Conversion of Methane to C_2 Hydrocarbons via Cold Plasma Reaction

Baowei Wang, Genhui Xu*

School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
[Manuscript received July 28, 2003; revised August 18, 2003]

Abstract: Direct conversion of methane to C_2 hydrocarbons via cold plasma reaction with catalysts has been studied at room temperature and atmospheric pressure. Methane can be converted into C_2 hydrocarbons in different selectivity depending on the form of the reactor, power of plasma, flow rate of methane, ratio of N_2/CH_4 and nature of the catalysts. The selectivity to C_2 hydrocarbons can reach as high as 98.64%, and the conversion of methane as high as 60% and the yield of C_2 hydrocarbons as high as 50% are obtained. Coking can be minimized under the conditions of: proper selection of the catalysts, appropriate high flow rate of inlet methane and suitable ratio of N_2 to CH_4. The catalyst surface provides active sites for radical recombination.

Key words: methane, C_2 hydrocarbons, cold plasma, catalyst

1. Introduction

Natural gas is an increasingly important fuel in energy and chemical supplies. With large increases in the worldwide natural gas reserves, it can be expected that natural gas will play an increasingly important role in energy and chemical supplies in the 21st century. The concentration of methane, as the second most important greenhouse gas, has been found to be significantly increased from 0.8 to 1.65 ppm for the past 200 years, and it was only after 1950 when major increment occurred [1]. This problem of greenhouse gas control has also attracted attention by the science community the world over. Since the 1980s, intensive research efforts have been made to develop the processes for the direct conversion of methane into more valuable hydrocarbons. The difficulty in direct methane conversion by catalytic and/or thermal processes is the strength of the methane C—H bond. The Gibbs free energy of methane is less than that of the products except C_2H_2 at the temperature of around 1873 K. It is one of the reasons why the high yield of these products (sufficient for the commercialization for the conversion process), can not be obtained [2].

Plasma chemical process especially cold plasma is a promising route for the synthesis of chemicals with high activation energy in that high energy can be supplied to plasma, and that many kinds of reactive particles, electrons, free radicals, ions metastable species and photons are produced in a plasma chemical processing system. Recently, the conversion of methane using non-equilibrium plasmas has attracted considerable attention. Nozaki et al. have succeeded in the growth of carbon nanotubes with atmospheric pressure glow discharge [3], and Liu et al. deposited the diamond-like carbon film using dielectric-barrier discharge (DBD) [4]. Considerable research efforts have been made on DBD conversion of methane into more useful chemicals including synthesis gas, gaseous and liquid hydrocarbons and oxygenates [5–9], and recently it was found that the use of starch significantly increases the selectivity to oxygenates [9]. Steam reforming of methane was investigated using ferroelec-
tric packed-bed reactor [10], pulse corona plasma was used to study methane conversion [11]. However, as the distribution of corona plasma was not continuous, the higher conversion and yield can not be achieved and the activity is lower and the effective plasma zone is smaller. Although some researchers paid much attention to microwave plasma for its strongpoint such as broad discharge spectrum, high energy density, and the ratio of electron temperature to ion temperature. C$_2$ hydrocarbons were synthesized via microwave plasma method in 1.33–13.3 kPa pressure [12] and vacuum operation does not favor industrial production. Formation of microwave plasma field needs very high electric field intensity under the normal pressure. Meanwhile, the experiment indicated that this methane plasma was easily converted into arc plasma, which made serious carbon deposition and continuous operations could not be obtained[13]. The higher conversion of methane and selectivity to C$_2$ hydrocarbons were achieved over porous C/SiC catalyst via the combination of microwave heating and microwave induced plasma in the same microwave applicator [14]. Microwave reforming of methane with carbon dioxide has been examined [15,16]. The microwave plasma has also been reported to be useful for the selective formation of acetylene [17,18].

In this paper, a direct, continuous, low-power selective and catalytic conversion of methane to C$_2$ hydrocarbons through cold plasma concerted catalysis by electric field enhancement was studied under the conditions of room temperature and atmospheric pressure.

