

# Methane Reforming with Carbon Dioxide

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## Introduction

The reforming of methane with carbon dioxide for the production of synthesis gas is appealing because it produces synthesis gas with higher purity and lower H<sub>2</sub>-to-CO ratio than either partial oxidation or steam reforming.<sup>1</sup> Lower H<sub>2</sub>-to-CO ratio is a preferable feedstock for the Fischer-Tropsch synthesis of long-chain hydrocarbons. On 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.<sup>2</sup> Commercially, nickel is used for methane reforming reactions due to its inherent availability and lower cost compared to noble metals. However, nickel also catalyses carbon formation via methane decomposition and CO disproportionation (Boudouard reaction).<sup>3</sup> Thus, notable efforts have been concentrated on exploring new catalysts, which are resistant to carbon formation. Sulphur passivated nickel catalysts and noble metals have been shown to exhibit resistance to carbon formation.<sup>4</sup> But the low activity of sulphur passivated nickel and the high costs and limited availability of the noble metals have limited their application.

There has been considerable interest in the catalytic properties of metal carbides. The production of metal carbides is abundant and their price is cheap compared to noble metals. It has been suggested that they can replace the rare and expensive noble metals in catalysis. Identifying better catalysts would reduce process costs for methanol, ammonia, and Fischer-Tropsch plants. The objective of this research is to develop new metal carbide catalysts for syngas production from methane reforming with carbon dioxide.

## The Catalyst Testing Unit

The catalyst testing unit is shown in Figure 1. The unit is computer-controlled and is located in a walk-in hood. The computer monitors alarms for CO and H<sub>2</sub>S, and for flows of reactive gases, hood velocity, ambient hood temperature, reactor temperature, reactor pressure,

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<sup>1</sup> van Kuelen, *et al.*, *Journal of Catalysis*, **166**, 306 (1997).

<sup>2</sup> Bradford and Vannice, *Applied Catalysis*, **142**, 73 (1996).

<sup>3</sup> Claridge, *et al.*, *Journal of Catalysis*, **180**, 85 (1998).

<sup>4</sup> Rostrup-Nielsen, *Journal of Catalysis*, **85**, 31 (1984).

and electric power. The unit automatically shuts down in the event of hood failure, or CO leak detection, or if a gas flow or the reactor temperature exceeds the preset operating ranges.

The unit has four lines of gas feed, each independently controlled. The reactor is a stainless steel tube (SS 304L) placed in a single-zone furnace. The catalyst samples are placed in the center of the reactor between quartz chips. The product stream is sampled immediately downstream of the reactor at the pressure of the reactor and at a minimum temperature of 150°C. The products are analyzed on-line, using a Hewlett-Packard 5890 gas chromatograph. The Hayesep D packed column is connected to a thermal conductivity detector, which provides quantitative analysis for CH<sub>4</sub>, He, CO<sub>2</sub>, CO, H<sub>2</sub>, and H<sub>2</sub>O. Helium is used as an internal standard for quantitative analysis.

## **Results**

Preliminary experiments were conducted to check the working condition of the catalyst testing unit. Two catalysts were used for this purpose. The first catalyst was Ni/Al<sub>2</sub>O<sub>3</sub> obtained from United Catalyst, Inc. and the second catalyst was Pt/ZrO<sub>2</sub>, which was prepared in-house. Prior to catalytic testing, blank reaction tests were performed without catalysts to determine the activity of the reactor and the thermocouple itself. Results show that the reactor and thermocouple were not catalytically active up to 750°C. However, at reaction temperatures 800 and 850°C, the % CH<sub>4</sub> conversions were 1.23 and 1.29%, respectively.

## **Commercial Catalyst**

The commercial Ni/Al<sub>2</sub>O<sub>3</sub> catalyst has a BET surface area of 1.5-5 m<sup>2</sup>/g and pore volume of 0.1-0.2 cc/g. It contains 14%-wt. Ni, 80-86%-wt. Al<sub>2</sub>O<sub>3</sub>, and less than 0.1%-wt. C. The catalyst pellets were crushed and sieved into grains of 0.3-0.6 mm (10-20 mesh) and 90-125µm (120-170 mesh) in size. Typically, 300 mg of the catalyst was tested. As recommended by United Catalysts, Inc., the commercial catalyst was pretreated by heating to 149°C and holding that temperature for 2 hours. Then, the temperature was raised to 204°C and CO<sub>2</sub> gas was passed through the reactor for 1 hour, before adjusting to the desired reaction temperature. The feed ratio used was CH<sub>4</sub>: CO<sub>2</sub>: Ar = 1: 3.7: 4.9 with a total feed rate of 170 cc/min. Both small and large particle-size catalysts were tested at various reaction temperatures ranging from high temperature (700°C) to low temperature (400°C) with increasing and decreasing temperature modes.

