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Ethylene production using a Pd and Ag–Pd–Y-zeolite catalyst in a DC plasma reactor

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Abstract

The interest in natural gas utilization has increased tremendously over the last decade. Natural gas is being looked at as an energy source, as well as a basis for the production of many chemicals. New technologies are needed for smaller scale, remote and niche applications to match many natural gas resources that will not be suitable for large-scale production of distillate products via syngas. Low temperature plasma reactors have been shown to be an effective method for the conversion of methane, and under some conditions have low power consumption. The advantage of low temperature processing potentially reduces the energy intensity of the process and therefore the cost. The feed reactants for this study consist of methane, hydrogen, and oxygen (less than 2.5%). For the dc plasma reactor using NaOH-treated Y-zeolite, the primary products are acetylene, hydrogen, and small amounts of carbon monoxide. However, recent efforts have focused on the in situ selective hydrogenation of the acetylene to ethylene. Palladium on a supported catalyst is commonly used in industry for the selective hydrogenation of small amounts of acetylene in the purification of ethylene produced in crackers. The addition of palladium to the NaOH-treated Y-zeolite maintains the same methane conversion (20–60%), but allows for the selective hydrogenation of the acetylene to ethylene. The catalyst is most selective around 45 °C, where it produces an ethylene to ethane ratio of about 4–1 with no acetylene. The addition of silver to the Pd–Y-zeolite serves two functions. It increases the ethylene to ethane ratio from 4 to at least 7, and as high as 11. In addition, the temperature at which the high ethylene to ethane ratio achieved is shifted to higher temperatures as well as extended over a wider temperature range. Ethylene yields as high as 30% and hydrogen yields as high as 40% have been obtained without attempting to optimize these yields; and it is expected, based on preliminary results, that higher yields can be obtained.

Keywords: Ethylene; Y-zeolite; Plasma reactor

1. Introduction

It is generally agreed that, for a variety of reasons, natural gas will become increasingly important as a source of energy, chemicals, and liquid fuels. Methane, the main component of natural gas, is extremely stable. Methane requires extremely high temperatures for reaction, as well as expensive co-reactants such as oxygen to initiate the reaction.

Methane can be activated by Group VIII metals and oxidized to syngas [1]. Therefore, most processes being implemented/investigated involve the production of synthesis gas from methane, followed by a process that utilizes the synthesis gas in the production of fuels or chemicals, i.e. Fischer–Tropsch and methanol synthesis. The cost of synthesis gas production can amount to about 60% of the total cost of the process. Much of this cost is for the production of oxygen. Cryogenic separation of air requires a very large-scale to lower its unit production cost, but it is still expensive even at these large scales.

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Plasmas have shown to be an effective method of converting methane to valuable chemicals such as C_2 hydrocarbons, hydrogen and carbon monoxide. Plasmas can achieve high conversions while maintaining high selectivities to the desired products. A plasma is an ionized gas that is generated by electrical discharges. The types of discharges used in this study can be termed cold or non-equilibrium plasmas. Cold plasmas are characterized by highly energetic electrons that exist at a very high temperature, while the bulk gas temperature remains low. The bulk gas temperature exists in the range 25–100 °C. The highly energetic electrons allow for reactions that thermodynamically would not occur at these low temperatures. This is advantageous because the feed gas does not have to be preheated to the extreme temperatures normally required for methane conversion.

In addition, the systems can run with little or no oxygen, eliminating the need for costly oxygen plants. The primary role of oxygen and hydrogen in the feed is to inhibit coke formation, which alters the discharge. There is no distinguishable change in methane conversion from 0.4 to 6% oxygen, only an increase in stability due to a reduction in carbon formation. Oxygen concentrations greater than 2 vol.% allow for stable operation.

Thus, a plasma system reduces two major obstacles needed for an economic process for methane conversion: (1) no energy intensive preheating/cooling (requiring large-scale energy integration) of the gas which may not be completely recoverable, and (2) small oxygen source needed (could be air or oxygen enriched air). However, the main products are still gases that present a similar problem concerning remote locations and the transportation of gases.

