Introduction
Ceria supported gold catalysts are among the most active catalysts known for the water gas shift (WGS) reaction with activities that are substantially higher than those of commercial Cu-based catalysts [1,2]. However, supported gold catalysts are susceptible to deactivation. We previously reported that the deactivation of Au/CeO₂ catalysts was caused by the deposition of carbonaceous species possibly formed on oxygen deficient sites [2]. We proposed that deactivation could be managed by conditioning the CeO₂ surface or by employing a dopant to minimize the oxygen deficiency. In this paper we explore the use of zirconia doping to suppress deactivation. Zirconia is reported to increase the mobility of oxygen on ceria surfaces [3]. This enhanced oxygen mobility could reduce the oxygen deficiency at the surface. In this paper, we used oxygen exchange experiments to investigate the role of zirconia on oxygen mobility.

Materials and Methods
The CeO₂-ZrO₂ supports were synthesized via decomposition of mechanically mixed (MM) and ball milled (BM) cerium and zirconium carbonates or hydrothermal synthesis of coprecipitated cerium and zirconium nitrates (CP). The resulting materials contained 10-40 mol% of ZrO₆ in CeO₂ and designated CeₙZr₁₋ₓO₂. These supports were used to prepare a series of 5 wt% Au/CeₓZr₁₋ₓO₂ catalysts via the deposition-precipitation method. The materials were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), in-situ Fourier Transform infrared (FTIR) and X-ray photoelectron spectroscopies (XPS), and sorption analysis. The isotopic oxygen exchange experiments were performed in a closed-loop gas recirculation system equipped with a mass spectrometer. The measurements focused on masses 32 (¹⁶O₂), 34 (¹⁶O¹⁸O), and 36 (¹⁸O₂). 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 reactions (10% CO, 22% H₂, 6% CO₂, 43% H₂, and 19% N₂).

Results and Discussion
Adding zirconia to the ceria support improved the activity maintenance (R_fina/R_initial) for the supported gold catalysts. In addition, the degree of activity maintenance varied significantly with the method used to prepare the support. For example, X-ray diffraction indicated that the CeₙZr₁₋ₓO₂-CP was a solid solution while the others contained segregated CeO₂ and ZrO₂ domains. Table 1 shows that the degree of deactivation was much lower for the CeₙZr₁₋ₓO₂-CP supported catalysts (solid solution with single phase) compared to the others prepared using CeₙZr₁₋ₓO₂-MM and CeₙZr₁₋ₓO₂-BM supports. To elucidate the effect of zirconia, the mobility of surface species on the supports was measured using isotope exchange experiments.

Table 1. Initial and final WGS rates at 240 °C for various Au/CeₓZr₁₋ₓO₂ catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Rate (µmol/g/s)</th>
<th>Final Rate (µmol/g/s)</th>
<th>R_fina/R_initial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/CeO₂</td>
<td>348</td>
<td>131</td>
<td>0.38</td>
</tr>
<tr>
<td>Au/Ce₉Zr₀.₁O₂ – MM</td>
<td>205</td>
<td>76</td>
<td>0.37</td>
</tr>
<tr>
<td>Au/Ce₉Zr₀.₃O₂ – BM</td>
<td>180</td>
<td>82</td>
<td>0.46</td>
</tr>
<tr>
<td>Au/Ce₉Zr₀.₆O₂ – CP</td>
<td>225</td>
<td>138</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Figure 1. Isothermal isotope oxygen exchange results measured at 400 °C for (a) Au/CeO₂ and (b) Au/Ce₉Zr₀.₆O₂-CP.

There was a greater degree of oxygen release, incorporation and exchange for the Au/Ce₉Zr₀.₆O₂-CP catalyst as compared to the Au/CeO₂ catalyst (Figure 1). These results are consistent with the addition of zirconia increasing the mobility of oxygen in the catalysts. The XPS results indicated that the formation of carbonates was reduced on zirconia compared to the ceria surface. Taken together, the results suggest that oxygen mobility played an important role in deactivation of the catalysts and in the formation of carbonate their surfaces.

Significance
The results from isotopic studies presented in this paper enhance our understanding of the mechanisms and driving forces for the deactivation of ceria supported gold, an important class of WGS catalysts.

References