571a Carbide and Nitride Supported Water Gas Shift Catalysts

Timothy E. King, Shyamal K. Bej, and Levi T. Thompson

The water-gas-shift (WGS) reaction is an important industrial reaction used to remove CO from synthesis gas during H_2 production. There is growing interest in its use in fuel processing applications. Molybdenum carbide and nitride has been demonstrated to be an active WGS catalyst. Recently we discovered that the introduction of a metal onto these carbide and nitride supports significantly improved the WGS activity. In fact, some formulations were more active than a commercial Cu-Zn-Al catalyst. Of the several factors affecting the performance of these materials, the amount and type of metal, and pretreatment conditions were the most influential. In this paper, we discuss the effect of these variables on selected carbide and nitride supported Ni and Pt catalysts. The pretreatment gas consisted of 100% H_2/He, 15% CH_4/H_2, or 100% NH_3 with temperatures ranging from 200-700 °C. The metal loading was varied between 0-8 wt %. Results were compared with those for unsupported Mo_2C and Mo_2N catalysts, and a commercial Cu-Zn-Al catalyst.

Catalyst activation occurred at temperatures in excess of 300 °C all gases. The mixture containing 15% CH_4/H_2 produced materials with the highest WGS activities. Pretreatment in H_2 at temperatures in excess of 450 °C resulted in a loss of activity. This loss in activity was a function of the Pt content; the higher the Pt content, the lower the activity loss. For catalysts pretreated in 15%CH_4/H_2, there was no appreciable loss in WGS activity. Similar results were seen when Mo_2N was used as a catalyst support.

Following pretreatment in 15%CH_4/H_2 at 590 °C, the WGS rates for the Pt/Mo_2C and Pt/Mo_2N catalysts increased with Pt loading. The results suggest a greater synergistic interaction was seen between Pt and the Mo_2N support than with the Mo_2C support at high loadings. For both carbide and nitride supports, the WGS rates saturated with a Pt loading of 7.5 wt. %. Unlike the supported Pt catalysts, the maximum loading possible for Ni on either Mo_2C or Mo_2N was approximately 1 wt. %.

The addition of a metal facilitated activation of the catalyst. Hydrogen TPR results indicated that the addition of Pt to Mo_2C lowers the reduction temperature by 50 °C when compared to unsupported Mo_2C. The addition of Pt or Ni lowered the recarburization temperature necessary to obtain the maximum WGS rate by 100 °C. Similar results were observed with the supported Ni catalysts. One explanation is that Pt and Ni participated in the dissociation of H_2 and this dissociated hydrogen spilled-over facilitating reduction of the support. Another possibility is that the metal assists in the dissociation of CH_4.

X-ray diffraction, temperature programmed reduction, pulsed chemisorption, thermal gravimetric analysis and BET surface area experiments were used to characterize the materials to gain further understanding. These and other results will be discussed.