DEACTIVATION OF SUPPORTED GOLD WATER GAS SHIFT CATALYSTS
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Introduction
An emerging application for the water gas shift (WGS) is in the production of hydrogen-rich gas for proton exchange membrane (PEM) fuel cells. The WGS is used to remove most of the CO, a poison to most fuel cell electrocatalysts, from the steam reforming and/or partial oxidation exhaust. The WGS reactor dominates the fuel processor mass, volume, and cost.

Catalysts composed of nanocrystalline gold particles supported on reducible oxides have been demonstrated to be highly active for a number of reactions including WGS. With regard to the activity, the gold particle size is very important, and its size must be small enough to lose metallic character and increase its electronegative character. The particle size dependency requires delicate preparation methods. The preferred method is deposition-precipitation. The support usually does not contribute to the catalytic activity, but synergetic effects have been observed in reducible oxide supported gold catalysts.

In some cases supported gold catalysts have been reported to be substantially more active for WGS than commercial Cu based catalysts. It has, however, also been observed that supported gold catalysts are very susceptible to deactivation and therefore may not be suitable for commercial application. It is claimed this deactivation is due to over-reduction of the support by the reformate. Results from our work are not consistent with this deactivation mechanism. These results along with a tentative mechanism for deactivation will be presented in this paper.

Experimental
Sample preparation. A 10 wt% Au/CeO2 catalyst was prepared using the deposition-precipitation method. A gold precursor (HAuCl4·3H2O) was deposited and precipitated onto the CeO2 support. The support was suspended in 100 ml of water with stirring. A Na2CO3 solution was used to keep the pH at 10 during precipitation. The catalyst was aged, carefully washed at 60 °C then dried at 80°C under vacuum for 6 h. The resulting material had a surface area of 120m2/g. The commercial Cu-Zn-Al catalyst was obtained from Süd Chemie Ltd.

Activity measurement. Approximately 15-30 mg of catalyst was loaded in a quartz microreactor. Silica was used as an inert diluent. The catalyst was reduced prior to the activity measurement with a mixture containing 4% H2 in N2. The catalytic properties were measured at atmospheric pressure and temperatures ranging from 200 to 240 °C using a reactant gas whose composition simulates reformate from gasoline partial oxidation (CO, H2O, CO2, H2 and N2 concentrations of 10, 22, 6, 43 and 19 mol%, respectively). An HPLC pump was used to feed H2O (0.04ml/min liq.) to the reactant. The space velocity was high enough to minimize transport limitations, and the particle size was adjusted to minimize the pressure drop as well as transport limitations. The effluents were analyzed using a SRI gas chromatograph with single Carboxen 1000 column.

Characterization. The catalyst was characterized using x-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) and sorption analysis. The XRD analysis was carried out using a Rigaku Rotaflex DMAX-B rotating anode x-ray diffractometer with a CuKα radiation source operated at 40 kV and 100 mA. In-situ FT-IR analysis was performed using a Mattson Galaxy 5000 spectrometer equipped with a Harrick high temperature reaction cell. The sample pellet included inert silica. A Micromeritics AutoChem 2910 was used for all sorption techniques.

Results and Discussion
The initial WGS activity for the Au/CeO2 catalyst was three times higher than that of a commercial Cu-Zn-Al catalyst, however, its activity decreased by more than 50 % during the first 12 hours on-stream when the CO conversion was limited to 15%. The deactivation rate was significantly slower when the catalyst was evaluated at CO conversions near 95%. Considering the excesses of H2O, H2, N2 and CO2, this result suggested that the CO content had the most significant effect on the deactivation behavior.

To explore the effect of CO, the Au/CeO2 catalyst was pretreated with H2, CO, and a mixture of H2 and CO (20% each balanced with N2). Figure 1 shows that H2 and CO alone didn’t affect to the initial deactivation behavior, however, the catalyst was deactivated severely when treated with the H2/CO mixture.

![Figure 1. The effect of H2/CO on deactivation of the WGS activity](image)

Figure 2. In-situ FT-IR spectra after CO/H2 treatment

![Figure 2. In-situ FT-IR spectra after CO/H2 treatment](image)
We used FT-IR spectroscopy to investigate the surface chemistry after the treatment with the CO/H₂ mixture. The spectra are shown in Figure 2, and they illustrate an increase in the amount of carbonate on exposure to the reactant or H₂/CO mixture. There are two possible mechanisms for carbonate formation. Consumption of the hydroxyls and CO₂ could explain the formation of Au-HCO₃ on the surface. Cerium carbonates could also be produced under the experimental conditions employed. Cerium carbonates have been identified on the surfaces of other supported noble metal catalysts during WGS⁵.

**Conclusions**

The gold catalyst was more active than a commercial Cu-Zn-Al catalyst, but deactivated very fast. We believe that this deactivation was due to formation of carbonates on the surface. Formation of the carbonate is typically reversible, and they were removed by calcination. The initial activity was fully recovered after the carbonates were removed.

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**References**


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**Figure 3.** Reaction rates for fresh and reactivated Au/CeO₂ catalyst

We propose that deactivation of the Au/CeO₂ catalyst was caused by poisoning of the active sites by carbonates formed during the WGS reaction. If carbonates deactivated the surface, calcinations should regenerate the activity. In Figure 3, the typical deactivation trend during the first 12 hour on stream is illustrated. Subsequently, we calcined the sample with air at 400 °C followed by reduction with 4% H₂/N₂, the same reduction treatment as that used for the fresh sample. The catalyst was regenerated, and in particular more than 95% of the initial activity was recovered following calcination.

**Figure 4.** Desorption of CO₂ during calcination of fresh and deactivated catalysts.

We monitored the CO₂ produced using calcinations using a mass spectrometer. A significant amount of CO₂ was measured as shown in Figure 4. This observation is inconsistent with calcination simply resulting in a re-oxidation of the over-reduced support. It suggests that adsorbed carbonates on the active sites reacted with oxygen in the air to produce CO₂. Reductions in the NO uptakes are also consistent with carbonates decreasing the density of active sites.