Figure 2 shows an example of a chromatogram obtained from testing the commercial catalyst. Pure component injections were used to identify the major peaks. Figures 3 and 4 show examples of the % CH<sub>4</sub> and % CO<sub>2</sub> conversions obtained from running the commercial catalyst. As expected, the % conversions increase as the reaction temperature increases. Moreover, the smaller particle size catalyst has higher % conversion compared to that of the larger particle size catalyst. It was also found that this catalyst is very stable.

It was hypothesized that there were three major reactions taking place: methane reforming, reverse water gas shift (RWGS), and carbon deposition. Reaction rates were calculated based on these reaction models. Figure 5 shows the reaction rates of the three reactions at various reaction temperatures. The order of increasing reaction rates is: rate of carbon deposition < rate of methane reforming < rate of RWGS.

### **Pt/ZrO<sub>2</sub> Catalyst**

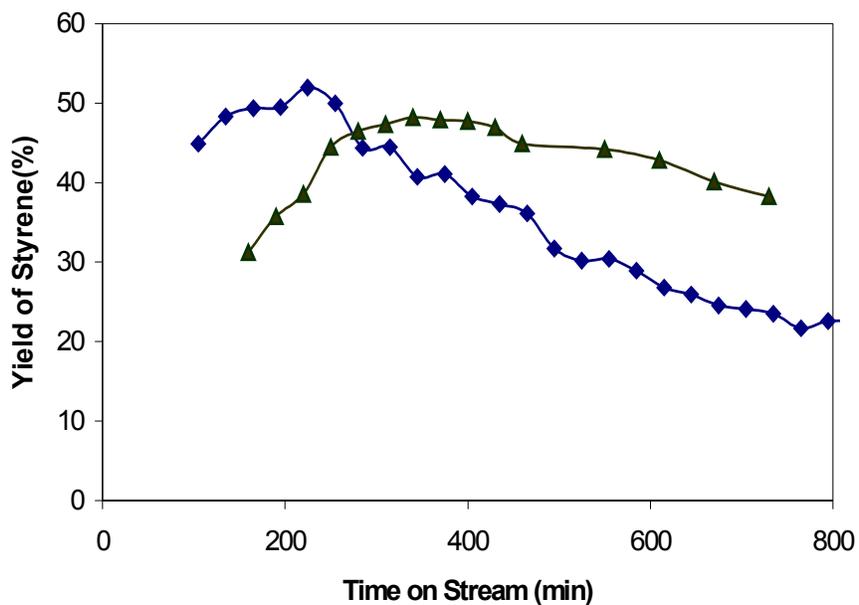
The Pt/ZrO<sub>2</sub> catalyst was prepared in our laboratory. Zirconium oxide powder, as received, was first calcined at 852°C for over 18 hours in flowing air. The calcined support was isostatically pressed into pellets at 6000 bar. The pellets were crushed and sieved to give grains having diameters between 0.3-0.6mm. The grains were impregnated with H<sub>2</sub>PtCl<sub>6</sub> solution to yield 0.31%-wt. Pt. The water was removed by heating the catalyst at 92°C for 2 hours in a rotating evaporator followed by drying overnight at 92°C in static air. The impregnated grains were calcined at 650°C for 15 hours. The BET surface area of the catalyst was determined to be 4-5 m<sup>2</sup>/g. The Pt/ZrO<sub>2</sub> catalyst was pretreated in flowing H<sub>2</sub> at temperatures between 400 to 800°C, *in situ*, before testing. The same reaction conditions, feed ratio, and feed rate used in testing the commercial catalysts were used in testing the Pt/ZrO<sub>2</sub> catalyst.

Results show very low % conversions for the Pt/ZrO<sub>2</sub> catalyst. Pretreating at higher temperatures with H<sub>2</sub> showed no significant effect on its conversion. Later, it was found that the catalyst was deactivating within 2 hours into the reaction. Thus, this prepared catalyst was found to be very unstable. No further study was made for this catalyst.

## Future Work

The catalyst testing unit was found to be in good working condition. Future work includes preparation and catalyst testing of molybdenum and tungsten carbide catalysts. A new experimental setup will be fabricated for the preparation of molybdenum carbide. Catalytic testing for  $\text{Co}_6\text{W}_6\text{C}$  catalyst is now in progress.

