

# Dry Reforming of Methane with Tungsten Carbide Catalyst

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## INTRODUCTION

In recent years, the dry reforming of methane for the production of synthesis gas using carbon dioxide has received considerable attention as compared to conventional steam reforming (1-5). Methane reforming with carbon dioxide is appealing because it produces synthesis gas with higher purity and lower H<sub>2</sub>/CO ratio than either partial oxidation or steam reforming. This lower H<sub>2</sub>/CO ratio is a preferable feedstock for the Fischer-Tropsch synthesis with iron catalysts (2,3). From the environmental perspective, methane reforming is enticing due to the reduction of carbon dioxide and methane emissions as both are viewed as harmful greenhouse gases. Besides, CO<sub>2</sub> is frequently a significant component of natural gas. Consequently, reforming with CO<sub>2</sub> eliminates extra processing steps for synthesis gas production.

Commercially, nickel is used for methane reforming reactions due to its lower cost compared to noble metals. However, nickel also catalyses carbon formation via methane decomposition and CO disproportionation (Boudouard reaction) (4). Thus, notable efforts have been concentrated on developing new catalysts, which are resistant to carbon formation. Sulfur passivated nickel catalysts and noble metals have been shown to exhibit resistance to carbon formation. But the low activity of sulfur passivated nickel and the high cost of noble metals promotes continued research for more active or less expensive catalysts.

Recently, there has been considerable interest in the catalytic properties of metal carbides (5,6). The production of metal carbides is abundant and their price is cheap compared to noble metals. Boudart suggested that they could replace the rare and expensive noble metals in catalysis (7). Identifying better catalysts would reduce process costs for methanol, ammonia, and Fischer-Tropsch plants. There have been reports of tungsten and molybdenum carbide catalysts being active for the methane dry reforming reaction without any significant deactivation at high pressures and temperatures (5). The purpose of this study is to investigate the performance of the cobalt tungsten carbide catalyst [Co<sub>6</sub>W<sub>6</sub>C] for the dry reforming of methane to produce synthesis gas and to understand the behavior of the reaction rates with varying partial pressures of methane and carbon dioxide.

## **EXPERIMENTAL**

The unsupported cobalt tungsten carbide [Co<sub>6</sub>W<sub>6</sub>C] catalyst was obtained from Nanodyne Inc. The details of the preparation procedure can be obtained from U.S. Patent 5,138,111 (8). The catalyst-testing unit is as shown in Figure 1 and is similar to that used by Liu *et al.* (9). The entire system is computer controlled from which most of the operating conditions can be set. The computer logs in data automatically at operator-determined intervals. The unit has four lines for gas feed, each being independently controlled by a mass-flow controller. The differential reactor consists of a silica-lined stainless-steel tube placed in a single-zone furnace. The silica lining on the stainless tubes was applied at Restek Corp. The catalyst is placed in the center of the reactor, with the quartz chips placed upstream and downstream of the catalyst. The product stream is sampled immediately downstream using a gas-sampling valve. There is a cooling system between the reactor outlet and the sampling valve. The products are analyzed on-line by a gas chromatograph (GC), which provides quantitative analysis for He, H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>O. Helium is used as the internal standard while argon serves as the carrier gas. The GC feed line from the sample loop is maintained at a temperature of 150 °C by wrapping the line with heating tapes. This prevents the water in the product stream from condensing before reaching the GC inlet. The reactor effluent (vapor phase) that is not passed through the GC is vented after passing through a scrubber. The entire unit is located in a walk-in hood. The computer continuously monitors alarms for CO and for flows of reactive gases, hood velocity, ambient hood temperature, reactor temperature, reactor pressure and electric power. The unit automatically shuts down in the event of hood failure, fire, power and air supply failure, or CO leak detection or if the gas flows or reactor temperature exceed any of the preset operating ranges.

## **RESULTS AND DISCUSSION**

The silica-lined stainless steel reactor tube was first packed with quartz chips without any catalyst (blank run) to determine the reactivity of the reactor at different temperatures and feed ratios. Results show that the CH<sub>4</sub> and CO<sub>2</sub> conversions for the blank runs are small. The conversions from the catalytic runs were obtained by subtracting the molar rates of formation of any species as obtained by the blank runs from those of the catalytic runs.

