

Production of Hydrogen and Carbon Nanotubes by Catalytic Decomposition of Methane

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Production of pure hydrogen from hydrocarbons, particularly methane, the major component of natural gas, has great practical importance. Traditionally, dry (with CO₂) reforming, wet (with H₂O) reforming, and partial oxidation of methane are employed to produce synthesis gas. Converting CO in synthesis gas using the water-gas shift reaction then produces a relatively pure hydrogen stream. However, this hydrogen still contains enough CO to poison the catalysts used in PEM electrochemical fuel cells. A reverse methanation reaction has to be carried out to reduce the CO concentration to sub-ppm levels. Non-oxidative catalytic decomposition of hydrocarbons to produce pure hydrogen is an alternative route to avoid the presence of CO. In the current investigation, nano-scale ferrihydrite and binary ferrihydrites supported on alumina were subjected to various pre-treatments, and were found to be effective catalysts for methane decomposition.

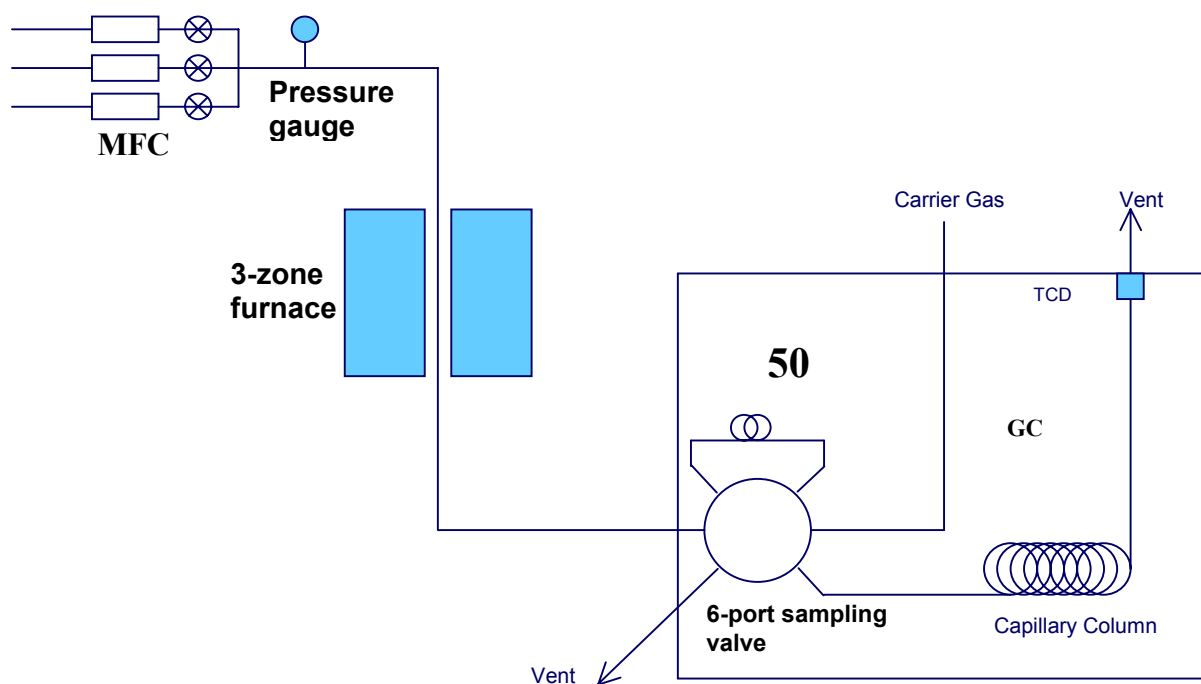


Figure 1: Schematic of experimental set-up for studying catalyst performance for decomposition of methane.

Figure 1 is a schematic of experimental set-up used for studying the catalyst performance. A calibrated volume of undiluted reactant (methane) stream is passed through a catalyst bed. The product gas stream did not contain any appreciable amounts of C₂ and higher hydrocarbons. Except in the case of non-catalytic (thermal) cracking, there was complete absence of any liquid products in all experiments.

