

Heterogeneous Catalysis

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On the Issue of the Deactivation of Au–Cerium and Pt–Cerium Water–Gas Shift Catalysts in Practical Fuel-Cell Applications**

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In recent years, nanostructured Au catalysts have attracted a lot of attention as potential candidates for the removal of poisonous carbon monoxide from synthesis gas streams, thus upgrading hydrogen gas to be used as fuel at the anode of low-temperature fuel cells. The interest in Au nanoparticles has been motivated by the pioneering work of Haruta et al., who demonstrated the extremely high activity of finely dispersed Au on reducible oxide supports for CO oxidation.^[1,2] Gold oxide systems have also been evaluated as potential catalysts

for the water–gas shift (WGS) reaction^[3–8] and the preferential oxidation of CO in H₂-rich fuel-gas streams.^[9–16] Among these catalysts, the combination of Au with nanoscale cerium oxide (ceria) has been shown to be the most active low-temperature WGS catalyst^[5,8] and one of the most selective preferential oxidation (PROX) catalysts^[14–16] for application at 80–120 °C.

Nanocrystalline ceria has unique properties as an oxide support, as it increases the activity of Au toward CO oxidation^[17] and the WGS reaction^[4,5] by more than two orders of magnitude relative to microcrystalline ceria. Similar findings have been reported by Gorte and co-workers for Pt-group metals on nanoscale ceria.^[18] Evidence in the literature has been mounting on the participation of the surface oxygen atoms of ceria in the catalysis of CO oxidation by dioxygen or water.^[4,19,20]

Deactivation with time-on-stream and/or in shut-down/restart operation currently plagues all known WGS catalysts based on ceria^[21–24] or copper oxide.^[25] Kim and Thompson reported fast deactivation of their Au–ceria catalyst, which they attributed to the blockage of the active sites by carbonates and/or formates formed during the WGS reaction.^[21] However, this fast extensive initial decline of activity of Au–ceria in the WGS reaction was not observed in a less H₂-rich gas composition.^[5] In their report on the deactivation of Pt–ceria with time-on-stream, Zalc et al. claimed that over-reduction of ceria cannot be avoided, thus rendering ceria-supported catalysts impractical for the WGS reaction in fuel-cell systems.^[22] Furthermore, in cyclic operation, including shut-down to room temperature and start-up of reactors, severe deactivation has been reported both for Pt–ceria^[23] and Au–ceria^[5] WGS catalysts. The activity of Pd–ceria and Pt–ceria for the WGS reaction can be partially recovered by reoxidation of the catalyst in oxygen at high temperatures (600 °C),^[24] but this process is not practical in the continuous operation of a fuel-cell system. To the best of our knowledge, no in situ remedy of the deactivation problem has been reported. Herein, we present a new way to stabilize the activity of Au–ceria catalysts for the WGS and PROX reactions under realistic operating conditions.

We started from the observation that Au–ceria catalysts have excellent stability with time-on-stream under PROX conditions at 120 °C.^[14] We further studied this type of catalyst in shut-down/start-up cycles of the PROX reactor under conditions that allowed water condensation on the catalyst. Interestingly, this did not affect the subsequent catalyst activity at 120 °C (Figure 1). After reaching steady state at 120 °C in the PROX reaction, the 0.28 AuCe(Gd)O_x catalyst sample was cooled to room temperature and held under a continuous flow of the same gas mixture for 2 h before being reheated to 120 °C. Stable CO conversion was recovered. The sample was then cooled down to room temperature and held in the flowing full gas stream for 6 h; again, no drop of activity was found after reheating at 120 °C. Excellent performance in the shut-down/start-up cycling of the PROX reactor was also observed with another Au–ceria (La-doped) sample (0.57 AuCe(La)O_x; Figure 1). Remarkable stability was further found for the 0.28 AuCe(Gd)O_x sample at higher conversions of CO when working with a higher O₂/CO ratio

