

Mobility of Surface Species on Supported Gold Water Gas Shift Catalysts: Isotopic Exchange of $^{18}\text{O}_2$ with ^{16}O of CeO_2 and $\text{CeO}_2\text{-ZrO}_2$

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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/CeO_2 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 CeO_2 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 mobility on CeO_2 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 $\text{CeO}_2\text{-ZrO}_2$ 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 ZrO_2 in CeO_2 , and designated $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$. These supports were used to prepare a series of 5 wt% $\text{Au/Ce}_x\text{Zr}_{1-x}\text{O}_2$ 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 ($^{16}\text{O}_2$), 34 ($^{16}\text{O}^{18}\text{O}$), and 36 ($^{18}\text{O}_2$). The catalytic properties were measured at atmospheric pressure and temperatures ranging from 200 to 240 °C using a reactant gas whose composition simulates reformat from gasoline partial oxidation reactions (10% CO , 22% H_2O , 6% CO_2 , 43% H_2 , and 19% N_2).

Results and Discussion

Adding zirconia to the ceria support improved the activity maintenance ($R_{\text{Final}}/R_{\text{Initial}}$) 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 $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2\text{-CP}$ was a solid solution while the others contained segregated CeO_2 and ZrO_2 domains. Table 1 shows that the degree of deactivation was much lower for the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2\text{-CP}$ supported catalysts (solid solution with single phase) compared to the others prepared using $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2\text{-MM}$ and $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2\text{-BM}$ 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 $\text{Au/Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts

| Sample | Initial Rate ($\mu\text{mol/g/s}$) | Final Rate ($\mu\text{mol/g/s}$) | $R_{\text{Final}}/R_{\text{Initial}}$ |
|---|--------------------------------------|------------------------------------|---------------------------------------|
| Au/CeO_2 | 348 | 131 | 0.38 |
| $\text{Au/Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2\text{-MM}$ | 205 | 76 | 0.37 |
| $\text{Au/Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2\text{-BM}$ | 180 | 82 | 0.46 |
| $\text{Au/Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2\text{-CP}$ | 225 | 138 | 0.61 |

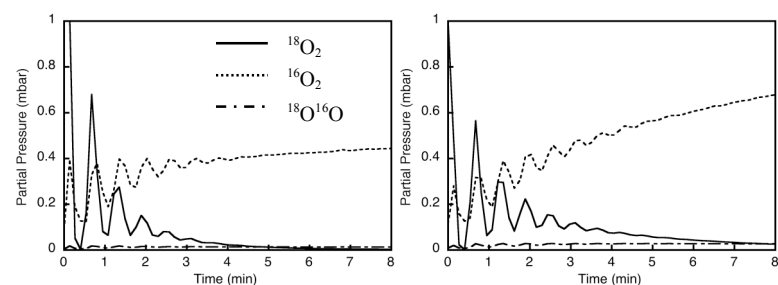


Figure 1. Isothermal isotope oxygen exchange results measured at 400 °C for (a) Au/CeO_2 and (b) $\text{Au/Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2\text{-CP}$.

There was a greater degree of oxygen release, incorporation and exchange for the $\text{Au/Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2\text{-CP}$ catalyst as compared to the Au/CeO_2 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-ceria surface 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

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