

# Hydrogen Production by Hydrocarbon Cracking

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## Introduction

The goal of this project is to develop catalysts and reaction conditions for catalytic cracking of hydrocarbons to produce hydrogen. Methane is the major component of natural gas. Traditionally, dry (with CO<sub>2</sub>) reforming, wet (with H<sub>2</sub>O) reforming and partial oxidation of methane is employed to produce synthesis gas and hydrogen is produced using the water-gas shift. In this project, we are exploring non-oxidative methods to produce hydrogen from hydrocarbon. Due to the lack of oxygen, there is no formation of carbon monoxide, which is a poison for catalysts used in fuel cells.

In the current project, nanoscale, binary, iron-based catalysts, supported on alumina, are being investigated to determine their activities for catalytic decomposition of hydrocarbons and reforming reactions.

## Catalyst synthesis

In previous work, our group has demonstrated that nanoscale, binary ferrihydrite catalysts are readily formed by co-precipitation techniques.<sup>(1,2)</sup> The metal component of these binary ferrihydrite (FHYD) catalysts typically consists of 90-95% iron and 5-10% of a secondary element. Characterization of FHYD<sub>90-95</sub>/M<sub>5-10</sub> (M = Si, Al, Mo, Cr) using a range of techniques (TEM, XRD, XAFS spectroscopy, Mössbauer spectroscopy, SQUID magnetometry) has established that:

1. Particle sizes in the as-precipitated state are typically in the range from 5 to 50 nm.
2. The secondary element is often concentrated at the surfaces of the particles.
3. Binary ferrihydrites resist agglomeration much better than pure ferrihydrite at elevated temperatures.

To date, we have synthesized binary FHYD/M catalysts with M = Mo, W, V, Pd, Ir, Ni, and Si. Pure ferrihydrite treated with a citric acid solution to promote chemisorption of organic ions at the particle surfaces<sup>(3)</sup> was also prepared. The surface organic ions also cause the ferrihydrite nano-particles to resist agglomeration at elevated temperatures.

Supported catalysts were prepared by first adding an aqueous solution of metal catalyst to a slurry of  $\gamma$ -alumina (150 m<sup>2</sup>/gram) and then precipitating metal oxyhydroxide on alumina by raising the pH of the slurry with ammonia. The slurry was washed with distilled water and dewatered. The paste was extruded and vacuum dried to form pellets.

For this report, we are limiting the discussion of reaction study results to the following three catalyst systems:

1. 5% Fe on alumina
2. 0.5% Mo - 4.5% Fe on alumina
3. 5% Mo on alumina

## Reaction and gas analysis system

Methane is a good carburizing agent and will carburize 304 and 316L stainless steel reactors rapidly. Hence, all of the current experiments were performed in quartz reactors. To quantify the gaseous reaction products, we use a six port sampling valve with a 50 microliter sample loop that does not saturate the TCD detector.

Methane can be cracked non-catalytically at higher temperatures. This thermal cracking reaction is dependent on the contact time and temperature. Since we have to use quartz wool to support the catalyst in the down-flow reactor, the amount of quartz wool used was kept constant to minimize any effect on the variation in contact time.

### **Catalyst pre-treatment**

The as-prepared, supported, iron catalyst exists in a ferrihydrite structure. Prior to reaction, the catalysts was subjected to the following three pretreatments.

- (1) The catalyst was oxidized under flowing air at 1000 °C.
- (2) The catalyst was reduced in flowing hydrogen (50ml/min) for two hours at 1000 °C to produce a metallic state.
- (3) The catalyst was first reduced to the metallic state in H<sub>2</sub> at 1000 °C, then carburized by treatment in flowing 20% CH<sub>4</sub> – 80% H<sub>2</sub> at 700 °C to produce metal carbide.

### **Results**

Figure 1 shows changes in methane and hydrogen concentrations by volume in the product stream as different catalysts in their reduced states are heated to increasing temperatures. It is clear that the catalysts have a profound effect in lowering the temperature for methane cracking as compared to thermal cracking over an alumina support with no added metal catalyst. Both the 5% Fe/Al<sub>2</sub>O<sub>3</sub> and the 0.5%-4.5%Fe/ Al<sub>2</sub>O<sub>3</sub> lower the methane decomposition temperatures by over 300 °C.

Though not so obvious, it is also noted that the product gas stream did not contain any appreciable amounts of C<sub>2</sub> and higher hydrocarbons. Since both hydrogen and methane are measured independently, it is seen that the product stream contains more than 98% of only these two gases. Except in the case of non-catalytic cracking, there was a complete absence of any liquid products in all experiments.