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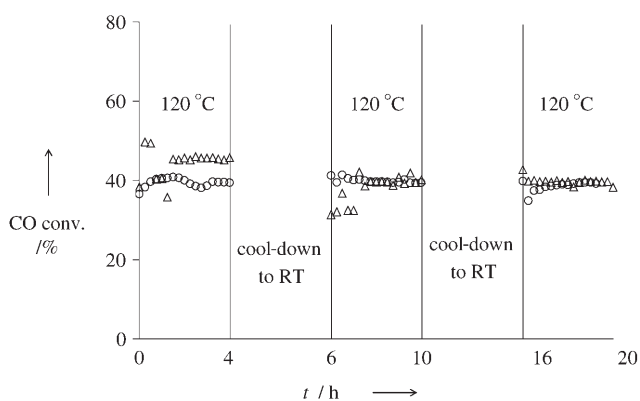


Figure 1. CO conversion versus time during a shut-down simulation of a PROX reactor using Au-ceria catalysts. Triangles: 0.28 AuCe(Gd)O_x; circles: 0.57 AuCe(La)O_x. Feed-gas mixture: 1:0.5:50:10:15:23.5 CO/O₂/H₂/H₂O/CO₂/He; W/F: 0.096 g s cm⁻³. conv. = conversion. W/F = catalyst weight/gas flow rate.

(see the Supporting Information). Similarly, a Pt-ceria catalyst prepared by deposition-precipitation on nanocrystalline ceria also shows a stable performance in the shut-down/start-up operation, except that the CO conversion is only 10% because of the lower selectivity of this catalyst toward CO oxidation.

In stark contrast to the above, shut-down under WGS reaction conditions severely deactivates the Au-ceria^[5] and Pt-ceria^[23] catalysts. Formation of cerium(III) hydroxycarbonate was identified by X-ray diffraction (XRD; see the Supporting Information). To probe the reasons for the deactivation of Au-ceria in the WGS shut-down process further, we conducted temperature-programmed oxidation (TPO) of a used catalyst, 5.8 AuCe(La)O_x, which was retrieved after shut-down in the full gas mixture. Fresh 5.8 AuCe(La)O_x was also tested for comparison. As shown in Figure 2, adventitious carbonates were present on both the fresh and used catalysts, with a peak for CO₂ centered at around 160 °C and a corresponding peak for H₂O at the same temperature. However, in the used catalyst only, another CO₂ elution took place, with a peak centered at a higher temperature (approximately 320 °C). Water was also eluted over the same temperature range. We attribute the second set of peaks

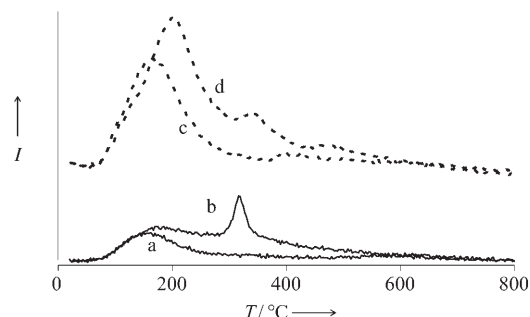


Figure 2. TPO profiles of 5.8 AuCe(La)O_x as prepared and after a WGS shut-down operation. a) CO₂ from the fresh catalyst, b) CO₂ from the used catalyst, c) H₂O from the fresh catalyst, d) H₂O from the used catalyst.

to the oxidative decomposition of cerium(III) hydroxycarbonate. We believe that this species forms and causes the deactivation of Au-ceria catalysts during WGS shut-down, thus explaining why activity could not be recovered when the WGS reaction was reheated to 300 °C after the stop-start cycle. This reaction gas mixture, containing no oxygen, can not bring about the decomposition of cerium(III) hydroxycarbonate. To examine the recovery of activity when cerium(III) hydroxycarbonate is decomposed, reaction rates over three materials were measured in the 11:26:26:7:30 gas mixture of CO/H₂O/H₂/CO₂/He. All samples were first aged in this gas mixture at 300 °C for 5 h. The reaction rate for the fresh 5.8 AuCe(La)O_x catalyst was 3.6 μmol CO₂ g_{cat}⁻¹ s⁻¹ at 175 °C. After treatment in the WGS shut-down/start-up process, the deactivated catalyst shows a rate of only 0.9 μmol CO₂ g_{cat}⁻¹ s⁻¹. When the deactivated catalyst was oxidized at 375 °C in 10:90 O₂/He to complete the decomposition of cerium(III) hydroxycarbonate, the WGS reaction rate at 175 °C was 3.3 μmol CO₂ g_{cat}⁻¹ s⁻¹, a value close to the fresh material. However, this process is not a practical way to regenerate the catalyst in fuel-cell applications.

