

Au catalysis – mechanistic and deactivation studies of water gas-shift reaction

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Introduction

The WGS reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$) is one of the important steps in the production of hydrogen from hydrocarbons. The reaction is becoming an alternative of the removal of CO from the stream in fuel cell applications. WGS catalysts that are applied commercially, are of two types: i) high temperature (400–500 °C) shift catalysts consisting of oxides of iron and chromium and ii) low temperature (200–400 °C) shift catalysts consisting of copper, zinc oxide and alumina.

Even though gold has long been regarded as an “inert” surface and bulk gold surfaces do not chemisorb many molecules, it has been shown in last decade [1] that gold supported catalyst has a high activity for reactions such as CO oxidation at sub-ambient temperature or water-gas shift reaction (WGS) at 125–175 °C. Au catalysts [2] that are nowadays intensively studied for the WGS reaction are: Au/Fe₂O₃, Au/CeO₂, Au/ZrO₂, and Au/TiO₂.

In our work, WGS reaction was performed with gold iron oxide-supported catalysts. Various steady-state experiments were carried out in 6-flow reactor. Moreover, surface species on the Au catalyst were identified by DRIFT FT-IR technique and stages of the WGS mechanism and the deactivation will be proposed. The various causes of deactivation were in detail investigated by applying different characterization techniques (e.g. DRIFTS, MS, TGA, TEM, BET, XRD) to as-received and spent catalysts at different times on stream. Formation of carbonate and carbonyl species, sintering, loss of Au and change of Fe₂O₃ support will be discussed.

Experimental

Steady-state experiments were performed in 6-flow apparatus at temperature range of 100 – 250 °C and pressure 1 bar. Au/Fe₂O₃ supplied by the University of Cardiff or World Gold Council (WGC) were studied for this reaction. Thermo Nicolet Nexus IR with corresponding OMNIC software with combination with MS were used to obtain Drift FT-IR spectra and MS analyses.

Results and Discussion

High activity of Au/Fe₂O₃ (Fig.1) was observed during the WGS reaction at low temperatures. Nevertheless, the commercial Cu-based catalyst showed higher activity at high temperatures. Furthermore, it is shown that the activity of Au/Fe₂O₃ for WGS reaction depends on the calcination temperature. The stability test performed at 200 °C revealed that Au catalyst gradually decreased in time, whereas the commercially available copper based catalyst did not show any deactivation besides the first 5 hours (Fig.2).

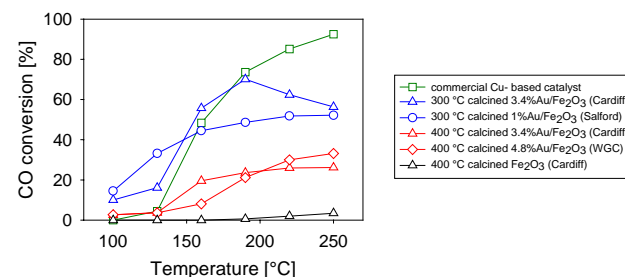


Fig.1 Water-gas shift reaction over Au catalysts and the commercial Cu-based catalyst as a function of the temperature. Feed composition: 0.5% CO, 1.5% H₂O, 98% He. Total flow rate: 55 ml/min.

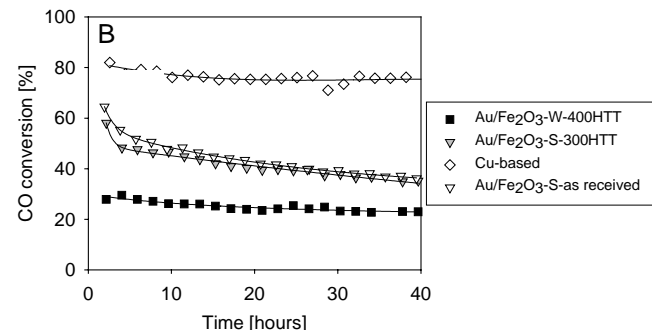


Figure 2. CO conversion obtained during the isothermal stability test of the water-gas shift reaction over Au/Fe₂O₃, Fe₂O₃ and Cu-based catalysts. The experiments were performed at 200 °C in the 6-flow set-up.

Conclusion

Even though the deactivation of Au/Fe₂O₃ appears to comprise several processes not all of them play a significant role of progress deactivation course observed herein. The formation of carbonate and carbonyl species occurs but not to a large extent and is not seen as the main cause of the Au/Fe₂O₃ deactivation. Neither severe agglomeration of Au particles nor the loss of Au takes place on the Au/Fe₂O₃ during the water-gas shift. The support suffers of severe changes during the water-gas shift reaction. In case that the fresh Au catalyst is supported on hematite, the support is reduced to the magnetite. The water-gas shift reaction over Au/Fe₂O₃ occurring via reduction-oxidation mechanism where the re-oxidation of the support appears to be a rate-limiting step. The significant loss of the surface area of the support is taking place during the water-gas shift reaction affects the catalytic performance and is the main cause of the Au/Fe₂O₃ deactivation.

