Elucidation of Structural and Catalytic Properties of Bimetallic Ni-Au for Pre-Reforming and On-Anode Steam Reforming of Hydrocarbons

Ya-Huei (Cathy) Chin, David L. King*, Yong Wang, Robert T. Rozmiarek, Hyun-Seog Roh, Jianli Hu, and Steve M. Heald
Pacific Northwest National Laboratory, Richland, WA 99354 (USA)
*David.King@pnl.gov

Introduction

Supported nickel catalysts are attractive for steam reforming of hydrocarbons due to their significantly lower cost relative to precious metal-based catalysts. Recent advancements in this area have demonstrated the potential for suppressing coke formation over the Ni surface by doping with a small amount of potassium, sulfur, or gold [1]. A previous Monte Carlo simulation study [1] examined the decoration of a Ni surface with Au atoms, and showed that Au preferentially occupied surface defects or grain boundaries on the Ni crystal. The elimination of high energy surface defects suppressed carbon nucleation. In the present study, we report an investigation of the chemical and structural modifications of nickel catalysts when Au is added at low concentrations as a promoter. Catalytic activity and activity maintenance for methane and butane steam reforming over supported Ni and bimetallic Ni-Au catalysts were examined in a microchannel reactor. In addition, to investigate the potential application of Au in promoting Ni anode SOFC internal reforming, a Au-modified Ni-YSZ anode was prepared and examined for activity and stability. Structural modifications as a result of Au addition to both supported Ni catalysts and Ni anode were investigated using X-ray absorption spectroscopy (XANES and EXAFS), XPS, DRIFT absorption, TEM, N_2O pulse reaction, and H_2 chemisorption in order to further understand this system and explain the catalytic results.

Results and Discussion

Figure 1a shows the Fourier transformed EXAFS spectra at Au L_3-edge for Ni-Au and monometallic Au supported on MgO-Al_2O_3, after oxidation at 500°C in air. The spectrum for Au/MgO-Al_2O_3 after reduction at 700°C is also shown. EXAFS analysis shows that oxidation at 500°C of the Ni-Au catalyst resulted in formation of segregated metallic Au clusters dispersed over MgO-Al_2O_3, Not surprisingly, analysis over Ni K-edge EXAFS indicates the presence of NiO oxidic species. Both samples provided spectra consistent with monometallic Au after reduction. TEM analysis provides further supporting evidence of such segregation of Au from Ni following oxidation.

Significant modifications to supported Ni-Au catalysts were observed following reduction at 700 °C. Figure 1b shows the Au L_3-edge Fourier Transform spectra over a series of 8.8% Ni/ MgO-Al_2O_3 catalyst samples promoted by varying amounts of Au. A new feature at 2.2 Å (uncorrected phase shift), which was ascribed to the bimetallic interaction of Ni-Au, appeared after reduction in 8%H_2/Ar at 700 °C for 2h. At a Au concentration below 0.2 wt%, the majority of the Au atoms were surrounded by Ni as the next nearest neighbor. Above 0.2 wt% Au, Au L_3-edge EXAFS indicates the presence of both Ni-Au and Au-Au interactions. The modification to the chemical environment and electronic states with addition of Au was further confirmed by XANES and apparent binding energy shift of Ni 2p core level photoelectron spectra.

As a result of this surface modification by Au addition, the steam reforming turnover rate of Ni dramatically decreases paralleled by a similar decrease in H_2 uptake via chemisorption and a reduction of N_2 formation in N_2O pulse reaction. Unlike the unpromoted 8.8% Ni/ MgO-Al_2O_3 sample, stability testing indicated that the Ni-Au bimetallic catalyst was stable under CH_4 steam reforming for over 6h with minimal coke deposition at a S/C of 1.25 and 650 °C, which is in agreement with a TGA reaction study carried out under severe deactivating conditions.

In addition to supported catalysts, Au modified Ni-YSZ anodes were examined to investigate the potential of using Ni-Au-YSZ anode for SOFC on-anode internal reforming. The goals are to suppress coke deposition without using excess steam and to lower the steam reforming activity for a better heat integration. This talk will cover the steam reforming activity and stability studies over both supported Ni-Au catalysts and Ni-Au anode. Spectrosopic and surface characterization results will be discussed to interpret the chemical and structural modifications of Au over Ni surfaces.

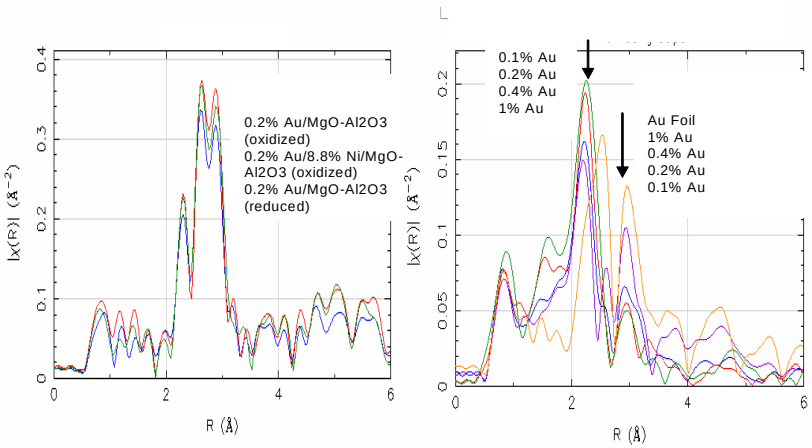

Figure 1a (left). Fourier transforms of Au L_3 EXAFS spectra over oxidized 0.2 wt% Au, 0.2 wt% Au/8.8 wt% Ni and reduced 0.2 wt% Au supported on MgO-Al_2O_3.
Figure 1b (right). Fourier transforms of Au L_3 EXAFS spectra over various Au promoted 8.8 wt% Ni MgO-Al_2O_3 after reduction in 8% H_2/Ar at 700 °C. Spectrum for Au foil is included for reference.

Generous support from the U.S. Department of Energy, Office of Fossil Energy, Solid State Energy Conversion Alliance (SECA) is gratefully acknowledged.

1 Bengaard, H.S., Nørskov, J. K., Sehested, J., Clausen, B.S., Nielsen, L.P., Molenbroek, A.M., and Rostrup-Nielsen, J.R., *J. Catal.* 209, 365 (2002).