The TPO of the used Au-ceria catalysts retrieved from the start/stop operation under PROX conditions did not show the presence of cerium(III) hydroxycarbonate (see the Supporting Information). This discovery motivated us to consider the addition of gaseous oxygen as a potential stabilizer of the WGS activity of Au-ceria as oxygen is the main variant in the gas composition between the PROX and WGS reaction conditions.^[26] Stability tests were carried out under the WGS reaction conditions with 0.5 mol % O₂ added into the feed-gas stream (see the Supporting Information). The long-term WGS stability of the 5.8 AuCe(La)O_x and 0.28 AuCe(Gd)O_x catalysts in the full reformate gas mixture (11:26:26:7:30 CO/H₂O/H₂/CO₂/He) with or without the addition of oxygen showed a clear trend of improved stability with the addition of 0.5 mol % O₂. The surface area of the used 0.28 AuCe(Gd)O_x catalyst when oxygen was added to the gas mixture was 123.6 m² g⁻¹, which is higher than the surface area (103.7 m² g⁻¹) of the used material after 50 hours on-stream without oxygen being present. It has been reported that the WGS gas composition controls the ratio of oxidized to neutral Au.^[5] In the absence of in situ characterization, it is difficult to establish the effect of the two different gas mixtures on the oxidation state of the Ce and Au components; in particular, we do not know whether stabilization of oxidized Au suppresses the sintering of the ceria nanoparticles. However, XRD analysis of the two used materials is indicative of the structural difference between them: the size of the ceria particle (based on <111> diffraction) of 0.28 AuCe(Gd)O_x exposed to the oxygen-laden gas mixture remained the same as for the fresh material (5.4 nm), whereas the size of the ceria particle grew to 5.8 nm in the sample used in the O₂-free WGS gas composition.

We ruled out a potential thermal effect from the addition of oxygen in the WGS reaction gas mixture. Whereas oxidation of H₂ or CO by the added oxygen would increase the bed temperature, the catalyst runs almost isothermally at 300 °C under the conditions used. For the hypothetical case in which the reactor would run adiabatically with the gas

composition used, we calculated an adiabatic temperature rise of 94 °C based on the combustion of 1 mol% CO with 0.5 mol% O₂ in the stream. Would operation at 400 °C therefore be the reason for the observed stability? Clearly, this is not the case as when the reaction was conducted at 400 °C in the full gas mixture without the addition of oxygen, the Au–ceria catalyst deactivated with time-on-stream (see the Supporting Information). The stabilization is not due to temperature rise. The maximum temperature increase in the gas film around the catalyst particles that results from the CO combustion reaction is <0.1 °C, and the maximum temperature gradient within the particles is 23.6 °C (see the Supporting Information). We propose that even such a small amount of oxygen in the reacting gas mixture can change the dynamic surface equilibrium of the Au–ceria catalyst and modify the amount of oxidized Au/Ce species, which in turn controls the structural stability and activity of the surface in the WGS reaction mixture. Further work is warranted to examine this behavior in detail.

