

Selective hydrogenation of acetylene to ethylene during the conversion of methane in a catalytic dc plasma reactor

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Previous studies have shown that plasma reactors can achieve high methane conversions while maintaining high selectivities towards acetylene and hydrogen. Palladium catalysts are commonly used in the selective hydrogenation of acetylene to ethylene. This paper discusses the use of Pd-Y zeolite for the in-situ selective hydrogenation of acetylene. Pd loading, presence of oxygen, and temperature play a large role in the selective hydrogenation of the acetylene.

1. INTRODUCTION

It is generally agreed that, for a variety of reasons, natural gas will become increasingly important as a petrochemical feedstock and source of liquid fuels. Natural gas reserves are abundant throughout the world. A limitation to the utilization of the reserves is the transportation of the natural gas to the desired location.

C₂ hydrocarbons consist of acetylene, ethylene, and ethane. Ethane is primarily used for the formation of ethylene by dehydrogenation, and ethylene has largely replaced acetylene as a petrochemical building block. The United States alone produces nearly 60 billion pounds of ethylene per year. Ethylene is highly reactive, due to its double bond, allowing it to be converted to a large assortment of products by addition, oxidative, and polymerization reactions. It is primarily used in the production of plastics, fibers, films, resins, adhesives, and elastomers [1], but it can also be oligimerized to liquid hydrocarbons.

Ethylene can be derived from many different feedstocks. The feedstock, and the resulting process, varies depending on the region. Table 1 lists different feedstocks used in the production of ethylene and their relative amounts in the United States. However, for Western Europe and Japan naphtha is the primary feedstock for the production of ethylene since natural gas is less abundant.

Table 1. Ethylene Feedstocks in the U.S.[2]

Ethane	27-30 billion pounds
Propane	8-10 billion pounds
Naphtha	10 billion pounds
Other	10 billion pounds

The thermal cracking of petroleum based naphtha with steam, known as pyrolysis, is used for over 97% of the worldwide production of ethylene. This process uses a feed stream that is a mixture of hydrocarbons and steam. The stream is preheated to a temperature of 500-650°C, and then raised to 750-875°C in a controlled manner in a radiant tube [3]. In the radiant tube the hydrocarbons crack into the major products: ethylene, olefins, and diolefins. Due to the high temperatures required for the endothermic reaction, an intensive energy input is required to drive the process. The large amount of by-products resulting from the use of the heavy hydrocarbon feedstock also requires oversized equipment for the resulting ethylene quantity.

The production of ethylene from ethane is also done by steam cracking. Not including methane, ethane requires both the highest temperature and the longest residence time to achieve acceptable conversion [3]. A typical ethane process operates near 60 % conversion of ethane and achieves an ethylene selectivity of 85%. This process uses the burning of the unwanted by-products to provide the necessary heat for the endothermic reaction. Over 10% of the ethane is thereby converted into carbon dioxide, and nitrogen oxides are also formed by the combustion. Production of ethylene by steam cracking is a large contributor to greenhouse gases [4]. It is desired, therefore, to introduce technologies that will reduce the emission of greenhouse gases during the production of ethylene.

It is already known that the use of methane as a petrochemical feedstock can lead to environmentally friendly technologies. The production of hydrogen by means of steam reforming is the only significant use of natural gas in the petrochemical industry. Steam reforming of methane is the industry's cleanest option for the production of hydrogen. Steam reforming of methane results in one carbon dioxide released for every four hydrogen molecules produced. On the other hand, the partial oxidation of coal results in a 1:1 production of carbon dioxide and hydrogen.

It has also been shown [5] that plasma reactors can activate methane at low temperatures. Low temperature plasmas offer the potential for efficient processes for direct conversion of methane to higher value products or the widely used intermediate, synthesis gas. The reaction is driven by highly energetic electrons that are created by applying an electric potential across the reaction volume. The low temperature plasma makes use of these excited electrons as initiators in what is predominantly a free radical pathway for conversion. The bulk gas temperature remains relatively low, allowing for unique, non-equilibrium product distributions. This paper will discuss the use of a dc plasma catalytic reactor for the production of C₂ hydrocarbons and/or synthesis gas (H₂ and CO).

2. EXPERIMENTAL

The experimental apparatus is similar to the system that has been described previously [5, 6]. The feed gases consisted of a combination of methane, oxygen, hydrogen, and helium. Helium was only used in initial experiments and for characterization studies of the catalyst. The feed gas flowrates were controlled by Porter mass flow controllers, model 201. The feed gases flowed axially down the reactor tube. The reactor is a quartz tube with a 9.0 mm O.D. and an I.D. of either 4.5 mm or 7.0 mm.