Figure 2 shows the effect of different pretreatments on 5%Fe/alumina catalysts for the same cracking reaction. For clarity, no methane concentrations are plotted (they are complimentary to the hydrogen concentrations). Oxidized Fe is not an active catalyst. However, under reaction conditions, it may be converted to metallic/carbide state, resulting in the observed activity. There is not much difference in activity between metallic and carbide phase. However, this may be due to rapid conversion of the metallic phase to carbide phase under reaction conditions. Thus, the catalyst state may be quite similar in both reaction experiments, even though they were pre-treated to produce different states. However, the carburized catalyst produced much more carbon and the experiment had to be stopped due to reactor clogging by carbon at temperatures above 850 °C.

### ***References:***

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2. G.P. Huffman, J. Zhao and Z. Feng, "Binary Ferrihydrite Catalysts," U.S. Patent Number 5,580,839, Dec.3, 1996.
3. J. Zhao, Z. Feng, F.E. Huggins, and G.P. Huffman, *Energy & Fuels*, **1994**, 8, 1152-1153.

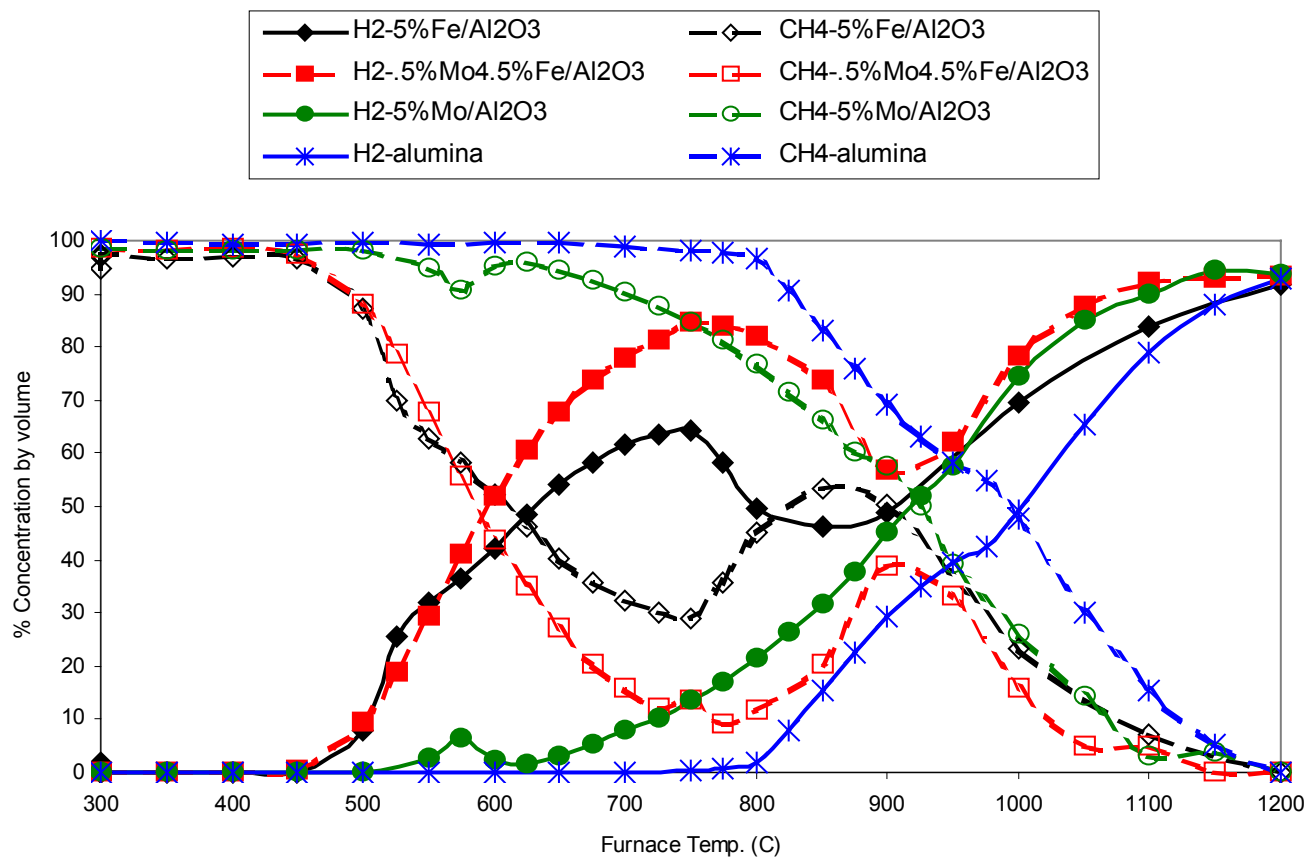


Figure 1. Catalytic CH4 cracking - Effect of catalyst - 5%Fe/Al2O3, 0.5%Mo/4.5%Fe/Al2O3 and 5%Mo/Al2O3 - Reduced in hydrogen at 1000C for 2 hrs.

