

Catalysis Science of Hydrogen Production via the Water-Gas Shift Reaction

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Abstract

Industrial hydrogen production is achieved by the water-gas shift (WGS) reaction ($\text{H}_2\text{O} + \text{CO} \leftrightarrow \text{H}_2 + \text{CO}_2$) [1]. Traditionally, the $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$ catalyst was used to perform the high temperature WGS and $\text{Cu-ZnO-Al}_2\text{O}_3$ catalyst to perform the low temperature WGS to enhance hydrogen production. The structure and promotion mechanism of Cu and Cr in the $\text{CuO-Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$ catalyst, however, are still not well understood due to the lack of surface characterization studies under reaction conditions [2-5].

The unsupported Fe_2O_3 , $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$ and $\text{CuO-Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$ catalysts were synthesized by co-precipitation from the corresponding aqueous nitrates. All the catalysts were investigated with modern cutting edge in situ, operando (Raman, XANES/EXAFS and near ambient pressure XPS) spectroscopy during the high temperature WGS reaction. Steady-State Isotopic Transient Kinetic Analysis (SSITKA) were performed to study its reaction mechanism.

The fresh, fully oxidized $\text{CuO-Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$ catalyst consists of surface Cr^{6+} species and bulk $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$, Cu^{2+} is enriched towards surface. During the WGS reaction, the surface Cr^{6+} extensively reduces to Cr^{3+} , the bulk $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$ transforms to bulk $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$ and Cu^{2+} reduces to metallic Cu^0 and migrates onto the surface. A surface FeO (Fe^{+2}) layer, however, is present during low-pressure WGS. The HT WGS catalyst operates via a redox reaction mechanism and the catalytic active site is the surface Fe species on $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$ that undergo the $\text{Fe}^{+2} \leftrightarrow \text{Fe}^{+3}$ redox cycle. The Cr promoter does not exhibit redox characteristics in the reaction environment and its only role is to increase the surface area of the dominant $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$ phase (textural promoter). SSITKA with $\text{CO}_2^{18}\text{-CO}_2^{16}$ isotopes further confirmed the WGS reaction follows a redox mechanism only involving surface oxygen species that are the most abundant reactive intermediates (MARI). These new insights have led to a new fundamental

understanding of the HT WGS catalysts and the development of a kinetic model that follows the surface Mars-van Krevelen mechanism.

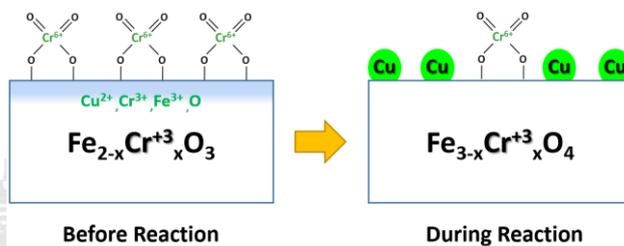


Figure 1 Schematic of $\text{CuO-Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$ catalyst before and during HT-WGS.

References

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