

The Influence of CO on the Deactivation of a Pt-Re-Mo Trimetallic Low Temperature Water Gas Shift Catalyst

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Introduction

This commercial monolithic Pt-Re-Mo catalyst is successfully being used for mid-temperature range (>300°C inlet) water gas shift (WGS) for on-site H₂ generation. However, in attempts to use this catalyst for low temperature WGS (<300°C inlet), the catalyst was found to be unstable during steady state operation. We observed decay rate to increase as reaction temperature decreases, H₂O concentration increases, or CO concentration increases. We also observed catalyst decay to be fully reversible by heating in a reductive gas. In prior work [1], we concluded surface oxidation of the Re/Mo promoters lead to the disruption of the trimetallic active cluster and subsequent catalyst decay. However, one piece missing from this mechanism is the role CO plays in catalyst deactivation during low temperature WGS (Figure 1), which is the focus of this current work. To gain insight into the low-temperature CO decay mechanism and identify the involved surface species, a series of activity and analytical measurements were performed on different metal combinations of the Pt-Re-Mo catalyst.

Materials and Methods

A stabilized zirconia support (Magnesium Electron Inc.) was impregnated with either Pt, Re, or Mo to create five catalyst formulations: 6%Pt, 2.5%Re-2%Mo, 6%Pt-2%Mo, 6%Pt-2.5%Re, 6%Pt-2.5%Re-2%Mo. A combination of wet precipitation and incipient wetness techniques were used to deposit the metals via amine solubilized platinum hydroxide, ammonium perhenate, ammonium molybdate precursors. The resulting material was dried for 8h at 120°C and calcined in air for 2 h at 550°C. The resulting catalyst was prepared as particles (250µm-500µm) and activated prior to each experiment in dry hydrogen at 350°C. The change in steady state activity at 250°C over a 16h period was measured in an electrically heated quartz tubular reactor (d_{tube}=13mm). An ATR reformat (11% CO, 10% CO₂, 38% H₂, 24% H₂O, bal N₂) was simulated by metering pure gases using mass flow controllers and purified demineralized water using a high performance liquid pump.

Results and Discussion

Independently, Re and Mo have little or no activity for WGS and have been found to primarily promote Pt activity for WGS. The promotion is believed to follow a bifunctional mechanism [2] involving the Pt-catalyzed reduction of MoO₃/Re₂O₇ into a partially oxidized state, which can then undergo a REDOX cycle that enhances the activation of water. Below 300°C, we hypothesize steam contained in the reformat over-oxidizes the Re/Mo leaving only the intrinsic activity of Pt (Figure 1, H₂O/H₂ vs. Activity). When the H₂O/H₂ ratio is maintained at an unstable level, we found CO concentration in the feed reformat to also increase decay rate (Figure 1, CO vs. Activity). It is likely CO influences the susceptibility of

the Re/Mo to oxidation by interacting directly with the promoters or indirectly by interacting with Pt.

Efficient promotion of WGS on Pt is more complex than the ability to undergo partial reduction. When comparing Pt-Mo and Pt-Re, we observed Re to more efficiently promote WGS on Pt than Mo. When formulated as a trimetallic combination a dramatic activity increase is observed. While this result is worthy of further investigation, it also provided some mechanistic evidence on the performance impacts of the bimetallic formulations and will be discussed in more depth. When combined with the other results in Figure 2, this result also provides insight into the role CO plays in catalyst decay. After a short decay as reformat replaces the dry hydrogen pretreatment gas, the Pt and Pt-Mo catalyst are both relatively stable with time. However, both the Pt-Re and Pt-Re-Mo catalyst experience significant decay during the 16h aging period. This result indicates the Re is intimately involved in the deactivation process on the catalyst surface. In addition to performance tests, analytical characterization of the surface including CO Chemisorption, Temperature Programmed Reduction, Transmission Electron Microscopy, and X-Ray Photoelectron Spectroscopy was performed to study changes in the catalyst during deactivation. A compilation of those results yields a preliminary understanding of how CO interacts with Re; either directly or interferes with the catalytic effect of Pt to keep the Re in its active partially reduced state.

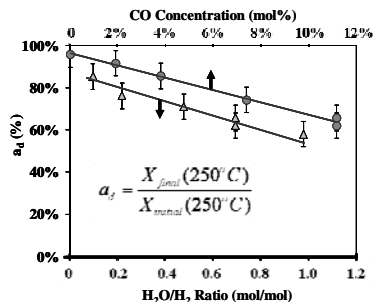


Figure 1: Influence of CO and H₂O/H₂ on Decay Rate

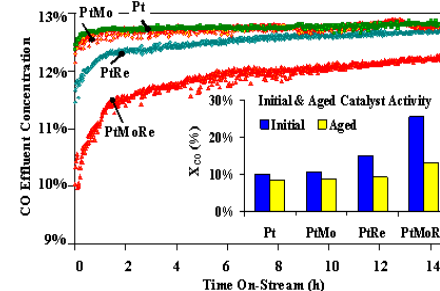


Figure 2: Influence of Catalyst Composition on Decay Rate

Significance

For low temperature WGS, this trimetallic Pt-Re-Mo catalyst provides a pathway for significantly higher activities that cannot be realized due to the instability issue. This catalyst also provides benefits inherent to precious metal catalysts including rapid activation in syngas, low pressure drop when used in monolith form, and stability during stop-start cycles. A thorough understanding of the low temperature decay mechanism will lead to the development of improved catalysts for low-temperature (<300°C inlet) water gas shift.

References

1. L. Dorazio, W. Ruettinger, M.J. Castaldi, R. Farrauto, *Topics in Catal.*, 51, 1-4 (2008).
2. H. Iida, A. Igarashi, *Applied Catalysis A: General*, 303, 48-55 (2006)