Fig. 1 shows a simplified flowsheet of a plasma process. The major feed components of the plasma system are the feed gases and electricity. Therefore, the plasma system might be coupled with a natural gas based power plant. The power plant could provide both power and natural gas to the system. It could be designed to run full time at a given production rate or designed to take advantage of off-peak times of the power plant.

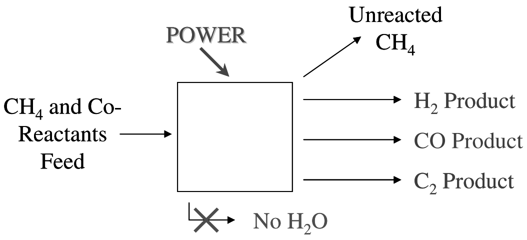

Fig. 1. Simplified flowsheet of plasma process.

2. Experimental

The experimental apparatus is similar to the system described previously [2,3]. The reactor is set up in a point to plane configuration, meaning that the top electrode is positioned concentrically within the reactor while the bottom electrode is a flat plate that also serves as a support for the catalyst. The distance between the two electrodes is 8 mm. The dc corona discharge is initiated by creating a potential difference between the two electrodes 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 [4,5]. The preparation of the Pd–Y-zeolite (chemical vapor deposition method) used in the initial experiments studying the effect of palladium metal on the selective hydrogenation of acetylene also has been described previously [6]. Subsequent preparations of Pd–Y and Ag–Pd–Y catalysts used the incipient wetness technique. At the low loadings used, there were no distinguishable differences in the performance of the catalyst when comparing chemical vapor deposition and incipient wetness.

The incipient wetness of the Y-zeolite was found by adding water to a known amount of catalyst until the catalyst could not take up any more water. A solution of tetraaminepalladium (II) nitrate was made such that for the amount of catalyst to be prepared, the amount of solution used for incipient wetness would provide the desired metal loading on the catalyst, 0.025 wt.% Pd–Y-zeolite. The catalyst was dried for 8 h in a 110 °C oven to remove the water. The catalyst was then subsequently calcined in air for a total of 6 h. The catalyst was heated to 350 °C over the first 2 h, then left at 350 °C for 4 h. This catalyst will be referred to as 0.025 wt.% Pd–Y-zeolite. The catalyst was reduced in flowing hydrogen at 350 °C prior to each experiment.

The silver–palladium Y-zeolite was prepared in a similar manner using the incipient wetness technique. Silver was added to the 0.025 wt.% Pd–Y-zeolite using silver nitrate. The incipient wetness of the catalyst was assumed to be the same as determined previously. The catalyst was dried and calcined in the same manner as the 0.025 wt.% Pd–Y-zeolite. A loading of 0.025 wt.% Ag on 0.025 wt.% Pd–Y-zeolite was prepared.

A furnace connected to a temperature controller is used to heat and maintain the reactor at the desired temperature. High methane conversions can be achieved at temperatures as low as room temperature; therefore, when the desired operating temperature is below 100 °C it is necessary to blow cooling air across the tube exterior in order to reduce the temperature, since the plasma itself heats the gas to some extent.

3. Results and discussion

As stated before, plasma reactors have been shown to be an effective method for the conversion of methane. Methane conversions in the range 15–70% have been achieved, depending on residence time and reactor configuration [3]. The feed consists of methane, hydrogen, and oxygen (less than 2.5%). The hydrogen and small quantities of oxygen are necessary to maintain stability of the streamer discharges by reducing carbon formation. When the parent Y-zeolite is being used, the major products of the reaction are acetylene, hydrogen and carbon monoxide. The reaction produces very little carbon dioxide, and water is undetectable. The product distribution does not vary over a temperature range 25–125 °C.