Another sequence of tests was conducted to investigate the effect of oxygen addition on the catalyst stability in the shut-down/start-up operation. The WGS reaction was carried out at 300 °C in the full 11:26:26:7:0.5:29.5 gas mixture of CO/H₂O/H₂/CO₂/O₂/He over 5.8 AuCe(La)O_x for 2 hours (Figure 3), and the CO conversion was over 65%. When the

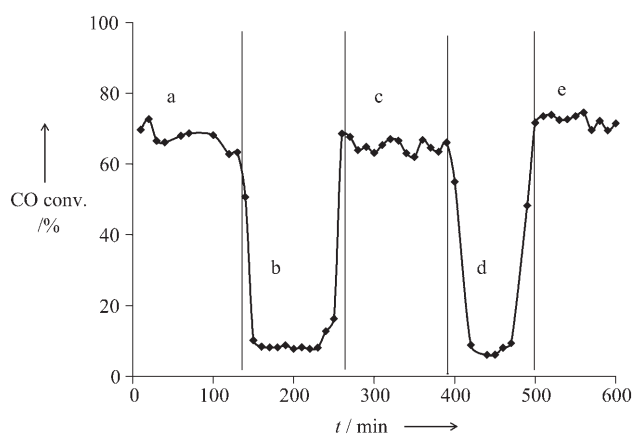


Figure 3. The effect of the addition of gaseous oxygen on 5.8 AuCe(La)O_x activity during a WGS shut-down/start-up operation. a) Reaction at 300 °C in feed gas; b) cool-down to room temperature in feed gas, except H₂O was preremoved; c) reaction at 300 °C in feed gas; d) cool-down to room temperature in feed gas; e) reaction at 300 °C in feed gas. Feed-gas mixture: 11:26:26:7:0.5:29.5 CO/H₂O/H₂/CO₂/O₂/He; S.V. = 30 000 h⁻¹. S.V. = space velocity.

heater was turned off, the same gas mixture, but without H₂O, was kept flowing through the reactor during the cooling transient (2 h), and the WGS reaction ceased. However, CO oxidation continued to occur at temperatures below 50 °C, thus accounting for the almost complete conversion of oxygen by CO oxidation. High CO conversion was recovered when the WGS reaction was restarted at 300 °C. The second cooling process was carried out in the full gas mixture (with 26% H₂O present). Even in the presence of the gradually condensing water vapor, CO oxidation also took place at low temper-

ature. Upon reheating, there was no decrease in the conversion of CO. Thus, shut-down/start-up in the full WGS gas mixture with the addition of 0.5 mol% oxygen does not affect the subsequent activity of the catalyst. Similar stabilization of the activity of the Au–ceria catalyst was observed in the shut-down (to room temperature)/start-up (at 150 °C) cyclic operation of the WGS reaction with 0.5 mol% O₂ present in the full WGS reaction gas mixture (see the Supporting Information). Both XRD and TPO analyses confirm that no cerium(III) hydroxycarbonate was formed during these cyclic tests.

How does oxygen prevent the deactivation of Au–ceria catalysts in the WGS reaction even during shut-down at room temperature? If oxygen stabilizes the activity, the oxygen concentration at the reactor outlet has to have a finite value. Otherwise, only a part of the catalyst bed can be under a higher oxygen potential, while the rest of the bed would deactivate as usual. The outlet oxygen concentration was estimated to be 930 ppm based on the rate of CO oxidation measured at 25 °C for this type of catalyst. The value measured experimentally was close at 726 ppm. Thus, oxygen is present throughout the catalyst bed and prevents the deactivation of ceria. From our findings, it appears that the oxygen potential of the gas, and not CO oxidation, is the critical factor for the observed stabilization, as clearly shown in Figure 4. Accordingly, in the shut-down process, CO was removed from the gas mixture during the cooling process to

