Stability of Gold-Ceria Catalysts in the Water-gas Shift and Selective CO Oxidation Reactions

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Gold-ceria catalysts have been shown to have excellent activity for low-temperature CO cleanup of reformate gas streams for PEM fuel cell use [1-4]. The maximum amount of gold necessary for activity in the water-gas shift and the selective or preferential CO oxidation (PROX) reactions is determined by the surface properties of ceria, specifically its oxygen ion vacancies. Various oxide dopants (La, Gd) of ceria are used to increase the number of oxygen defects of ceria.

Catalyst synthesis methods include deposition-precipitation (DP) of gold onto ceria particles as well as preparation of bulk catalysts by the urea gelation/co-precipitation (UGC) method. Details about the preparation techniques can be found in refs. 1-4. Different tests to check the stability of gold-ceria over a wide range of temperatures and different WGS gas compositions were conducted. In a 120-hour long stability test of the 4.7Au-Ce(La)O_x (DP, 650 ^oC calcined) sample at 300 ^oC, little deactivation with time-on-stream was observed in a reformate-type gas mixture containing 7 % CO-38 % H_2O-11 % CO_2-40 % H_2-He (space velocity 6,000 h^{-1} (NTP)). Only initially, there was a drop in activity of ~ 15%. Characterization of the used catalyst found that the ceria crystallite size (7.1nm) had increased only slightly, while the gold crystallite size grew from 4.6 to 6.8 nm. Therefore, the initial activity loss is not due to the growth of gold particles. The gold crystallite size has little effect on the catalytic activity, as reported before [1-3, 5].

Figure 1 shows the CO conversion vs. time plot over three catalysts 8Au-Ce(La)O_x (UGC), 4.7Au-Ce(La)O_x (DP), and 0.44Au-Ce(La)O_x (DP, NaCN) in a gas mixture containing 5 % CO-15 % H_2O-35 % H_2-He, at 250°C and at a space velocity of 15,000 h^{-1} (NTP) for 100 h. Sodium cyanide was used to leach out weakly bound gold from the 4.7%Au –sample; more than 90% of gold was thus removed. Yet the sample with 0.44%Au was more active than the parent one [1], as is shown in Fig.1. The conversion dropped ~20 % in the first 10 h and was then stabilized with very slow further decay. The ceria surface area loss was also ~20%, matching the activity loss.

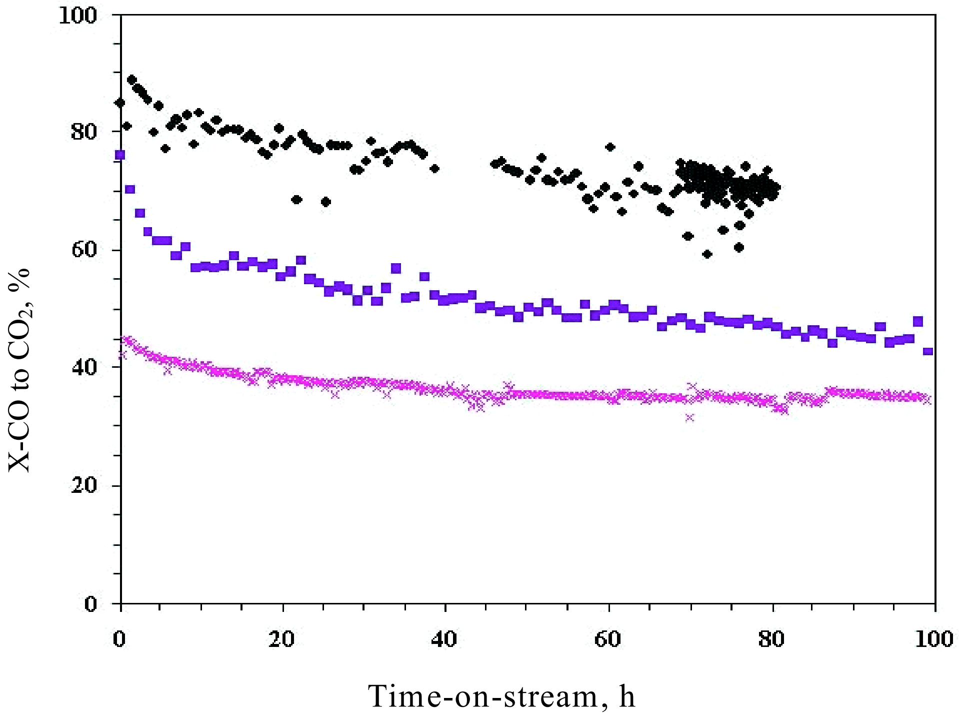

Figure 1. Stability of gold-ceria WGS catalysts.

