

Methane Dry Reforming: Effects of Pressure and Promoters on Carbon Formation

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INTRODUCTION

Natural gas, estimated to last well into the 21st Century, is composed mainly of methane and it is in direct competition with coal and oil as a fuel for the production of electricity. Use of natural gas which contains more hydrogen and fewer carbons than coal and oil will significantly reduce pollutants such as CO₂, SO_x, NO_x, and trace elements such as Sb, As, Be, Cl, Cd, Co, Cr, Pb, Hg, Mn, Ni, and Se.

In recent years there have been considerable efforts to develop catalysts for converting natural gas to fuels, fuel additives, and chemicals. Oxidative coupling of methane to ethane and ethylene and subsequent conversion of these chemicals to liquid fuel is one approach that has attracted great interest.^{1,2} A key to success for an economically viable process is the development of a catalyst that converts methane selectively into higher hydrocarbons, preferably ethylene, at a higher yield than current technology.

Early work at NETL demonstrated that it is possible to convert methane to higher hydrocarbons (C₂⁺ products) via oxidative coupling of methane, in which oxygen and methane were fed over a catalyst.^{3,4} Despite intensive efforts in this area, little progress has been achieved, mainly because the products of methane conversion, ethane and ethylene, are more reactive than methane and are converted to carbon oxides at a lower temperature compared to methane.⁶

The other method of producing fuels, fuel additives, and chemicals is via production of synthesis gas (a mixture of carbon monoxide and hydrogen) by steam reforming, partial oxidation, or dry reforming. Reforming methane combined with the water-gas shift reaction produces syngas suitable for synthesis of ammonia, methanol, Fischer Tropsch products, and chemicals. The cost of syngas production in converting natural gas to liquid fuels is more than 60% of the total cost. Therefore, reducing the cost of syngas will significantly affect the economics of gas to liquids processes. Most of these reactions are carried out catalytically and the development of new and novel catalysts is very important for utilization of natural gas, particularly for producing liquid fuels.

Recently many researchers have concentrated their efforts toward catalytic reforming of methane with carbon dioxide. This process can be very useful for converting thermal energy into chemical energy. For example, energy losses in combustion/gasification systems and in advanced gas turbines can be captured by reacting natural gas with the by-product of combustion (CO₂) over a catalyst producing syngas which can be converted into liquid fuels and chemicals, ultimately increasing the system efficiency. Although this concept has many environmental and economic incentives, unfortunately, there are no commercial processes for reforming of methane with CO₂. The main problem is that there are several carbon-forming reactions associated with this concept that deactivate the conventional steam reforming, nickel-based, catalysts. Nickel catalyzes carbon formation via hydrocarbon decomposition and CO disproportionation reactions, which greatly contributes to catalyst deactivation, specifically at higher pressures. Methane conversion decreases as the pressure increases due to water formation via the reverse water-gas shift reaction. Therefore, the challenge is to develop a catalyst which exhibits a high selectivity toward hydrogen and carbon monoxide without forming carbon. In this paper we report the preparation and testing of catalysts for dry reforming of methane to syngas at atmospheric and at higher pressures with and without promoters.

EXPERIMENTAL

Tungsten carbide catalyst was prepared as described in the U.S. patent 5321,161 by mixing 12 grams (0.03 mole) of tungsten hexachloride (WCl_6) with 8.6 grams (0.09 mole) of guanidine hydrochloride, $HN=C-(NH_2)_2 \cdot HCl$.⁷ The mixture was heated from room temperature to 200 °C in two hours, held at this temperature for two hours, then the temperature was raised to 750 °C for seven and one-half hours and held at this temperature for two hours under nitrogen. Molybdenum carbide catalyst was prepared by temperature-programmed reduction of molybdenum oxide in a flow of 11.6% ethane or methane in hydrogen at a flow rate of 55 ml/min.

The nickel-based catalysts were prepared from water soluble nitrate solutions with proper metal ratios. A 0.3-m long quartz (1/2" stainless steel tube used for higher pressure) reactor tube (6.35-mm o.d., 4.0-mm i.d.) with a quartz thermocouple well was used as a fixed-bed reactor with 0.01-0.5 grams of catalyst (-28/+48 mesh) held in place by quartz wool. A thermal conductivity detector was used with a 1-m by 3.2-mm-o.d. stainless steel molecular sieve 5A column and a 3.66-m by 3.2-mm-o.d. stainless steel HayeSep C (80/100 mesh) column at isothermal oven temperatures of 120 and 50 °C, respectively. Argon was used as carrier gas at 20 ml/min.