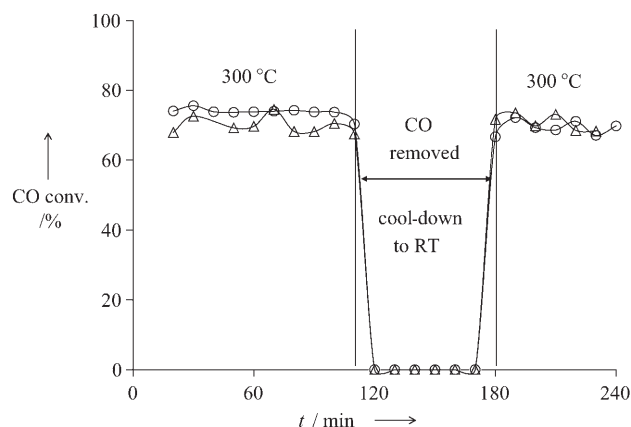


Figure 4. A stable WGS shut-down/start-up operation with 5 AuCe(La)O_x and 0.64 AuCe(Gd)O_x catalysts in the presence of added oxygen (CO was removed during the cooling process). Circles: 5 AuCe(La)O_x; triangles: 0.64 AuCe(Gd)O_x. Feed-gas mixture: 11:26:26:7:0.5:29.5 CO/H₂O/H₂/CO₂/O₂/He; S.V. = 30 000 h⁻¹.

eliminate the effect of CO oxidation. Almost all of the oxygen added broke through at the exit of the reactor when the temperature was lower than 60 °C (hydrogen oxidation is also quenched at temperatures lower than 60 °C). When CO was added into the gas and the WGS reaction was restarted at 300 °C, full recovery of the activity was achieved. Evidently, the added oxygen oxidizes Ce^{III} to Ce^{IV}, thus preventing the formation of cerium(III) hydroxycarbonate. The TPO profile of the used 5 AuCe(La)O_x catalyst retrieved from this process is shown in Figure 5. CO₂ elution from the used catalyst is

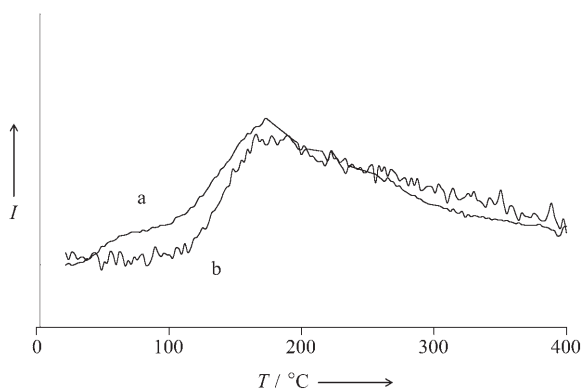


Figure 5. TPO profiles of fresh and used 5 AuCe(La) O_x catalyst after a WGS shut-down operation (CO was removed during the cooling process). a) Elution of CO_2 from used material, b) elution of CO_2 from fresh material. Test gas: 20:80 O_2/He ($50\text{ cm}^3\text{ min}^{-1}$ (NTP)); heating rate: 5°C min^{-1} .

similar to the fresh material, thus proving that cerium(III) hydroxycarbonate did not form in the oxygen-laden WGS reaction gas mixture.

During the shut-down/start-up process, the addition of 0.5 mol% O_2 to a 10:10:60:7:13 gas mixture of $CO/H_2O/H_2/CO_2/He$ did not stabilize the WGS activity of PtCe(La) O_x (see the Supporting Information). Pt-ceria has a much higher light-off temperature for CO oxidation than Au-ceria and does not sustain CO oxidation under shut-down conditions. It is possible that the oxygen potential in this particular gas mixture with very high H_2 content (60%) is not high enough to keep Pt-ceria free of carbonate. The oxygen potential was changed by varying the ratio of O_2/H_2 (Figure 6). We found that the addition of 1 mol% O_2 in the 11:26:26:7:30 gas mixture of $CO/H_2O/H_2/CO_2/He$ was enough to stabilize this type of catalyst and prevent its deactivation. The higher concentration of oxygen gave better recovery than 0.5 mol% O_2 , thus confirming that the oxygen potential is the key factor