2. Experimental

The experimental apparatus has been previously described [7,8]. The reactor was made of a quartz tube with a 10 mm inside diameter. An Omega K-type thermocouple with a quartz thermowell was attached to the inside wall of the reactor to monitor the reactive gas temperature. All experiments were carried out under atmospheric pressure. The flow rates of feed gases were regulated by mass flow controller D07-7A/ZMM, and mass flow display device D08-4C/ZM had been calibrated with soap film flowmeter. The flow rates of exhaust gases were regulated by soap film flowmeter. The feed gases were mixed and then introduced into the reactor. The feed gases and the exhaust gases were analyzed by an on-line gas chromatograph (HP 5971A). A quadrupole mass spectro-graph (Balzers MSC200) was used as the detector and monitor of hydrocarbon production.

3. Results and discussion

3.1. Optimization of operation parameters

Figure 1 shows that the conversion of methane first increases and then decreases with the increase of electrode spacing under the constant voltage and inlet flow rate of methane. When the electrode spacing is 5 mm, the conversion of methane reaches its maximum. When the electrode spacing is less than 5 mm, carbon deposition can easily reduce the electrode spacing. The reason is that the available energy of methane increases when the electrode spacing decreases; furthermore, the hydrogen in methane would be completely eliminated, and thus carbon was formed which caused the stop of the reaction.

![Figure 1. Methane conversion vs. electrode spacing](image)

Reaction conditions: temperature 297 K, voltage 40 kV, flow rate of CH$_4$ 70.55 ml/min

In figure 2 it is shown that the conversion of methane decreases and the selectivity to C$_2$ hydrocarbons increases with the increase of the inlet flow rate of methane. The reason for this is that the available energy of methane and the radicals produced by methane dissociation are decreased when the flow rate of methane is increased, and the residence time
decreased. However, methane may be completely stripped of hydrogen if the flow rate of methane is much too low, which would result in carbon deposition. Therefore, the conversion can not be too high, and the optimum flow rate of methane is a constant 60–80 ml/min under the appropriate voltage.

Figure 2. Conversion of methane and selectivity to C<sub>2</sub> hydrocarbons vs. flow rate of methane

Reaction conditions: temperature 297 K, voltage 38 kV(AC)

Figure 3 shows that the conversion of methane is sensitive to the voltage. If the voltage increases, the available energy increases for the methane dissociation. The concentration of the methane dissociation radicals leads to the increase of conversion. After the conversion reaches its maximum, the amount of methane dissociation radicals becomes too high; Under this condition some radicals would adsorb on the catalyst surface and formed carbon after complete hydrogen elimination. The conversion of methane after this point decreased because a part of the electrical energy would be absorbed by the carbon. Therefore, the optimum voltage is 38 kV under the alternating current field.

Table 1 shows that the conversion of methane and the ratio of carbon deposition decrease with the increasing of the N<sub>2</sub> to CH<sub>4</sub> ratio. The reason for this is that the probability of nitrogen collision with radicals increases when the ratio of N<sub>2</sub> to CH<sub>4</sub> increases, which causes the number of excessive radicals decrease. Although the addition of nitrogen decreases the conversion of methane, it can effectively prevent carbon deposition. Since the ionization energy of nitrogen (1503.2 kJ/mole) is higher than that of methane and C<sub>2</sub> hydrocarbons, the nitrogen can not be dissociated under the supplied electrical power. Therefore, the optimum ratio of N<sub>2</sub> to CH<sub>4</sub> is between 0.5–1.0.

Table 2 shows that the conversion of methane over V<sub>2</sub>O<sub>5</sub> catalyst is better than that of non-catalytic reaction and other catalyst catalyzed reaction. For other catalysts except V<sub>2</sub>O<sub>5</sub>, the conversion of methane is even lower than that without catalyst, while the selectivity to C<sub>2</sub> hydrocarbon is much higher than that of non-catalytic reaction. For LaBaO, ZnO
and La$_{0.8}$Sr$_{0.2}$CrO$_3$ catalysts, the selectivity to ethylene is much higher than that over V$_2$O$_5$, MoO$_3$/ZSM-5 and without catalysts. The yield of C$_2$ hydrocarbons over V$_2$O$_5$ catalyst is much higher than that over other catalysts and without catalyst, however, the yield of ethylene is lower than that of other catalysts and without catalyst. The ratio of carbon depositions obviously decreases in plasma catalytic reaction. This suggests that the performance of catalyst under plasma would be further investigated.