Acetylene is the primary C_2 hydrocarbon. Due to safety and the onset of ethylene production and utilization as the primary petrochemical source, acetylene is not the most desired C_2 product. Work has been successful for the in situ selective hydrogenation of the acetylene to ethylene by the addition of Pd to the parent Y-zeolite [6]. Fig. 2 shows the effect of the addition of palladium and silver to the parent Y-zeolite. Methane conversion is independent of metal loading; however, C_2 selectivities are very dependent

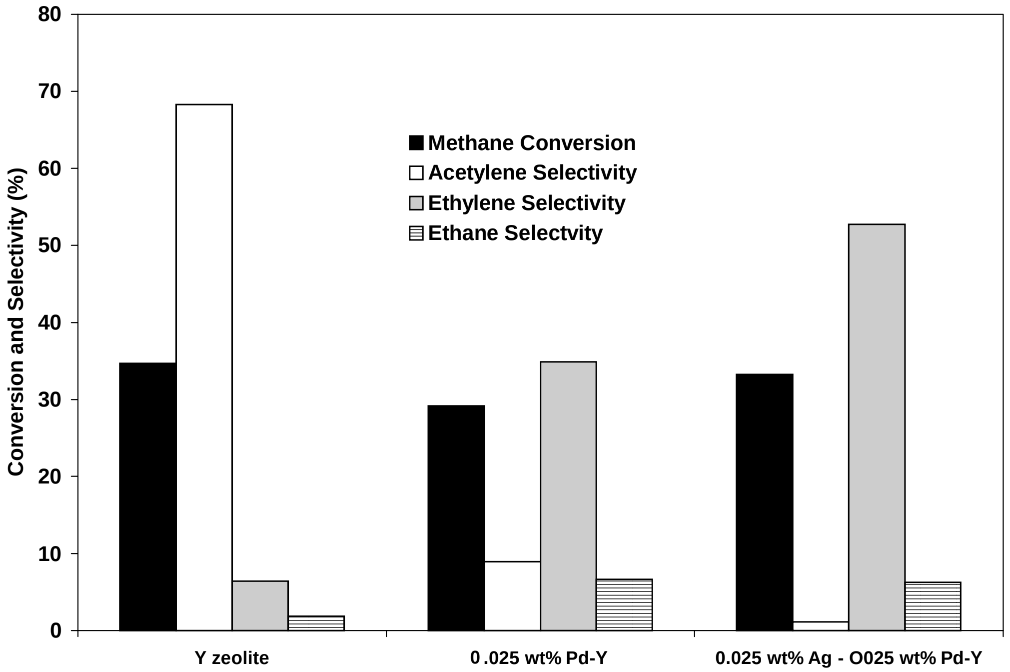

Fig. 2. Effect of metal loading on C_2 selectivity. 1/1 H_2/CH_4 with 2% O_2, 1.2 s residence time, 4.55 W. 7 mm ID, 0 psig. Temperature optimized for each catalyst to produce the highest selectivity of C_2H_4.