A point to plane electrode configuration was employed, meaning that the top electrode is a wire point electrode and the bottom electrode is a flat plate that also serves as a

support for the catalyst. The top electrode is positioned concentrically within the reactor, and the gap between its tip and the plate is 8.0 mm. The dc corona discharge is created using a high voltage power supply (Model 210-50R, Bertan Associates Inc.).

The preparation and characterization of the NaOH treated Y zeolite has been discussed elsewhere [7, 8]. Palladium was added using chemical vapor deposition according to the following procedure. The NaOH Y zeolite was calcined at 400°C, then mixed with the appropriate amount of palladium acetylacetonate to achieve the desired Pd loading (ranging from 0.025 to 1%). The mixture was then heated slowly under vacuum to a temperature of 130°C to disperse the palladium throughout the NaOH Y zeolite. This Pd on NaOH Y zeolite will henceforth be referred to as Pd-Y zeolite. The Pd-Y zeolite was then calcined for the final time to a temperature of 350°C.

The fresh catalyst is pretreated in the reactor before each experiment. The NaOH Y zeolite is heated at 250°C to remove any moisture from the catalyst. The Pd-Y zeolite is reduced in 30 ml of hydrogen for 4 hours. The temperature is slowly ramped to 350°C during the first two hours, then held at 350°C for the final two hours.

As mentioned before, this system operates at low temperatures. A furnace around the reactor is used to heat the system to the desired temperature. However, when the desired operating temperature is below 373 K it is necessary to use cooling air across the tube exterior to control the temperature since the plasma itself does heat the gas to some extent. The temperature measured on the outside has been calibrated against the internal temperature of the reactor, and has been discussed elsewhere [7, 8].

The product gases are passed through a dry ice/acetone bath that allows for any condensable organic liquids to be separated from the product gases. It should be noted that the dc system does not produce any measurable liquids, including water. The effluent gases can be analyzed on-line by either a gas chromatograph or a mass spectrometer.

3. RESULTS and DISCUSSION

The catalytic dc plasma reactor has shown to produce high yields of C₂ hydrocarbons, hydrogen, and carbon monoxide at reasonable methane conversions. It is desired, due to many factors, to shift the acetylene production to ethylene. Pd supported catalysts are commonly used for the selective hydrogenation of acetylene to ethylene. These catalyst usually convert acetylene at low concentrations in ethylene streams to ethylene with a very high selectivity. The Pd-Y zeolite prepared by CVD was used to study the in-situ production of ethylene from acetylene (where the acetylene comes from the conversion of methane). Figure 1 shows the effect of different Pd loadings on methane conversion and acetylene, ethylene, and ethane selectivity.

The methane conversion is fairly independent of Pd loading when compared to the parent Y zeolite. The C₂ selectivities vary greatly depending on the Pd loading. As the Pd loading is increased, the amount of acetylene that is hydrogenated increases until all of the acetylene is hydrogenated at 1.0 wt% Pd. At low Pd loadings, ethylene is the major hydrogenated product, while at the high loadings ethane predominates. This dependence is believed to be due to the amount of Pd available for hydrogenation to ethylene and ethane. It is thought that low amounts of palladium and small Pd ensembles favor the hydrogenation to ethylene, while excess Pd and large Pd clusters allow for the produced ethylene to be further

hydrogenated to ethane. Acetylene's adsorption strength is higher than that of ethylene, resulting in the desorption of ethylene before it can be further hydrogenated to ethane when metal site availability is limited. However, the 1.0 wt% Pd loading has larger Pd ensembles that lead to the formation of ethane.

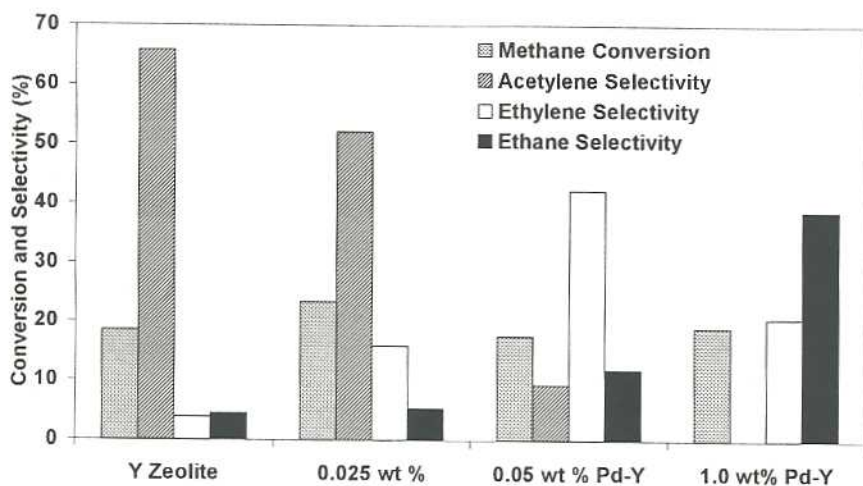


Figure 1. Effect of different Pd loadings on methane conversion and hydrocarbon selectivity. 2/1 H_2/CH_4 with 2% O_2 , 7200 hr^{-1} , 3.9 watts, 45°C

