SUPPORTED BINARY CATALYSTS FOR
DEHYDROGENATION OF METHANE

Naresh Shah1, Frank E. Huggins1, Devadas Panjala1,
Gerald P. Huffman1, A. Punnoose2, M.S. Seehra2

1University of Kentucky, Lexington, KY 40508-4005
2West Virginia University, Morgantown, WV 26506-6315

Introduction
Production of pure hydrogen from hydrocarbons, particularly methane, the major component of natural gas, has great practical importance. Traditionally, reforming and partial oxidation of methane are employed to produce synthesis gas, which, when followed by water-gas shift conversion of the CO in synthesis gas to CO2 and the consequent removal of CO2 produces a relatively pure hydrogen stream. However, this hydrogen stream still contains enough CO to poison the catalysts used in PEM electrochemical fuel cells. A reverse methanation reaction has to be carried out to reduce the CO concentration to sub-ppm levels.

Catalytic decomposition of undiluted methane to pure hydrogen and carbon was carried out in absence of any oxidizing medium with a variety of alumina supported binary metal catalysts. Nanoscale, binary, 0.5%M-4.5%Fe (M = Pd, Mo or Ni) catalysts supported on alumina reduced the decomposition temperature of undiluted methane by 400-500 °C relative to non-catalytic thermal decomposition. The product stream comprised of over 75-volume % of hydrogen and unconverted methane at reaction temperatures of 700 °C. The efficient removal of carbon from the catalyst surface in the form of nanotubes is believed to be the key factor influencing catalyst performance.

Figure 1 is a plot of hydrogen production by catalytic decomposition of methane at various reactor temperatures using pure Fe, pure Mo and binary Mo-Fe catalysts. The role that binary metals play in methane decomposition is clearly evident. Similar plots of hydrogen production by methane decomposition using other binary metal catalysts (Ni-Fe and Pd-Fe) show significantly higher activity than either Fe or the other secondary metal (Ni, Pd) alone.

This paper primarily deals with characterization of these highly active nanoscale binary alumina supported catalysts using a variety of analytical techniques, viz. x-ray absorption fine structure (XAFS) spectroscopy, x-ray diffraction (XRD), Mössbauer spectroscopy, and scanning (SEM) and transmission (TEM) electron microscopy. The synthesis and pre-treatment of the catalysts, as well as SEM/TEM characterization of the produced nanotubes, have been reported elsewhere.

As-prepared catalysts
Mössbauer and Fe K-edge XAFS spectroscopies confirmed that the iron in vacuum-dried, alumina-supported catalysts exists in the ferrihydrite structure. The radial structure functions of the Pd and Ni EXAFS indicate the presence of only one nearest neighbor oxygen shell implying either very small particles of oxide on alumina or incorporation in ferrihydrite. XAFS analysis indicates that Mo exists in the +6 oxidation state, probably as MoO3.

Pre-reduced catalysts
The as-prepared or pre-oxidized catalysts were not active for methane decomposition. The catalysts were activated by reduction at 700 °C for two hours and cooling in flowing hydrogen. However, Mössbauer and Fe EXAFS spectroscopic data showed that for all the catalysts, the reduction of Fe to the metallic state is not complete at 700 °C probably because iron reacted with the alumina support to form hercynite. Pre-reduction at 1000 °C is required to complete the reduction of all the Fe to metal. XRD studies of catalysts reduced at 700 °C only yielded lines due to the γ-alumina support, except for Pd-Fe, in which lines due to metallic Fe were also observed (figure 2). Both Pd XANES and Fe Mössbauer data showed that at 700 °C, Pd is easily reduced to metallic state and its presence appears to facilitate the reduction of Fe. Both Ni and Mo are partially reduced to the metallic state. Mössbauer spectroscopy showed the presence of a Fe3Mo phase in Mo-Fe/Al2O3 catalysts and the enhanced formation of a NiFe austenite phase in reduced Ni-Fe/Al2O3 catalysts. STEM investigation of the reduced catalyst further confirms the formation of alloy phase. Figure 3 shows a dark field STEM image and Al, Fe and Mo K-edge EDS maps of a pre-reduced Mo-Fe catalyst. Overlap of Mo and Fe images confirm formation of nanoscale Mo-Fe metallic alloy particles.
Catalysts after on-stream exposure

Exposure of the pre-reduced catalysts to flowing methane at 700 °C did not result in any significant changes in the XAFS spectra. Although methane is a carburizing atmosphere and the catalysts are very active in decomposing methane to produce large amounts of elemental carbon in form of nanotubes, the catalysts retain their metallic states. As shown in figure 4, XRD studies indicate that γ-alumina undergoes a phase transformation to δ-alumina when the pre-reduction step is carried out at a higher temperature (1000 °C instead of 700 °C). Besides lines due to alumina, XRD studies showed lines due to graphite and Fe_3C in all samples after on-stream exposure. Mössbauer spectroscopy indicated formation of austenite phase possibly due to incorporation of carbon in iron and/or stabilization by the secondary metal. A small amount (0-20%) of iron was also found in metallic state. Substantial amounts of iron were still in unreduced Fe^{2+} state probably as hercynite (FeAl_2O_4) spinel due to reaction of the iron with the support.

Acknowledgement. This research was supported by the U.S. Department of Energy through both the Division of Fossil Energy (FE) under the National Energy Technology Laboratory (NETL) and the Division of Energy Efficiency and Renewable Energy (EE) under the Office of Advanced Automotive Technologies, under contract No. DE-FC26-99FT40540.

References