The unsupported cobalt tungsten carbide catalyst was tested for activity at various temperatures and feed ratios. The particle size of the catalyst used was less than 38 microns. The catalyst was found to be very stable at 850 °C for a period of over 90 hours with a feed ratio of CH<sub>4</sub>/CO<sub>2</sub> = 1 (Figure 2). The CH<sub>4</sub> and CO<sub>2</sub> conversions increased steadily with time at 850 °C and then stabilized at 82% and 78% respectively, with a H<sub>2</sub>/CO ratio close to 1. When the reaction temperatures were subsequently decreased, the conversions were found to decrease, but were also stable. A similar trend was observed for the H<sub>2</sub>/CO ratio, which decreases as reaction temperature decreases. These trends lead to a working hypothesis that the catalyst is undergoing certain phase transformations. Evidence to these transformations will become apparent when the X-ray diffraction patterns of the catalyst are obtained. The carbon balances obtained for the continuous experiments were better than 98%.

The catalyst was tested for activity at different partial pressures of CH<sub>4</sub> and CO<sub>2</sub> at 600, 550 and 500 °C. Figures 3 and 4 show the effects of varying the partial pressures of CH<sub>4</sub> and CO<sub>2</sub> on the reaction rates of methane reforming ( $r_{MR}$ ), reverse water gas shift ( $r_{RW}$ ), and carbon deposition ( $r_{CD}$ ) at 600 °C. Similar trends were observed at lower temperatures. The reaction rates increase initially with increasing partial pressure, but later on approach a constant value as the partial pressures reach a higher value. These observations suggest a Langmuir-Hinshelwood model for rate kinetics.

## **FUTURE WORK**

The future work includes testing the catalyst over a wider range of temperatures for different partial pressures of CH<sub>4</sub> and CO<sub>2</sub>. The short-term goal includes modeling the rate expressions to fit the Langmuir-Hinshelwood model for rate kinetics. The long-term objectives include (1) carrying out mixed reforming studies by introducing steam into the feed mixture and (2) X-ray diffraction studies of the fresh and used catalysts, in collaboration with Prof. M. Seehra at West Virginia University.

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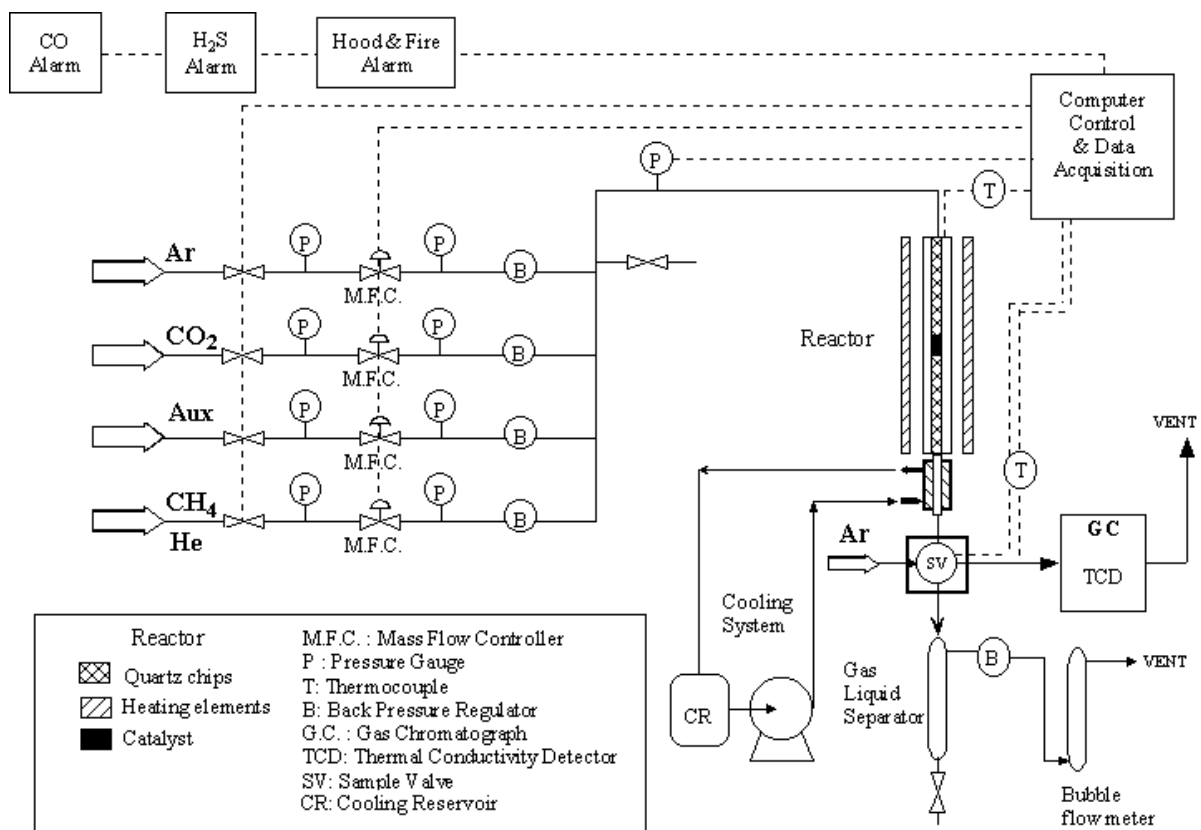


