2+</sup> oxygenation site and χ<sub>Fe</sub>C<sub>3</sub> chain propagation site for higher alcohols synthesis. This finding paves the way towards the rational design of practically relevant dual site catalysts with enhanced intrinsic activity and functionality.

Acknowledgements

Funding for this work was provided by the U.S. Department of Energy under Award Numbers DE-FG3606GO86025, DE-FC2608NT01923, and the U.S. Department of Agriculture under Award number AB567370MSU.