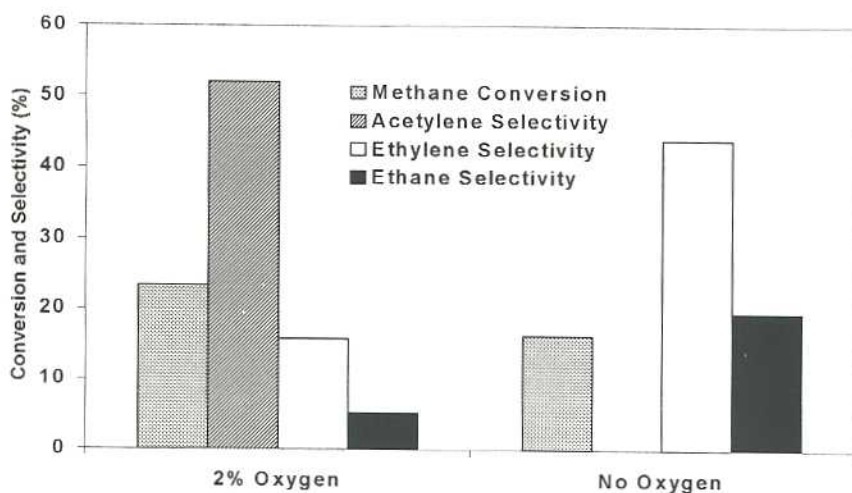


Figure 2. Effect of oxygen on methane conversion and hydrocarbon selectivity. 0.025 wt% Pd-Y zeolite, 2/1 H_2/CH_4 with x% O_2 , 7200 hr^{-1} , 3.9 watts, 45°C

It was also found that oxygen plays a major role in the selectivity of the hydrogenation catalyst, probably via production of carbon monoxide. Previous researchers found that carbon monoxide reduced the hydrogenation of ethylene to ethane because of its higher adsorption strength than ethylene.[9]. In our studies we noticed a large effect on selectivity when carbon monoxide is present; however, it was not the usual inhibition of ethylene hydrogenation, but rather acetylene hydrogenation (Figure 2 and 3).

As seen from Figures 2 and 3, carbon monoxide affects the hydrogenation of acetylene to ethylene and ethane. When oxygen is removed from the feed, all of the acetylene is hydrogenated. Carbon monoxide seems to reduce the number of Pd sites that are available for the hydrogenation of acetylene. Similarly, when the system is operating without oxygen and carbon monoxide is injected in the system, acetylene (not present before) becomes the major product and immediately disappears upon removal of carbon monoxide.

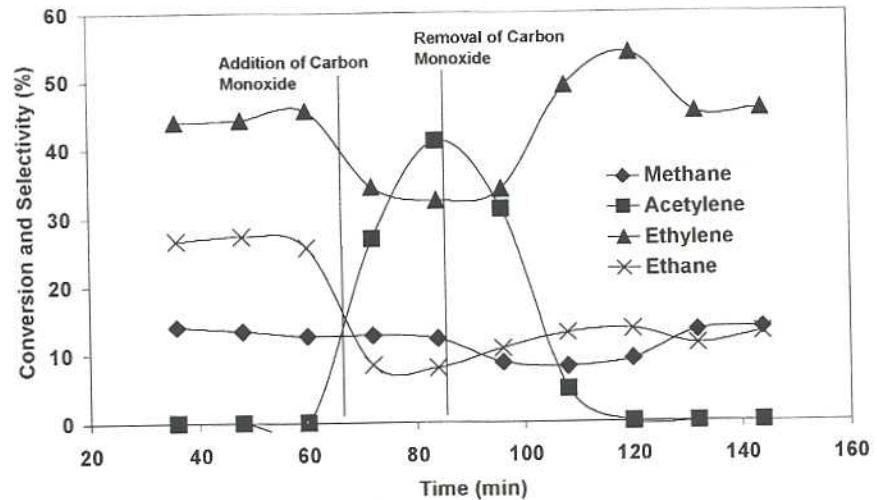


Figure 3. Effect of addition and removal of carbon monoxide on methane conversion and hydrocarbon selectivity. 0.025 wt% Pd-Y zeolite, 2/1 H₂/CH₄ with x% O₂, 7200 hr⁻¹, 3.9 watts, 45°C