Figure 1. Flow sheet of the catalyst-testing unit

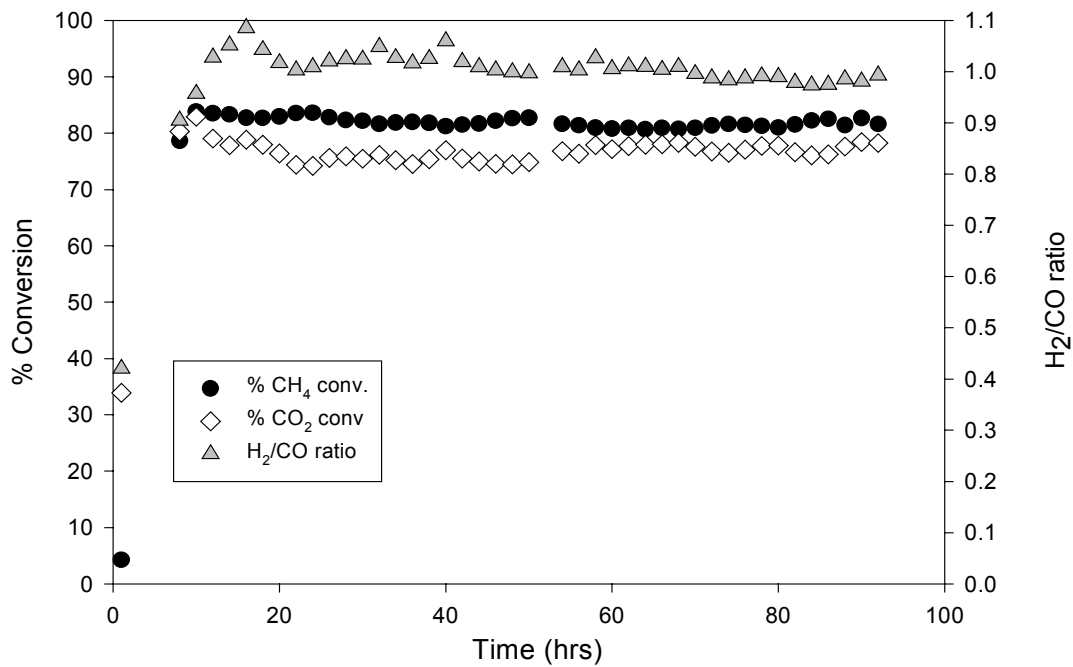


Figure 2. Lifetime study of the Co<sub>6</sub>W<sub>6</sub>C catalyst for the dry reforming reaction (850 °C, particle size < 38 microns, P<sub>CH<sub>4</sub></sub>= 1 bar, P<sub>CO<sub>2</sub></sub>= 1 bar)

