

Reaction-Relevant Gold Structures in Au-CeO₂ and Au-Fe₂O₃ Catalysts and Structure sensitivity of the Water-Gas Shift Reaction

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Introduction

Au-CeO₂ and Au-Fe₂O₃ are among the most active catalysts reported to date for the catalytic oxidation of carbon monoxide by water in low-temperature WGS [1-5], the specific activity of these materials on two supports are the same and only Au-O-Ce and Au-O-Fe species are the active sites for the reaction [6]. Recently we reported the gold structural evolution in Au-CeO₂ under WGS conditions [7] and a strong shape effect of CeO₂ single crystals on the Au-CeO₂ activity for the WGS [8]. In this work, fundamental studies of the gold structural evolution during WGS and shape effects of Fe₂O₃ nanocrystals are reported to further probe the activity/stability of active sites at the nano-scale. We follow the gold structural evolution in-situ with reaction temperature and gas composition using XANES and EXAFS, and examine the shape effect of Fe₂O₃ crystals on Au-Fe₂O₃, trying to identify the similarity of Au-O-Ce/Fe sites responsible for the observed activity. Detailed microscopy studies using the aberration-corrected microscopes at ORNL complement this investigation.

Materials and Methods

2at.% Au-Fe₂O₃ was purchased from the World Gold Council (WGC) and 0.7at.% Au-Fe₂O₃ was obtained by leaching weakly bound gold from the parent 2at.% Au-Fe₂O₃. Nano iron oxide single crystals with different crystal shapes were prepared and gold was introduced by deposition-precipitation. Low-temperature WGS reaction activity tests were conducted at atmospheric pressure with the catalyst in powder form in a packed-bed flow reactor. The gas streams were analyzed by a HP-5890 gas chromatograph equipped with a thermal conductivity detector. Several techniques such as in-situ XANES/EXAFS/XRD, XPS, TPR and HREM were used to characterize the catalysts. On the other hand, Au deposited on Fe₃O₄ (111) in UHV was examined to investigate the importance of the atomic scale interaction of the metal and oxide using STM/STS.

Results and Discussion

From results of XPS and in-situ XANES/EXAFS, the fresh leached materials only retain strongly bound oxidized gold species. This is further confirmed by aberration-corrected HREM images. The coordination number (CN) of Au-Au grows after the WGS reaction, together with a decrease in CN of Au-O. Redispersion of gold on the iron oxide surface is observed after subsequent reoxidation in O₂/He. Similar reduction/redispersion phenomena were recently found on gold-ceria catalysts for the WGS reaction [7], as shown in Figure 1. Catalytic tests show that the initial activity (fully dispersed gold in Fe₂O₃) is maximum. STM/STS work focuses on the interaction of Au with the Fe₃O₄ (111) surface. Current data

show that gold atoms stabilized on a magnetite (111) surface after high-temperature annealing change the electronic properties of the iron oxide surface, consistent with the strong interaction found in powder samples. These results as well as data from catalytic activity tests, XRD, XPS and H₂-TPR analyses of gold-iron oxide samples will be discussed to explain the significance of Au-O-Fe sites for WGS activity. To maximize and stabilize the active sites by optimizing the design and synthesis of catalysts, more detailed investigation of gold supported on iron oxides with different shapes is underway, results of which will be included in the presentation.

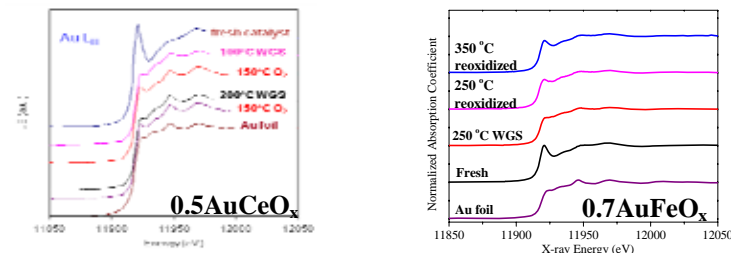


Figure 1. XANES data showing gold structural evolution in 0.5AuCeO_x and 0.7AuFeO_x catalysts under WGS conditions and various redox treatments. Gas mixture: 5%CO-3%H₂O-He; contact time: 0.36g.s/cc.

Significance

[Au-O-Ce] and [Au-O-Fe] species, not metallic gold, catalyze the WGS. The on-stream deactivation of gold-based samples is due to the loss of Au-O-support interaction instead of the formation of carbonate or gold particle sintering, which are the prevailing explanations in most of the pertinent literature. Redispersion of gold species in the used sample by oxidizing it at 350-400°C, can recover the activity. Increasing the oxygen potential in the reformat gas stabilizes the active sites and, in turn, the catalytic performance. Oxygen-assisted WGS operation is recommended for future process designs.

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