**Figure 1. Effect of  $\text{CO}_2$  on Dehydrogenation of Ethylbenzene with  $\text{Fe}/\text{Al}_2\text{O}_3$  Catalyst**



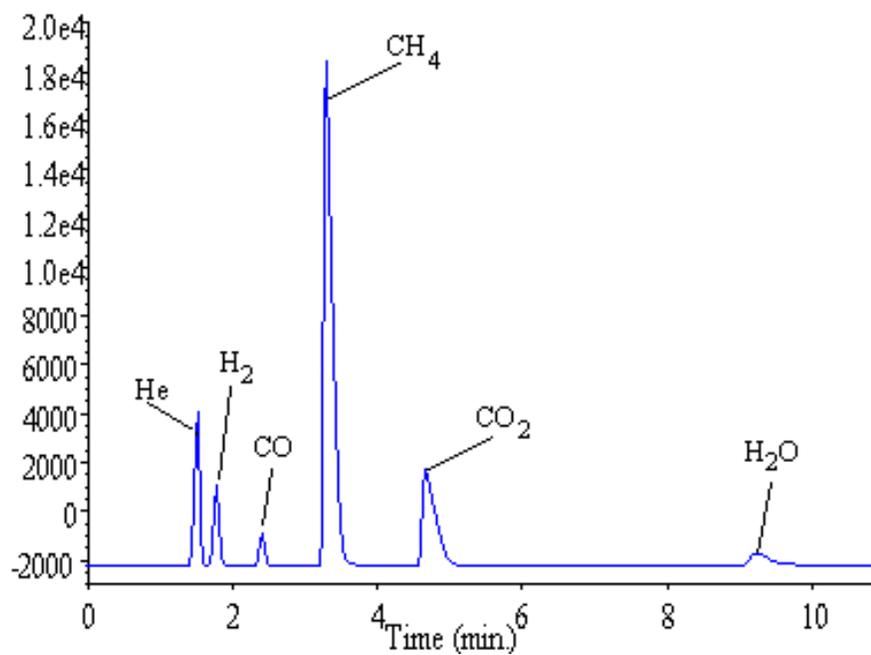
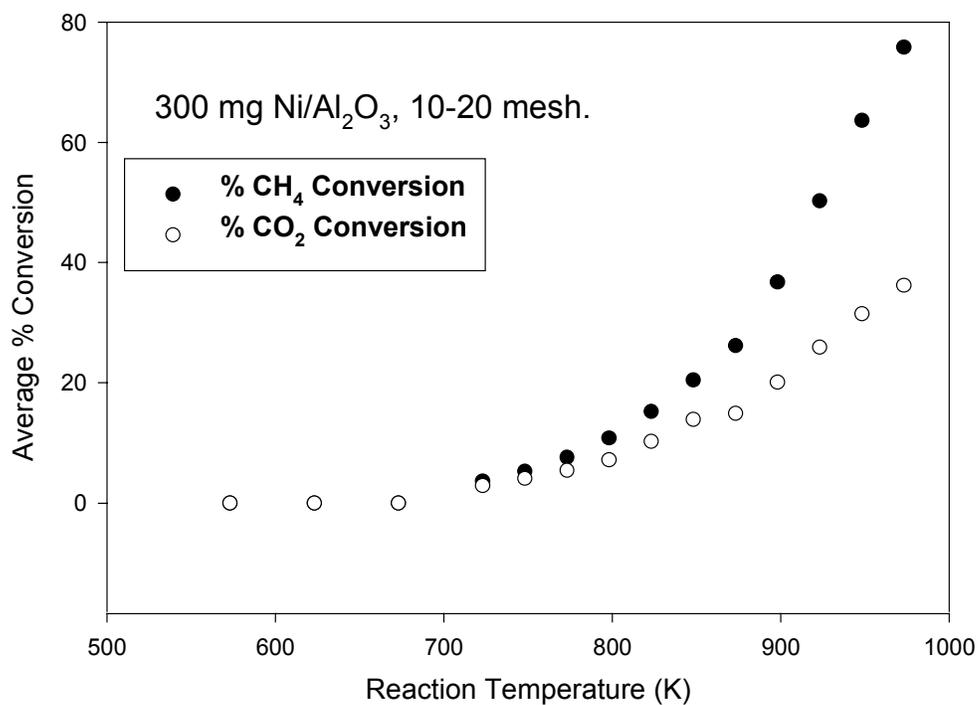
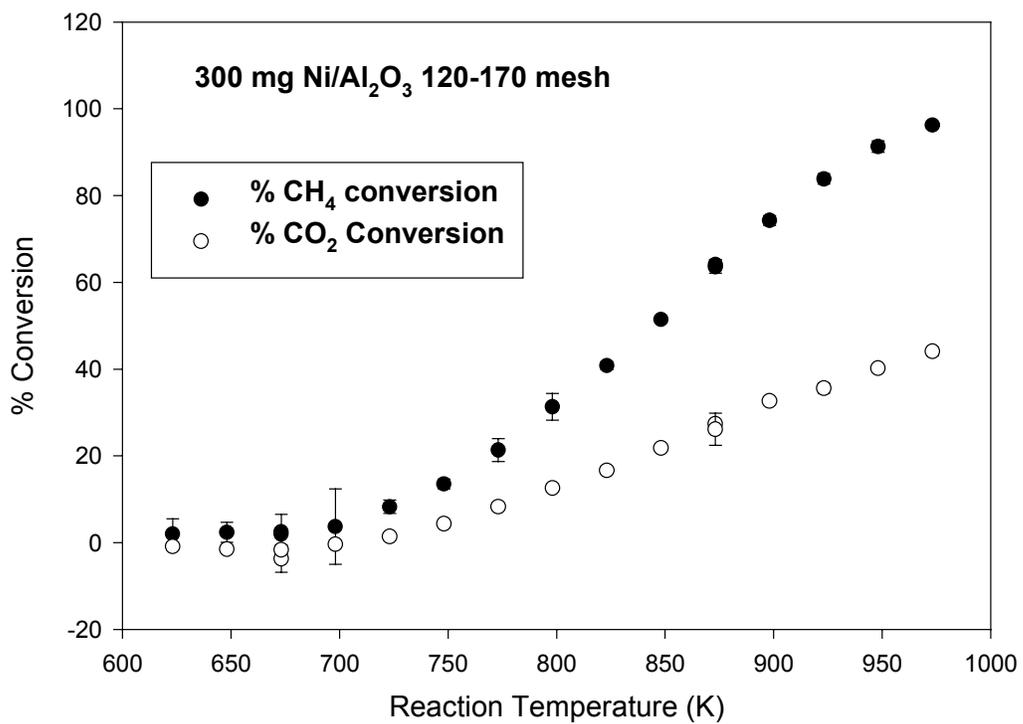