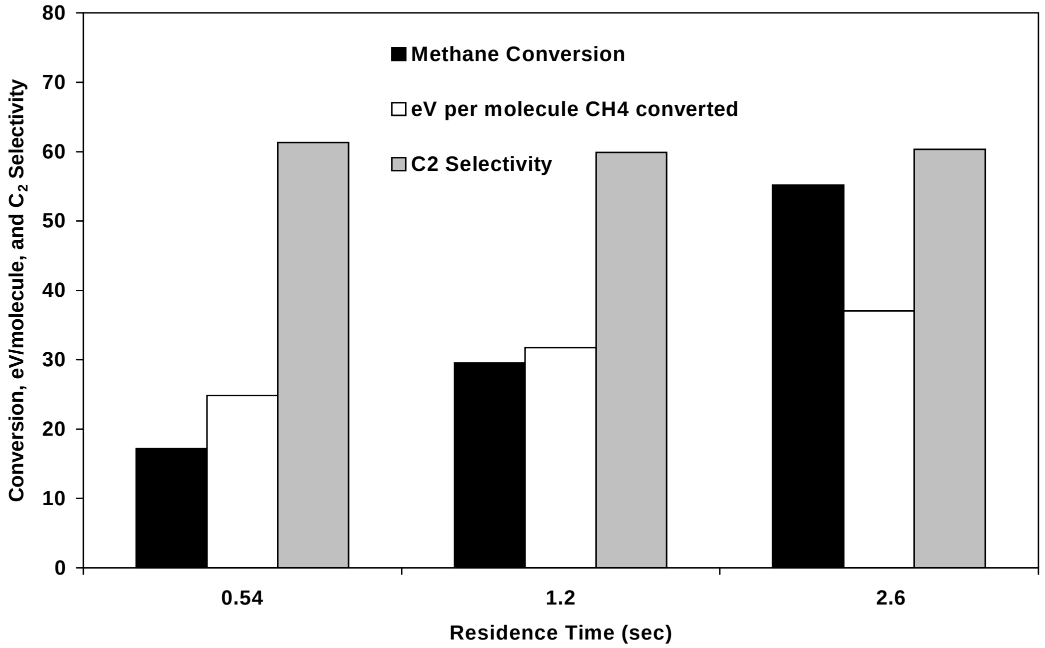

Fig. 3. Effect of residence time on methane conversion, power consumption, and overall C_2 selectivity. 0.025 wt.% Ag–0.025 wt.% Pd–Y-zeolite, 1/1 H_2/CH_4 with 2% O_2, 4.55 W. 7 mm ID, 0 psig.

upon metal loading. The 0.025 wt.% Pd–Y selectively hydrogenates the acetylene that is produced in the gas phase into ethylene and ethane. The optimum temperature for ethylene production with the 0.025 wt.% Pd–Y-zeolite is 45 °C. The addition of 0.025 wt.% Ag to the 0.025 wt.% Pd–Y-zeolite increases the selectivity of ethylene by reducing the over hydrogenation to ethane. In addition, silver shifts the optimum temperature for ethylene production to 85 °C.

It is desired to produce a high yield of ethylene. This can be achieved by having high methane conversions and maintaining high selectivities. A characteristic of the plasma process is that the products do not vary as the methane conversion increases or decreases. Fig. 3 shows that as the residence time is increased the methane conversion increases without any effect on overall C_2 selectivity. Thus, the C_2 yield increased from 10 to 30% over the residence time variation of 0.54–2.6 s. However, there is an increase in the energy consumption (eV per molecule of CH_4 converted). This is a measure of the amount of power that is input as compared to the number of methane molecules converted.

It is the decrease in the methane throughput that results in the increase in eV per molecule shown in Fig. 3. One way to increase the methane throughput is to increase the methane fraction in the feed. Fig. 4 shows the results of varying the feed composition. Once again, the methane fractional conversion does not vary significantly, but the increase in the feed partial pressure of methane results in a decrease in eV per molecule of methane converted (the power input is constant). In addition, there is an increase in the overall C_2 selectivity resulting in an increase in C_2 yield.

To put the current results into context, a number of economic scenarios may be formulated to assist in determining the direction for optimization of a hypothetical process. A simplified initial economic analysis similar to the analysis outlined by Douglas [7] is presented. It states that the first step is determining the economic potential of the process. The economic potential is defined as the difference between the product values and the raw material costs. In this case, electricity is considered as a raw material (this could be considered as the natural gas required to generate