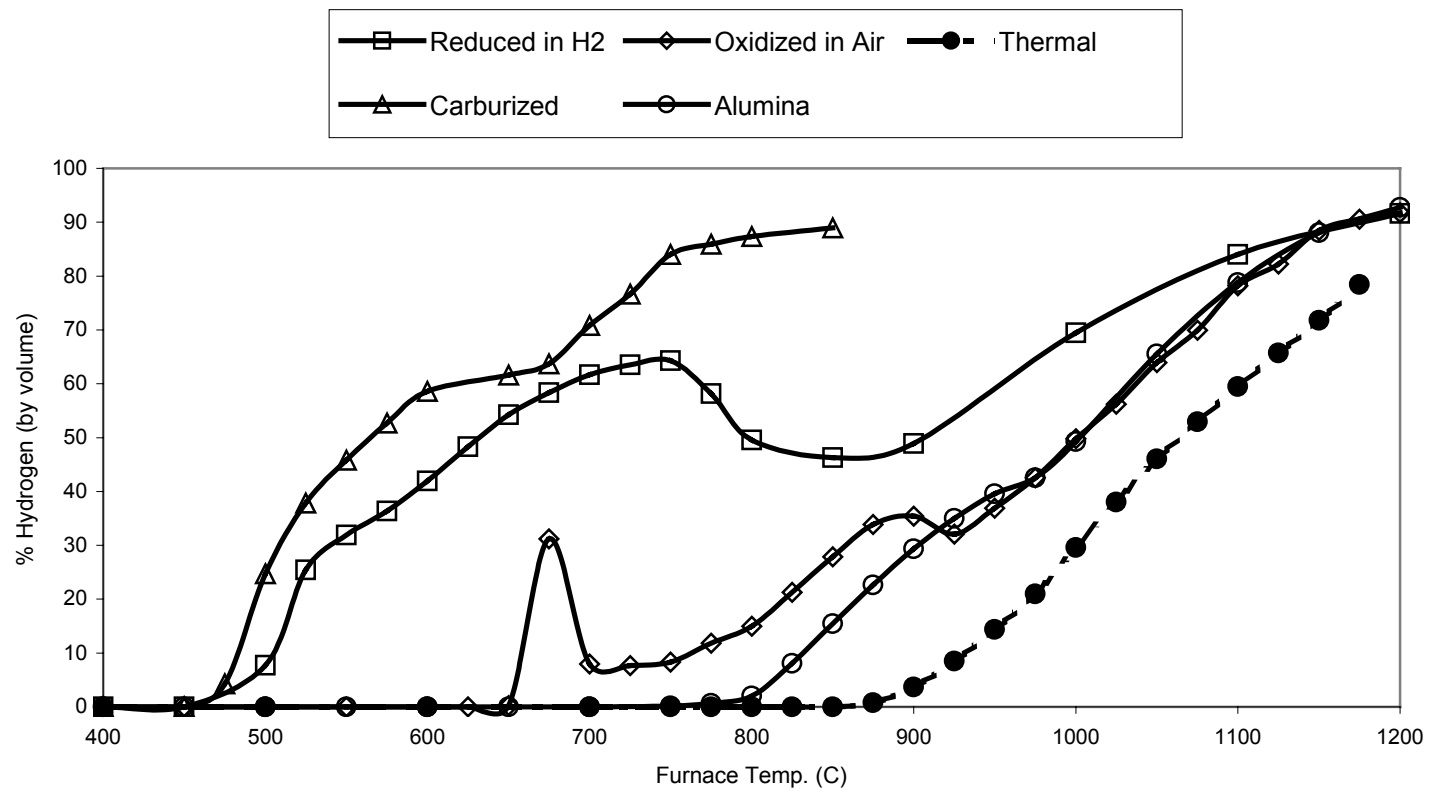


Figure 2. Hydrogen production from CH<sub>4</sub> cracking - Thermal and 5%Fe/Al<sub>2</sub>O<sub>3</sub>.