RESULTS AND DISCUSSION

A series of carbide and Ni-based catalysts were prepared and tested at several reaction conditions for reaction of methane with CO_2 . Pure SiC was tested at 950 °C and no significant methane or CO_2 conversions were observed. Higher activity was obtained for pure tungsten carbide, which was tested at 650, 750, and 850 °C as shown in Figure 1. At temperatures of 650 and 750 °C methane and CO_2 conversions were less than 15% and H₂/CO ratio was about 0.2. A dramatic increase in CH_4 and CO_2 conversions plus a H₂/CO ratio of 1.1 was obtained at higher temperatures of 850 and 950 °C (not shown). Methane conversion of less than 15% and CO_2 conversion of less than 17% were obtained for commercially produced Mo_2C . However, when molybdenum carbide was prepared by temperature-programmed reduction of molybdenum (VI) oxide with a mixture of 11.6% ethane or methane in hydrogen, methane and CO_2 conversions of more than 90% were obtained at 950 °C and 1.0 atm. A lower H₂/CO was obtained at lower temperatures. Molybdenum carbide catalyst was tested for 16 hrs and the results are shown in Figure 2. Higher catalytic activity was observed for the catalyst prepared with ethane mixture compared to that prepared with methane mixture. Molybdenum carbide supported on TiO_2 was prepared by mixing MoO_3 with TiO_2 in an ethyl alcohol slurry. The dried mixture was reacted with 11.6 vol.% ethane in hydrogen to form carbide. About 90% of methane and 100% of CO_2 were converted to hydrogen and CO with a ratio of 1.0 and the test continued for 2.5 hours at 900 °C without deactivation or forming significant amounts of carbon.

We also tested two commercial nickel-based catalysts. The results for R-67 are shown in Figure 3. Similar results were obtained for G-56B catalyst. Although these catalysts showed a similar activity and selectivity compared to carbide and noble metal catalysts at temperatures higher than 850 °C, none of the experiments lasted more than five hours because a significant amount of carbon formed on the catalyst bed plugging the reactor tube. Zero activity in Figure 3 means that there was no flow due to carbon formation that plugged the reactor. We prepared a series of Ni-based catalysts promoted with alkali and alkali earth metals which were tested for more than 360 hours at 850 °C and at atmospheric pressure. The amount of carbon deposition was reduced significantly due to addition of alkali and alkali earth metals. The promoted catalyst was tested at 7 and 13 atm for 6 hours. Methane and CO_2 conversions decreased as the pressure increased.

CONCLUSIONS

A series of carbide and Ni-based catalysts were prepared and tested at several reaction conditions for reaction of methane with CO_2 . The Ni-based and carbide catalysts were very active and selective for producing syngas. However, a significant amount of carbon formed on the commercial Ni-based catalysts, plugging the reactor after five hours on stream. The amount of carbon deposition was reduced significantly due to addition alkali and alkali earth metals. Methane conversion decreased as the pressure increased, due to water formation via the reverse

water-gas shift reaction. Molybdenum carbide catalyst appeared to be stable for ten hours, at atmospheric pressure, and after that methane and CO₂ conversions slowly decreased due to oxidation of molybdenum carbide to molybdenum oxide.

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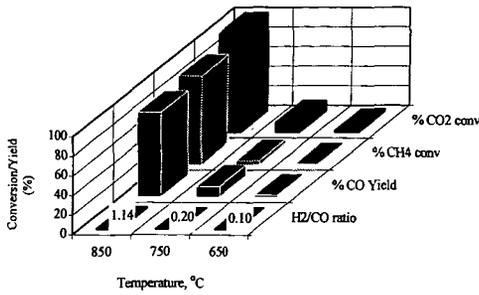


Figure 1. Effect of temperature on dry reforming of methane over Tungsten carbide, $CH_4/CO_2=1.15$, GHSV = $5040 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$

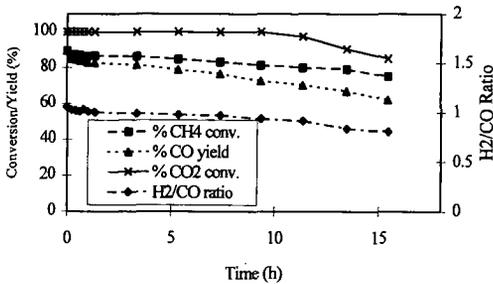


Figure 2. Dry reforming of methane over molybdenum carbide, $CH_4/CO_2=1.16$, GHSV = $5040 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ at $850 \text{ }^\circ\text{C}$

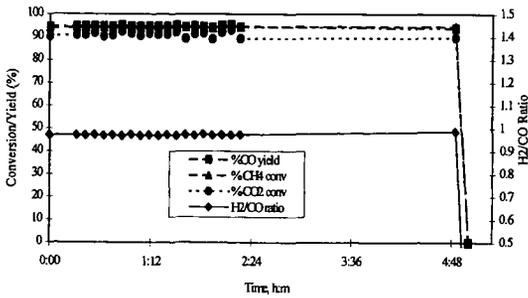


Figure 3. Dry reforming of methane over Ni-based catalyst (R-67), CH_4/CO_2 ratio = 1.1, GHSV = $5040 \text{ cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, at $750 \text{ }^\circ\text{C}$, no flow after 5 hours.