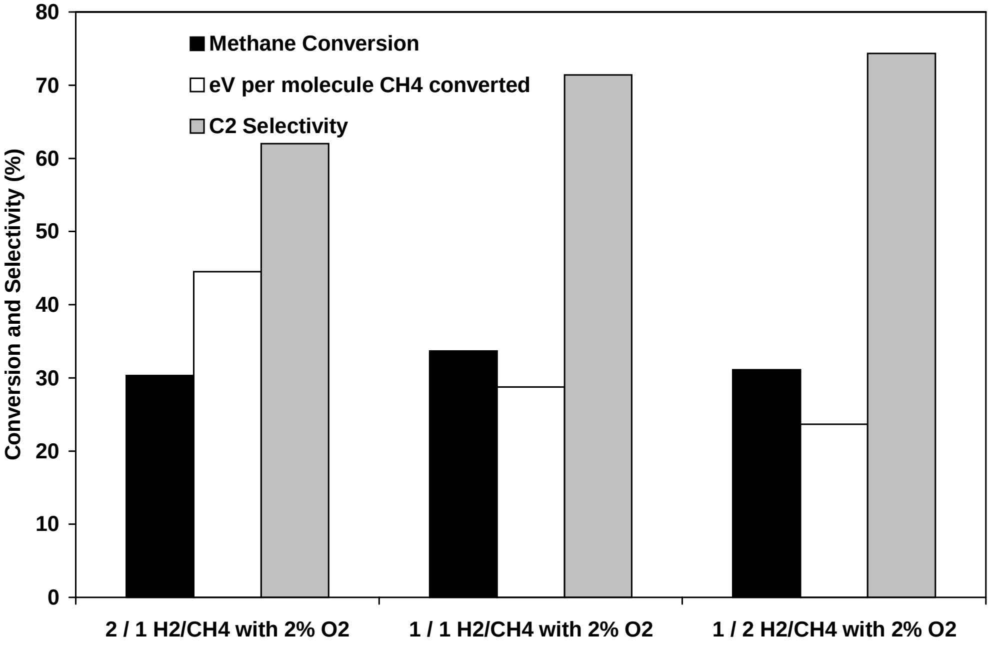

Fig. 4. Effect of feed composition on methane conversion, power consumption, and overall C_2 selectivity, 0.025 wt.% Pd–Y-zeolite, 4.55 W. 7 mm ID, 0 psig.

the power). A co-production (electricity and chemicals) process can be envisioned if the plasma conversion process were to be incorporated with a natural gas-based peaking power plant. Low temperature plasmas can be started up and shut down quite rapidly, and operation only during off-peak power hours is possible. It might be assumed that the cost of the electricity would be no greater than the off-peak price. The natural gas cost would be associated with the contract price of the power plant; however, the excess gas during off-peak could come at a substantially reduced cost. Table 1 shows the energy costs of the process for different conversions based on a power consumption for the conversion of 10 eV/molecule. It is assumed that the valuable products, ethylene and hydrogen, are separated out of the product stream and the remaining stream may be fed directly to the power generation plant. Thus, the only cost of the feed natural gas is for the converted portion of methane. An off-peak electricity cost of $ 0.025/kW h and natural gas costs of $ 0.50 and $ 2.50/MMBtu were assumed for the analysis.

The valuable products consist of C_2 hydrocarbons and hydrogen. For the products values, ethylene has a value of $ 0.015/mole, and the Department of Energy has projected a production goal for hydrogen of $ 0.002/mole [8]. Table 2 shows a summary of the value of the product stream from the plasma process. For a given feed composition and reactor conditions, the product selectivities are independent of methane conversion. Hydrogen and ethylene selectivities of 75 and 65%, respectively, were used for this analysis.

Table 1
Energy cost of plasma process

100 kg[a] of CH_4 feed	Electricity cost[b] ($ 0.025 kW h)	Natural gas feed cost[c]	
		$ 0.50/ MMBtu	$ 2.50/ MMBtu
10% Conversion	$ 0.84	$ 0.05	$ 0.25
25% Conversion	$ 2.09	$ 0.13	$ 0.63
50% Conversion	$ 4.19	$ 0.25	$ 1.27

[a] 20 kg CH_4 = 44.5 lb CH_4 = 1264 g mole = 1000 ft^3 CH_4 = 1 MMBtu.

[b] Based on power consumption of 10 eV/molecule of methane converted.

[c] Reactor feed.

Table 2
Product values

100 kg of CH_4 feed	Value of products	
	Hydrogen	Ethylene
10% Conversion	\$ 0.38	\$ 0.61
25% Conversion	\$ 0.94	\$ 1.52
50% Conversion	\$ 1.87	\$ 3.05

Table 3
Economic potential

100 kg of CH_4 feed	Product value − energy cost	
	\$ 0.50/MMBtu	\$ 2.50/MMBtu
10% Conversion	\$ 0.10	−\$ 0.10
25% Conversion	\$ 0.24	−\$ 0.26
50% Conversion	\$ 0.48	−\$ 0.54

Table 3 shows that it is necessary to get the natural gas at a reduced cost to produce a profit at this power consumption level. Economic potential is calculated as the difference between the value of the products (ethylene, hydrogen and ethane) and the cost of the electricity and the consumed methane. The electrical cost is the major portion of the energy cost (>90%); therefore, if the electrical costs can be reduced then the economic potential will increase dramatically. Fig. 5 shows the effect of electrical cost (eV per molecule of methane converted) on profit margin, with the other factors held constant.