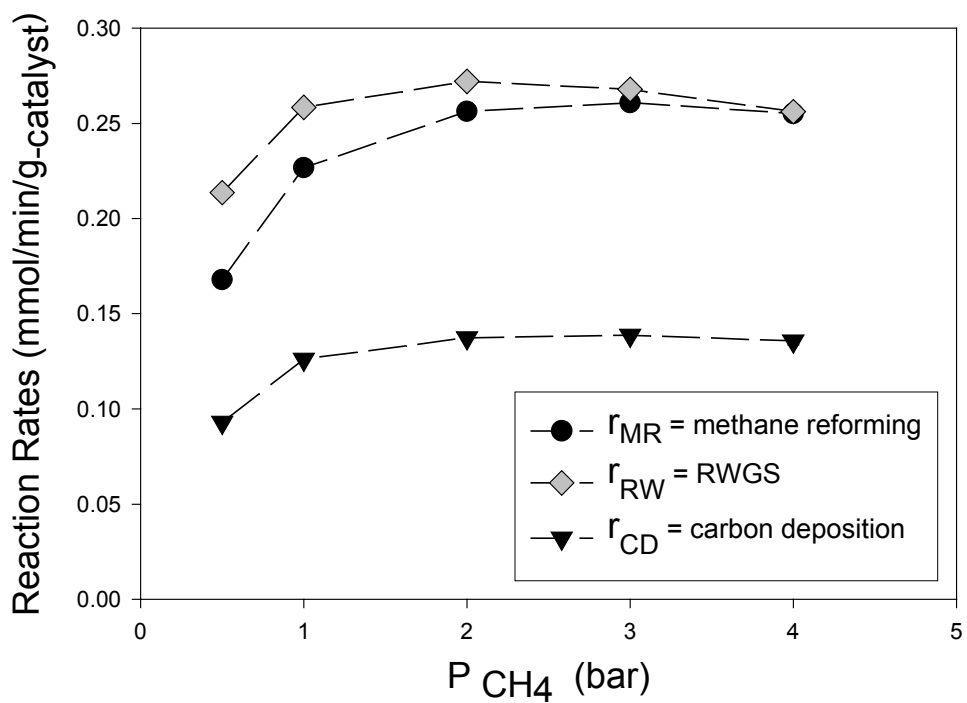


Figure 3. Effect of varying  $P_{CH_4}$  on the reaction rates ( 600 °C, particle size < 38 microns,  $P_{CO_2}$ = 1 bar)

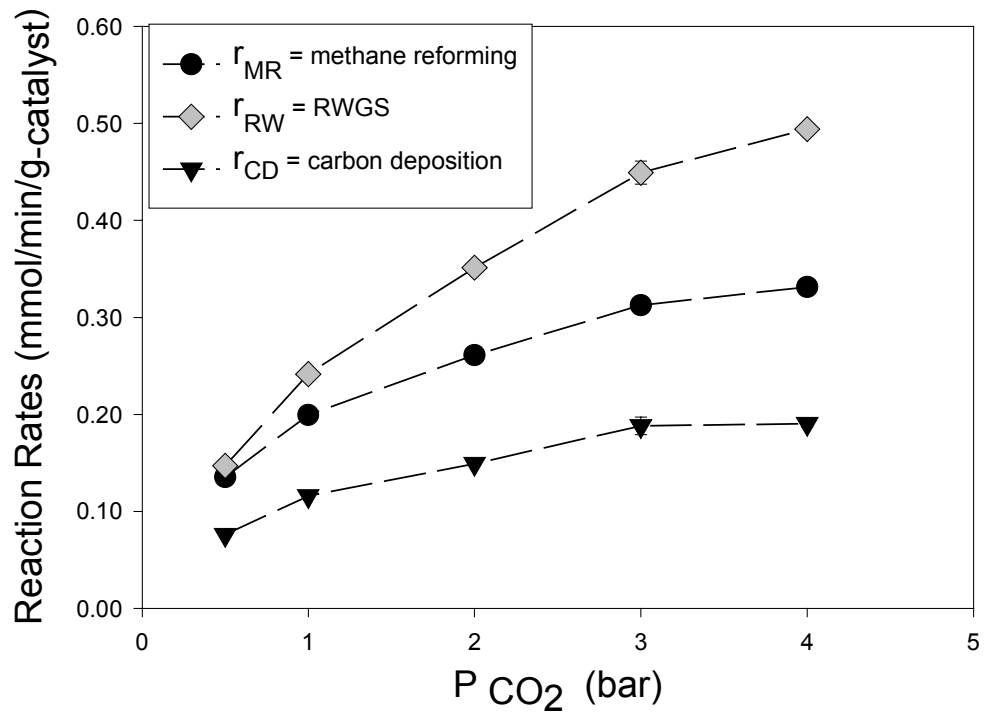


Figure 4. Effect of varying P<sub>CO<sub>2</sub></sub> on the reaction rates (600 °C, particle size < 38 microns, P<sub>CH<sub>4</sub></sub>= 1 bar)