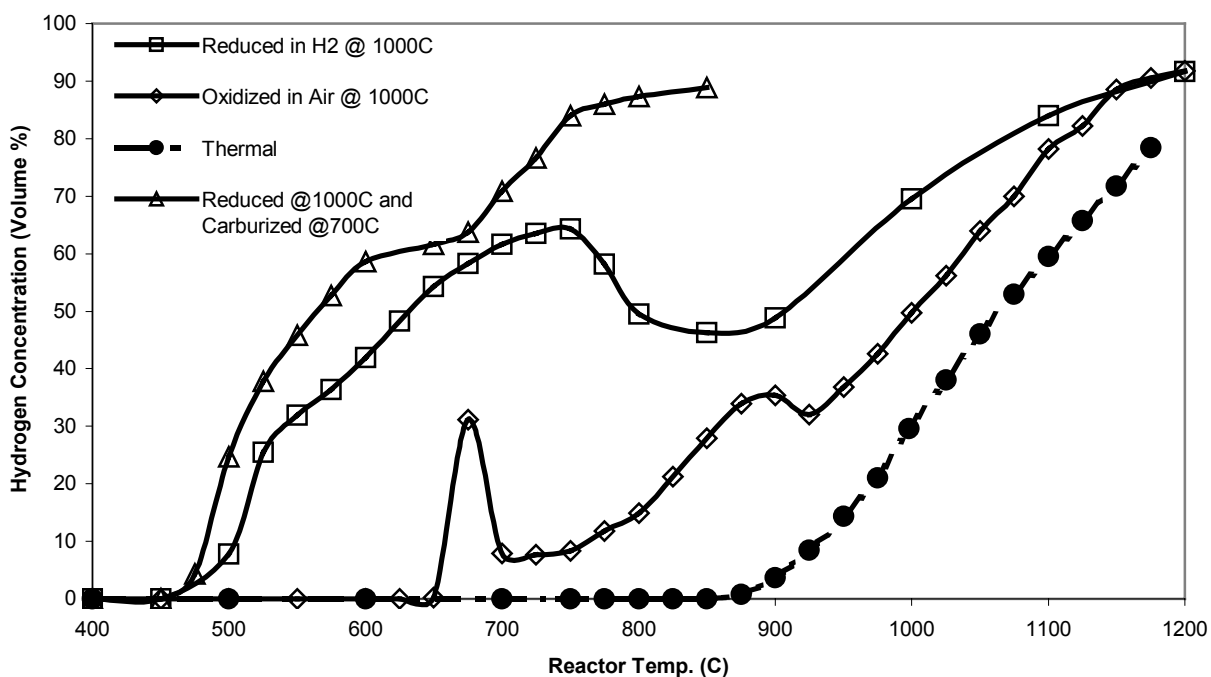


Figure 2: Effect of different pretreatments on catalytic methane decomposition using 5%Fe/alumina catalysts.

Figure 2 shows the effect of different pretreatments on 5%Fe/alumina catalysts for the methane cracking reaction. For clarity, no methane concentrations are plotted; they are complimentary to the hydrogen concentrations ($\%CH_4 = 100 - \%H_2$). Oxidized Fe is not an active catalyst. However, under reaction conditions, it shows some activity, which may be due to partial conversion to metallic/carbide state. There is not much difference in activity between the pre-reduced catalyst and the pre-reduced and pre-carburized catalyst. This may be because the metallic phase converts to the carbide phase under reaction conditions. That is, the catalyst state may be essentially the same in both reaction experiments, even though they were pre-treated to produce different states. Only the reduction pre-treatment was carried out for most of the subsequent experiments.

Figure 3 compares the observed H_2 concentrations as a function of increasing temperature for all of the different catalysts tested after a reduction pre-treatment at 700 °C. All of the binary catalysts cause substantial reductions in the methane, decomposition temperature. The largest decrease, 500 °C, is produced by the 0.5%Pd-4.5%Fe/ Al_2O_3 catalyst. It is apparent that the bimetallic supported catalysts are significantly more active than the monometallic supported catalysts.