The conversion results presented in this paper have electrical consumptions higher than 20 eV/molecule. However, the dc system and an ac system [9] have produced significantly lower power consumptions under different conditions. To date, the dc systems lowest power is 13 eV/molecule converted. There has not yet been any investigation into the optimization of the dc power supply, which could reduce the power consumption of the process. The ac system has thus far been found to be capable of electrical consumptions as low as 2.5 eV/molecule, thus producing hydrogen at a cost of \$ 0.002/mole (at the DOE target). Again, there has been no effort to optimize the power supply and transformer associated with the ac plasma process.

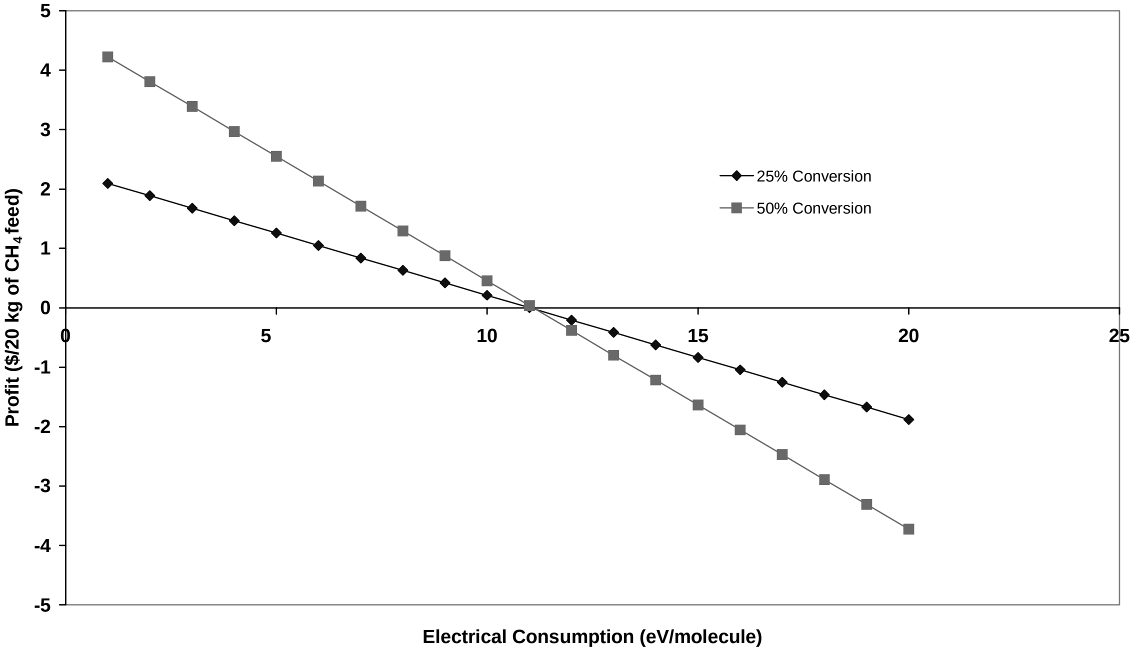

Fig. 5. Effect of electrical consumption on profit. Hydrogen selectivity, 75%; ethylene selectivity, 65%; ethylene, \$ 0.015 mole; hydrogen, \$ 0.002 mole; electricity, \$ 0.025 kW h; natural gas, \$ 0.50/MMBtu.

4. Conclusions

The catalytic dc plasma reactor can achieve high methane conversions while also maintaining high selectivities. One niche market might be to synergistically incorporate with a natural gas-based power plant. The electrical requirements have not yet been optimized; doing so would increase the profit ratio. If hydrogen is not the primary objective, the initial acetylene that is produced in the gas phase can be selectively hydrogenated in situ to ethylene by the use of palladium on the parent Y-zeolite. Also, further increases in selectivity and operating temperature are achieved by the addition of silver. The system has achieved ethylene yields as high as 30%, with similar hydrogen yields and little production of combustion products CO_2 and H_2O. It is expected that the C_2 yield can be further improved with optimization.

Acknowledgements

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