The operating temperature plays a large role in the activity of the Pd catalyst, Figure 4. As the temperature is increased from room temperature to 100°C, the acetylene is completely hydrogenated to ethylene and ethane. Ethylene goes through a selectivity maximum at around 50°C. Above 50°C, the selectivity decreases due to the over hydrogenation to ethane. At temperatures above 95°C, ethane is the only C₂ hydrocarbon produced. Therefore, it is desirable to operate at low temperatures at which good conversions can still be achieved in the plasma discharge.

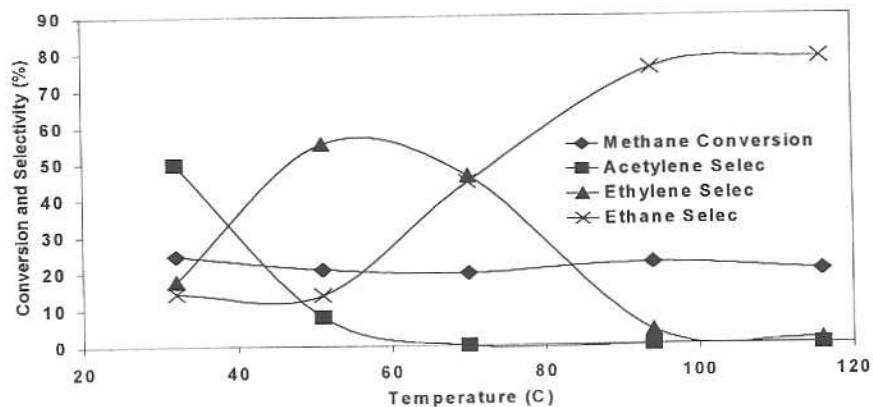


Figure 4. Effect of temperature on methane conversion and hydrocarbon selectivity. 0.025 wt% Pd-Y zeolite, 2/1 H₂/CH₄ with no O₂, 7200 hr⁻¹, 3.9 watts

4. CONCLUSIONS

The addition of palladium to the Y zeolite used in the catalytic dc plasma reactor allows for the hydrogenation of acetylene to ethylene and ethane. Currently, operating around 50°C and without oxygen allows for greater selectivity control to the desired ethylene. Further studies and characterization should allow for further improvements in the selectivity of ethylene in the hydrogenation of acetylene.

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REFERENCES

1. McKetta, J.J., ed. *Encyclopedia of Chemical Processing and Design*. Vol. 20, 1986, Marcel Dekker: 1984. 88-159.
2. Greenberg, K., *Domestic ethylene market stays strong*, in *Chemical Market Reporter*. 1999. p. 4,12.
3. Gerhartz, W., *Ullman's Encyclopedia of Industrial Chemistry*. Vol. A10, 1987, Weinheim: VCH. 45.
4. Jacoby, M., *New ethylene process is environmentally-friendly*, in *C&EN*. 1999. p. 6.
5. Liu, C.J., R.G. Mallinson, and L.L. Lobban, *Nonoxidative methane conversion to acetylene over zeolite in a low temperature plasma*. *Journal of catalysis*, 1998. **179**: p. 326-334.
6. Gordon, C.L., L.L. Lobban, and R.G. Mallinson, *The production of hydrogen from methane using tubular plasma reactors*, in *Advances in hydrogen energy*, C. Gregoire-Padro, Editor. 2000, Kulmer.
7. Liu, C.-J., A. Marafee, B.J. Hill, G. Xu, R.G. Mallinson, and L.L. Lobban, *Oxidative coupling of methane with ac and dc corona discharge*. *Industrial & Engineering Chemistry Research*, 1996. **35**(10): p. 3295-3301.
8. Marafee, A., C.-J. Liu, G. Xu, R.G. Mallinson, and L.L. Lobban, *An experimental study on the oxidative coupling of methane in a direct current corona discharge reactor over Sr/La₂O₃ catalyst*. *Industrial & Engineering Chemistry Research*, 1997. **36**: p. 632-637.
9. Price, G.L. and Y.H. Park, *Deuterium tracer study on the effect of CO on the selective hydrogenation of acetylene over Pd/AL₂O₃*. *Industrial Engineering and Chemical Research*, 1991. **30**: p. 1693-1699.