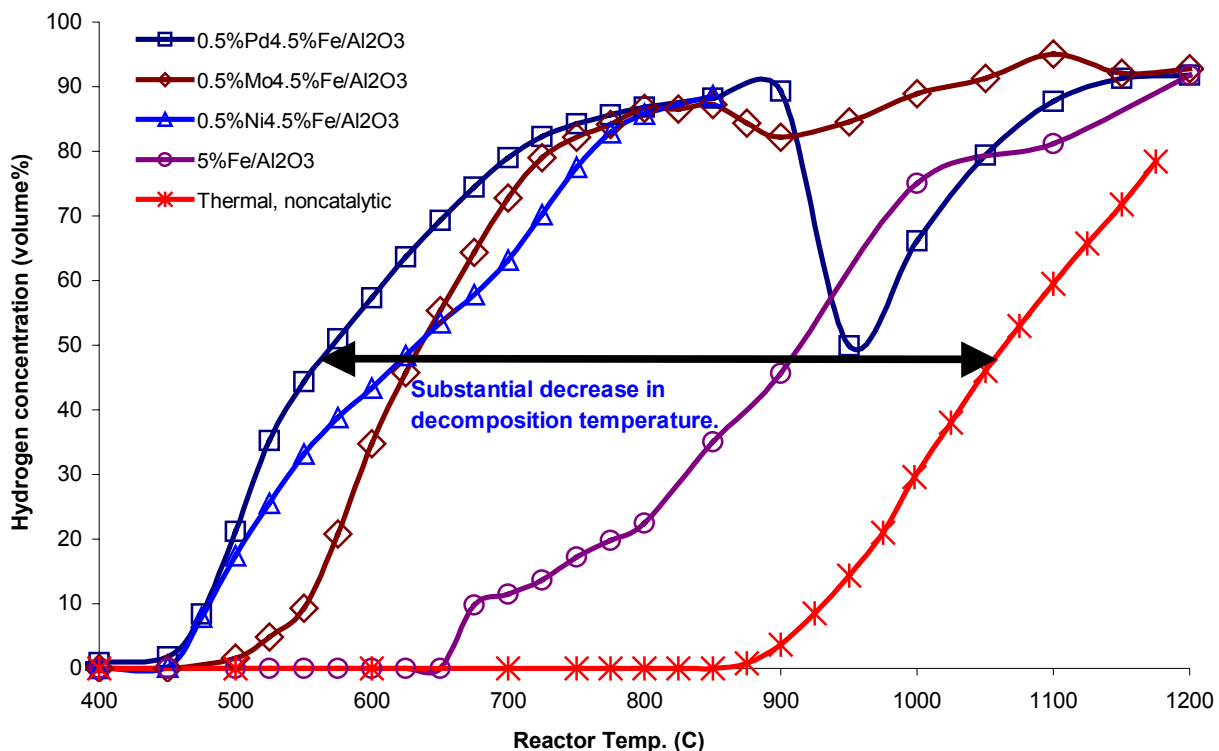


Figure 3. Comparison of alumina supported binary Pd-Fe, Mo-Fe and Ni-Fe catalysts pre-reduced at 700 °C for hydrogen production.

Decomposition of methane converts a gaseous methane inlet stream to a gaseous hydrogen outlet stream and a solid carbon. It is believed that methyl radicals polymerize to form cyclic and aromatic precursors to graphitic soot particles. During non-catalytic, thermal decomposition experiments, we found that smooth and shiny graphitic film covers the entire heated section of the reactor as well as the catalyst support and quartz wool. It is very difficult to remove this film. Exposure to a strong oxidizer (air, rather than CO₂ or steam) at relatively high temperature (>700 °C) is required to oxidize this tenacious film. Exposure to this strongly oxidizing atmosphere also oxidizes the metallic catalyst and it has to be re-reduced to recover its activity for methane decomposition.

The form of carbon produced is quite different for catalytic decomposition of methane at lower (~700 °C) temperatures. Figure 4 is an SEM image showing that the most (>90%) of the carbon formed under these conditions is in the form of carbon nanotubes. Carbon fibers (Figure 5) were observed in very small amounts (< 5%) and only at higher reactor temperatures, where the catalysts are not so active.

High-resolution transmission electron microscopy (HRTEM) showed that the nanotubes were multi-walled and that most of the nanotube ends did not contain catalyst particles (figure 6). This indicates that the binary metallic catalyst particles are anchored at the support surface and the nanotubes continue to grow upwards from the catalysts particles. However, quite a few

nanotubes were observed that contained metallic Fe particles within the tube (figure 7). EDX spectra showed that such particles did not contain the secondary element, indicating poorer metal-support anchoring for catalyst particles containing only iron and suggesting that the secondary element may play a critical role in the anchoring mechanism. This topic is under further investigation.

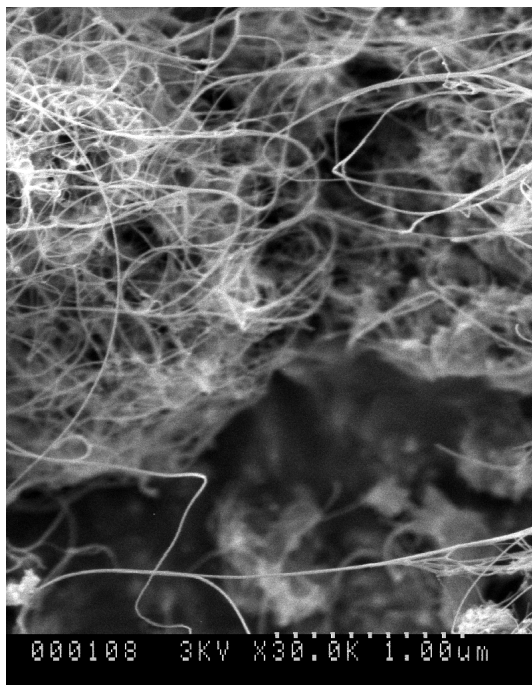


Figure 4. SEM image of multi-walled carbon nanotubes grown by decomposing undiluted methane over pre-reduced (at 1000C) 0.5%Mo4.5%Fe/Al₂O₃ catalyst at 900 °C reactor temperature.