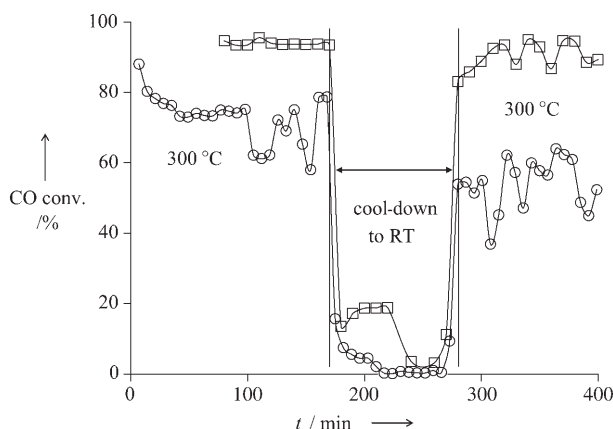


Figure 6. Oxygen potential effect on Pt-ceria WGS shut-down/start-up activity. Catalyst: 2.2 PtCe(La) O_x ; squares: 1 mol% O_2 in feed gas; circles: 0.5 mol% O_2 in feed gas. Feed-gas mixture: 11:26:26:7:0.5:29.5 or 11:26:26:7:1:29 $CO/H_2O/H_2/CO_2/O_2/He$; S.V. = $50\,000\text{ h}^{-1}$; catalyst was run at 300°C for 3 h, then cooled to room temperature during shut-down with gas flowing for approximately 2 h, then reheated to 300°C .

controlling the deactivation of ceria-based catalysts. Pt-ceria catalysts require a higher oxygen potential to stabilize their WGS activity relative to Au-ceria catalysts. This behavior may be attributed to over-reduction of ceria caused by Pt.^[22] There was no improvement in the Pt-ceria stability by adding 0.5 mol% O_2 in the gas stream in a time-on-stream stability test at 300°C , but the CO conversion was increased. Hence, the selectivity to CO oxidation was higher than hydrogen oxidation at 300°C (see the Supporting Information).

In summary, we have reported herein that in the presence of a small amount of gaseous oxygen Au-ceria or Pt-ceria catalysts show remarkable stability in the WGS reaction in the full fuel-gas mixture both at low and high temperatures and, very importantly, in a cyclic shut-down/start-up operation. Therefore, nanostructured Au-ceria or Pt-ceria materials can be developed as active and stable catalysts for the WGS reaction. As Au-ceria catalysts are also very active for the PROX reaction, it is possible to combine the WGS and PROX reactors in one unit containing the Au-ceria catalyst. This approach has a clear advantage for application to fuel-gas clean-up for fuel-cell use under realistic operating conditions.

Experimental Section

High-content (≈ 5 atom%) Au-ceria catalysts were prepared by deposition/precipitation of Au onto nanocrystalline ceria prepared separately (see the Supporting Information), whereas low-content (< 0.6 atom%) Au-ceria catalysts were prepared either by leaching weakly bound Au from the high-content Au-ceria samples with a solution of sodium cyanide^[4] or by a one-pot gelation/coprecipitation (UGC) method using urea as the precipitation agent.^[14] The catalysts are denoted as $a\text{ AuCe(La)}O_x$ or $a\text{ AuCe(Gd)}O_x$, where a is the Au content in atomic percent, Ce(La) O_x is 10 atom% La-doped ceria, and Ce(Gd) O_x is 10 atom% Gd-doped ceria. The PtCe(La) O_x catalyst was prepared by incipient wetness impregnation (IMP) of the same nanocrystalline ceria. WGS reaction tests were conducted at atmospheric pressure in a heated quartz-tube microreactor containing the catalyst powder as a packed bed. The feed- and product-gas streams were analyzed by a HP-6890 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The WGS gas mixture molar composition was 11:26:7:26:30 $CO/H_2O/CO_2/H_2/He$; whereas the molar composition of the gas mixture for the PROX reaction was 1:0.5:10:15:50:23.5 $CO/O_2/H_2O/CO_2/H_2/He$. Characterization techniques used include Brunauer-Emmet-Teller (BET), XRD, and TPO analysis. TPO was used to investigate the carbon deposition or carbonate presence in the used catalysts. The catalysts in fine-powder form were oxidized at a heating rate of 5°C min^{-1} from room temperature to 400 or 800°C in 20:80 O_2/He ($50\text{ cm}^3\text{ min}^{-1}$ at normal temperature and pressure (NTP)). An on-line residual gas analyzer (MKS-model RS-1) was used to detect CO, CO_2 , H_2O , and O_2 .

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