3.2. Cold plasma activation of methane

Product selectivity is directly influenced by the flow rate, power, pressure of the reaction system, distribution of electrical field and the energy density of the reaction zone. Our experimental data suggest that the major initial reaction is C—H bond breaking with concomitant formation of CH$_3^+$, CH$_2^+$, CH$^+$, H$^+$ and C at the high energy density zone. CH$_3^+$ and CH$_2^+$ radicals are desirable for the formation of ethane and ethylene from methane. They are low-energy processes because they predominate at low power levels in the bond C—H breaking reaction. Selectivity can be optimized in the cold plasma reaction because CH$^+$ and as a result H$^+$ and C can be largely minimized. Increasing the flow rate and decreasing the power can suppress the undesirable species such as CH$^+$, H$^+$ and C. The recombination of radicals CH$_3^+$, CH$_2^+$, CH$^+$ may be responsible for the formation of products by equations (1) to (8):

\[
\begin{align*}
  \text{CH}_3^+ + \text{CH}_3 & \rightarrow \text{C}_2\text{H}_6 \quad (1) \\
  \text{CH}_2^+ + \text{CH}_3 & \rightarrow \text{C}_2\text{H}_4 \quad (2) \\
  \text{CH}^+ + \text{CH}^+ & \rightarrow \text{C}_2\text{H}_2 \quad (3) \\
  \text{CH}_3^+ + \text{CH}^+ & \rightarrow \text{C}_2\text{H}_4 \quad (4) \\
  \text{CH}_3^+ + \text{CH}_2 & \rightarrow \text{C}_2\text{H}_4 + \text{H}^+ \quad (5) \\
  \text{CH}_3^+ + \text{CH}^+ & \rightarrow \text{C}_2\text{H}_4 \quad (6)
\end{align*}
\]

CH$_3^+$ + CH$^+$ \rightarrow C$_2$H$_2$ + H$_2$ \hspace{1cm} (7)

CH$_2$ + CH$^+$ \rightarrow C$_2$H$_2$ + H$^+$ \hspace{1cm} (8)

Production of acetylene can be promoted by preventing the formation of carbon. However, under low energy density and in a small plasma zone, the amount of methane cracked is little, and the probability of reaction (1), (2), (3) and (4) is even less. Methane collision with radicals is mainly responsible for the formation of products by equations (9) to (13):

\[
\begin{align*}
  \text{CH}_4 + \text{CH}_3^+ & \rightarrow \text{C}_2\text{H}_6 + \text{H}^+ \quad (9) \\
  \text{CH}_4 + \text{CH}_2^+ & \rightarrow \text{C}_2\text{H}_4 \quad (10) \\
  \text{CH}_4 + \text{CH}_2 & \rightarrow \text{C}_2\text{H}_4 + 2\text{H}^+/\text{H}_2 \quad (11) \\
  \text{CH}_4 + \text{CH}^+ & \rightarrow \text{C}_2\text{H}_4 \quad (12) \\
  \text{CH}_4 + \text{CH}^+ & \rightarrow \text{C}_2\text{H}_2 + \text{H}^+ + \text{H}_2 \quad (13)
\end{align*}
\]

Considerable research has been carried out by surface catalytic activation for the oxidative coupling of methane at elevated temperature over oxide catalysts. These catalysts for OCM are not active in plasma reaction [12]. It indicated that different mechanisms were involved in the two different processes. The thermodynamic temperature in our plasma reactor is much lower (<373 K) than that of the OCM processes, whereas the electronic temperature in our cold plasma reaction is 2500–50000 K. Catalysts in the plasma process primarily play the role of providing surfaces for the adsorption of methane, CH$_3^+$, CH$_2^+$, CH$^+$ and H$^+$.
radicals produced in the plasma zone and facilitating the desorption of H$_2$ and C$_2$ hydrocarbons, which perhaps can prevent C$_2$ hydrocarbons from producing higher hydrocarbons.

4. Conclusions

Methane can be cracked into radicals via direct, continuous, low power cold plasma under mild temperature and atmospheric pressure. The selectivity to C$_2$ hydrocarbons can reach as high as 98.64%, and conversions of methane as high as 60% can be obtained. Coking can be minimized under the conditions of selecting proper catalysts, appropriately high flow rate of inlet methane and suitable mole ratio of N$_2$ to CH$_4$.

References