Diamonds: 8Au-Ce(La)O_x(UGC); Crosses: 4.7Au-Ce(La)O_x(DP); Squares: 0.44Au-Ce(La)O_x(DP, NaCN).

Space velocity: 15,000 h^{-1} (NTP); feed gas: 5%CO-15%H_2O-35%H_2-He;

reaction temperature: 250 °C; all catalysts calcined in air at 400 °C, 4h.

The catalyst stability under shutdown conditions was also tested to simulate fuel cell operation under cyclic conditions as shown in Figure 2. When a typical Au-Ce(La)Ox catalyst was cooled down from 300 °C to room temperature in the full fuel gas (containing 26%H_2O), it lost more than 50% of its activity, as shown by reheating in the fuel gas to 300 °C. Formation of cerium hydroxycarbonate was identified by XRD. Shutdown in dry gas preserved the activity. By comparison, gold-titanium oxide and gold-zirconium oxide did not show any deactivation in shutdown-startup cycles. However, these catalysts have inferior steady-state activity at 300 °C to gold-ceria.

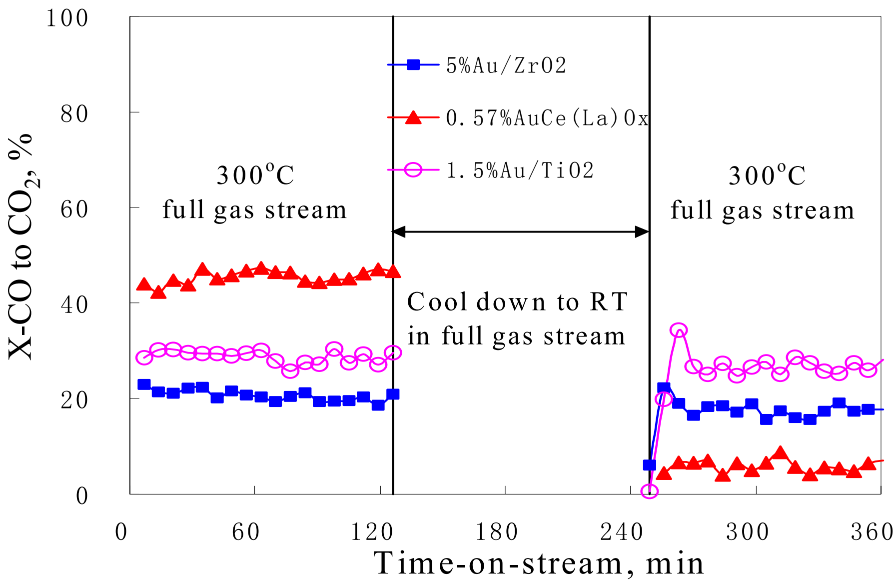

Figure 2. Processor shutdown simulation.

Gas composition: 11%CO-26%H_2O-7%CO_2-26%H_2-He; space velocity: 50,000 h^{-1}(NTP).

The stability of both the as prepared and leached gold-ceria catalysts under CO-PROX reaction conditions is excellent as shown in Figure 3 for 24 h-long tests at 120 °C. No loss of CO oxidation activity or selectivity for either catalyst was observed.

As shown above H_2O plays a very important role in the deactivation of gold-ceria samples in WGS reaction under shutdown conditions. Interestingly, shutdown under PROX conditions, did not affect the subsequent catalyst activity at 120 °C. A sample 0.28AuCe(Gd)Ox was prepared by single-pot UGC synthesis and tested in a gas mixture of 1% CO-0.5% O_2-50% H_2-10% H_2O-15% CO_2-bal He at 120 °C [5]. After reaching steady state, the CO conversion was ~45% and the selectivity ~34%. Then the sample was cooled to room temperature and held for 2 hours, before it was reheated to 120 °C. As shown in Figure 4, only a slight drop in CO conversion (~5%) was observed and the selectivity was unchanged. The sample was cooled down to room temperature again and held in the full gas for 6 hours; again, no drop of activity was found after restarting the reaction at 120 °C.

