Gas-induced Stability of Ceria-based Water-gas Shift Catalysts

Weiling Deng, Howard Saltsburg, Maria Flytzani-Stephanopoulos
Department of Chemical and Biological Engineering
Tufts University, Medford, MA 02155

Xianqin Wang, Jonathan Hanson, José A. Rodriguez
Chemistry Department
Brookhaven National Laboratory, Upton, NY 11973

Nanostructured gold-ceria catalysts are among the most active materials for the low temperature water-gas shift reaction. Different techniques can be used to prepare highly dispersed gold in cerium oxide with or without dopants. We have recently reported that a strong interaction between gold and ceria is responsible for the WGS reaction activity [1,2]. Gold is stabilized in oxidized form in ceria; the amount of stabilized gold correlates with the number of surface oxygen defects of nanoscale ceria.

In highly reducing environments, the gold-ceria interaction can be lost, zerovalent gold is formed, ceria defects are annealed, and deactivation follows. This happens readily above 300 °C, but much less at lower temperatures. The catalysts after use in various WGS gas mixtures were characterized by XPS to examine the oxidation state of gold, which changed with the reaction conditions. As shown in Figure 1, in more oxidizing atmospheres (line a and b), ionic gold is clearly seen in the used samples. However, when used in a more reducing WGS atmosphere (line d), the peak of Au(0) became sharper. Gold particle growth from 5.0 to 7.2 nm was measured in this sample.

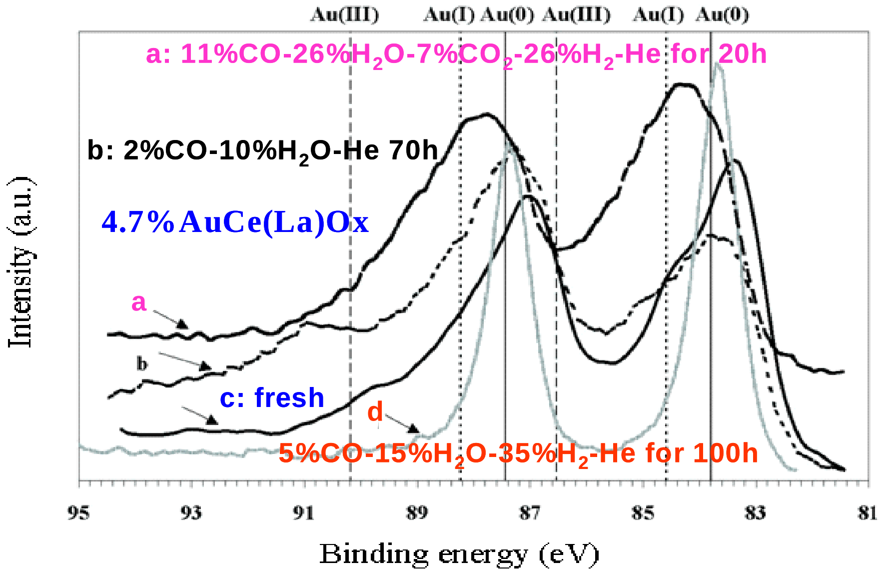

Figure 1. XPS of as prepared and used 4.7Au-CL(DP); calcined at 400°C, 10h.

The most serious stability issue with ceria-based catalysts is formation of cerium(III) hydroxycarbonate during shutdown to room temperature [2]. However, we have found that addition of a small amount of oxygen (0.5 mol%) in the feed gas can fully stabilize the WGS activity of Au-nano ceria in realistic reformate gas streams, and prevent the formation of cerium(III) hydroxycarbonate at low temperatures. Shutdown to room temperature with water condensation is now possible without any activity loss for the gold-ceria catalysts. In Figure 2, the WGS reaction was carried out at 300 ^{o}C in the full gas mixture over 5.8AuCe(La)O_x for 2 h. The CO conversion was over 65%. When the heater was turned off, during the cooling transient (2 h), the same gas mixture except for H_2O was kept flowing through the reactor. WGS reaction ceased. However, the CO oxidation reaction continued to occur to temperatures below 50 ^{o}C, which accounts for the nearly full conversion of oxygen by the CO oxidation reaction. High CO conversion was recovered when the WGS reaction was restarted at 300 ^{o}C. The second cooling was carried out in the full gas (with 26%H_2O present). Even in the presence of the gradually condensing water vapor, at low temperature, the CO oxidation reaction also took place. Upon reheating, there was no decrease in the conversion of CO. Thus, shutdown-startup in the full WGS gas mixture with 0.5 mol% oxygen added does not affect the subsequent activity of the catalyst. Similar stabilization of the gold-ceria catalyst activity was observed in shutdown (to RT)-startup (at 150 ^{o}C) cyclic operation of the WGS reaction with 0.5%O_2 present in the full WGS reaction gas mixture. Both XRD and TPO experiments confirm that no cerium(III) hydroxycarbonate was formed during these treatments.