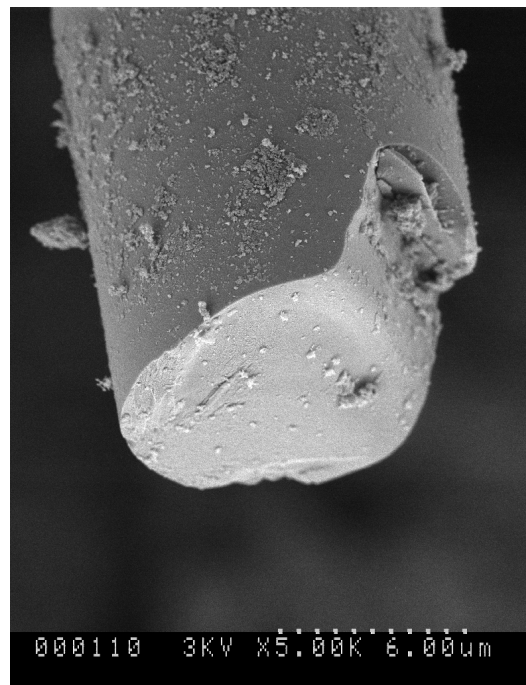


Figure 5. SEM image of carbon nano-fiber (whisker) grown by decomposing undiluted methane over as-prepared 0.5%Pd-4.5%Fe/Al₂O₃ catalyst at 850 °C reactor temperature.

In conclusion, it has been demonstrated that alumina supported binary Fe-Pd, Fe-Mo, and Fe-Ni catalysts are quite active for catalytic decomposition of methane, yielding a pure hydrogen stream and a potentially valuable carbon nanotube byproduct. Reduced activity of these catalysts due to carbon deposition can be recovered by an oxidative regeneration step. If this regeneration is carried out with CO₂, it yields a rather pure CO stream, which is valuable for many C1 reactions.

A more detailed summary of this work has been prepared and submitted to *Energy & Fuels*. Presentations on the work have recently been made at the American Chemical Society meeting in San Diego and at the North American Catalysis Meeting in Toronto. A patent disclosure has also been filed.

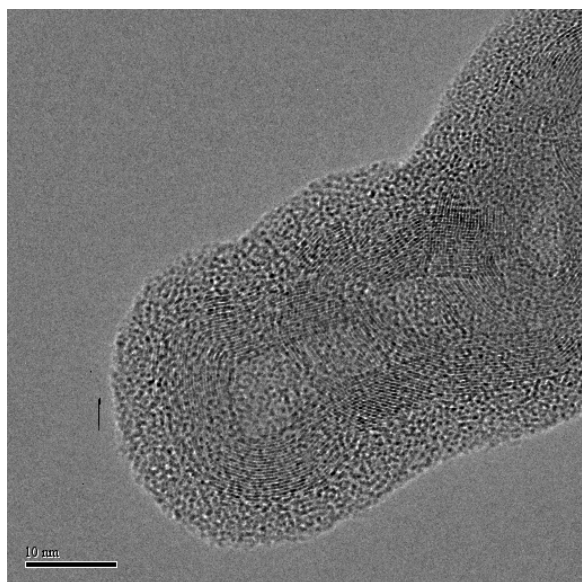


Figure 6. HRTEM image of multi-walled carbon nanotubes grown by decomposing undiluted methane over as-prepared 0.5%Pd-4.5%Fe/Al₂O₃ catalyst at 600 °C reactor temperature. Note the absence of any metallic particle at the nanotube ends.

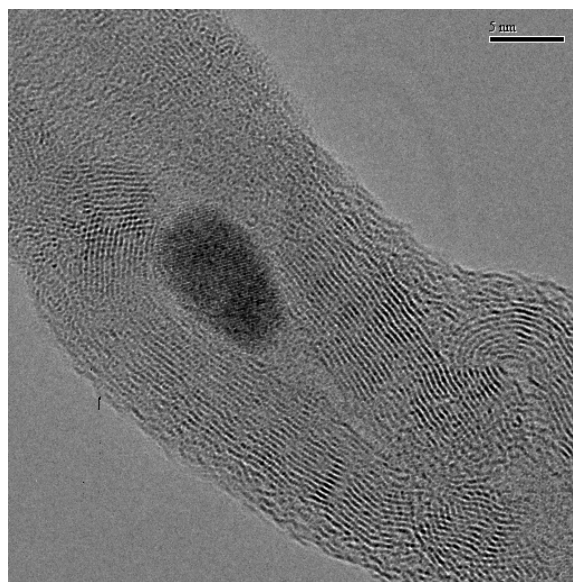


Figure 7. HRTEM image of multi-walled carbon nanotube grown by decomposing undiluted methane over pre-reduced (at 1000C) 0.5%Mo-4.5%Fe/Al₂O₃ catalyst at 600 °C reactor temperature. An EDX spectrum showed the particle to be pure Fe.