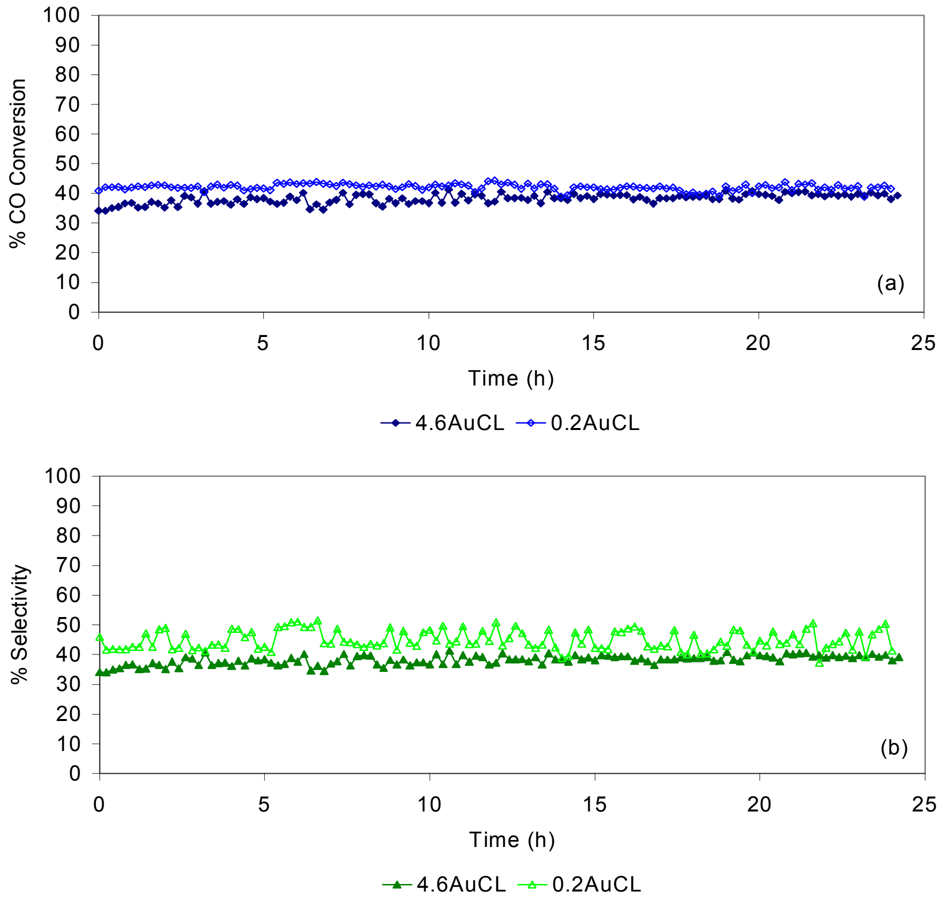

Figure 3. Stability of gold-ceria catalysts under PROX conditions for 24 hours at 120 °C. W/F = 0.096 g·s/cm^3; 1% CO-0.5% O_2-50% H_2-10% H_2O-15% CO_2-bal He.