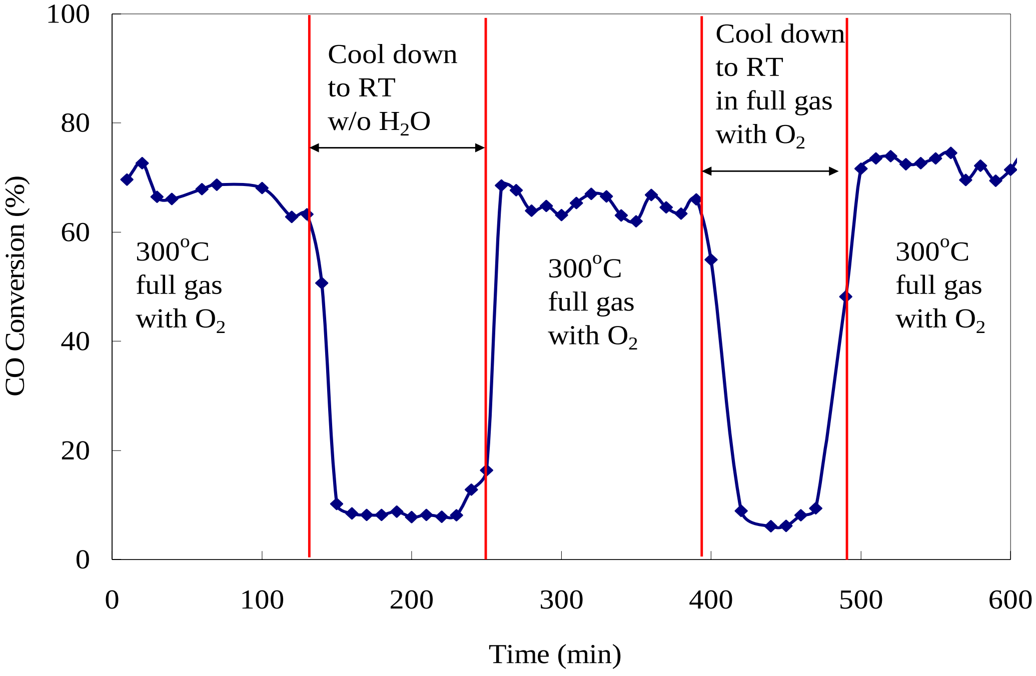

Figure 2. Gaseous oxygen addition effect on 5.8AuCe(La)O_x activity during WGS shutdown – startup operation. Gas mixture: 11%CO-26%H_2O-26%H_2-7%CO_2-0.5%O_2-He; S.V. = 30,000 h^{-1}

The key is the CO oxidation reaction by oxygen that is very fast and not quenched at room temperature. On the other hand, gaseous oxygen addition can not stabilize platinum-ceria catalysts after shutdown to room temperature in the full WGS gas mixture since the light off temperature of CO oxidation over platinum-ceria is much higher than that for gold-ceria.

In this presentation, we will show evidence of the dynamic response of gold-ceria catalysts to different gas environments accompanied by structural characterization by various techniques, including *in situ* XANES and EXAFS.

References

1. Q. Fu, H. Saltsburg and M. Flytzani-Stephanopoulos, *Science* 301 (2003) 935.
2. Q.Fu, W.Deng, H. Saltsburg, M. Flytzani-Stephanopoulos, *Appl. Catal. B*, 56 (2005) 57-68.
3. W. Deng, M. Flytzani-Stephanopoulos, 19th NAM paper # O-305, Philadelphia, PA, May 22-27, 2005.