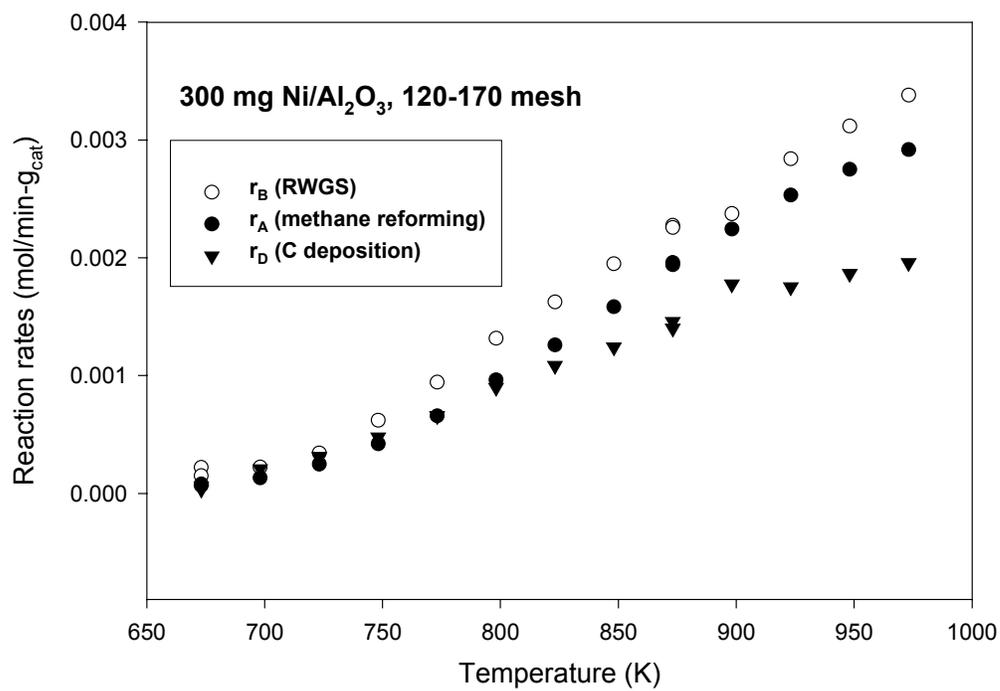
Figure 2- A typical chromatograph obtained from Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (120-170 mesh size).  
Reaction conditions: T= 700 °C; feed ratio = CH<sub>4</sub>: CO<sub>2</sub>:Ar = 1:3.7:4.9



**Figure 3- Conversion plots for large particle size commercial catalyst with decreasing temperatures**



**Figure 4- Conversion plots for small particle size commercial catalyst with decreasing temperatures.**



**Figure 5- Reaction rates of methane reforming, RWGS, and C-deposition with decreasing temperature using small particle size commercial catalyst.**