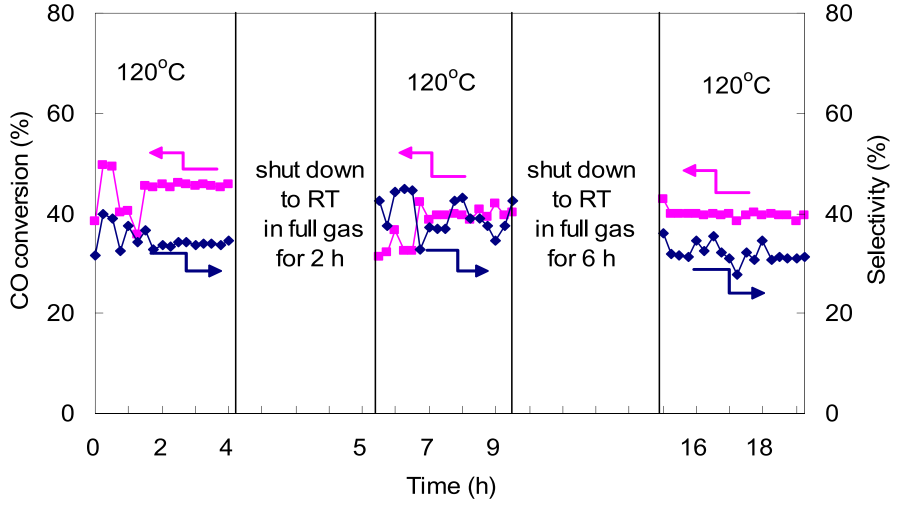

Figure 4. Shutdown simulation of PROX reaction over 0.28%AuCe(Gd)Ox. W/F: 0.096 g.s/cm^3; 1% CO-0.5% O_2-50% H_2-10% H_2O-15% CO_2-bal He.

H_2-TPR was conducted to determine the reducibility of the surface oxygen of the gold-ceria catalysts. We found that oxidation of reduced leached gold-ceria samples takes place readily at room temperature, by O_2, H_2O or air, but not by CO_2. However, only one third of the oxygen storage capacity can be restored at room temperature. When oxidized at higher temperature (350 °C), almost all of it is recovered.

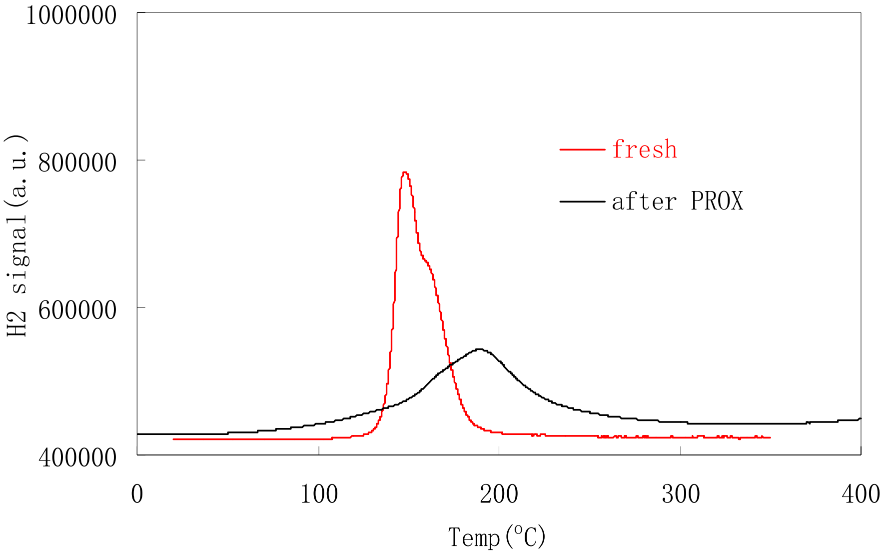

Figure 5. H_2-TPR profiles of $0.28AuCe(Gd)O_x$ before and after the PROX reaction.
Test condition: 20% H_2/N_2, 50 cm^3/min (NTP), 5 °C/min.
PROX condition: W/F = 0.096 $g \cdot s/cm^3$;
1% CO-0.5% O_2-50% H_2-10% H_2O-15% CO_2-bal He up to 120 °C for 17 h.

Figure 5 compares the H_2-TPR profiles of 0.28AuCe(Gd)Ox, as prepared (400°C-calcined) and after use in the CO-PROX reaction. The as prepared material contains ionic gold; its reduction begins around 120 °C [2,3]. After 17 h in the PROX reaction full gas mixture, reduction of the used sample starts at ~50 °C, but a broader peak extending to 300 °C is observed. The hydrogen consumption over these two samples is similar, 677μmol/gcat for the as prepared, and 680μmol/gcat for the used one. Thus, under this reaction condition, part of gold changed oxidation state but no loss of activity was observed. Leaching the used $0.28AuCe(Gd)O_x$ sample with a sodium cyanide solution left 0.20%Au in the catalyst.

Structural analyses and activity data from used catalysts will be presented to aim at rationalizing the WGS and PROX catalyst formulations from the performance stability viewpoint.

References

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