Co-Generation of C$_2$+ Hydrocarbons and Synthesis Gas from Methane and Carbon Dioxide using Dielectric-Barrier Discharge Plasma Reactor without Catalyst at Low Temperature

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ABSTRACT

Co-generation of C$_2$, hydrocarbons and synthesis gas from methane and carbon dioxide has been an important issue in tackling the global warming effects from the two greenhouse gases. Dielectric-barrier discharge (DBD) plasma technology has been proposed to improve the process involving conversion and utilization of both methane and carbon dioxide. In this paper, a study on the effects of CH$_4$/CO$_2$ feed ratio, total feed flow rate, and discharge voltage on performance of DBD plasma reactor without catalyst at low temperature were addressed. The three factors in the DBD reactor showed significant effects on the reactor performances, i.e. methane conversion, synthesis gas and C$_2$+ hydrocarbons selectivities. With the DBD plasma reactor without catalyst, the C$_2$+ hydrocarbons (ethane, ethylene, acetylene, and propane) and synthesis gas (hydrogen and carbon monoxide), were produced from methane and carbon dioxide at low temperature with promising performances. Co-feeding carbon dioxide to the methane feed stream reduced coking and enhanced methane conversion. Methane and carbon dioxide conversions were influenced significantly by the discharge voltage. High discharge voltage, low CH$_4$/CO$_2$ feed ratio, and low total feed flow rate were suitable for the co-generation over DBD plasma reactor with potential performances.

Keywords: dielectric-barrier discharge, plasma discharge reactor, CH$_4$-CO$_2$ conversion, synthesis gas

1. INTRODUCTION

The studies on conversion and utilization of methane and carbon dioxide are widely researched in the field of C1 chemistry. Several technologies have been proposed to improve the efficiency and utilization of methane and carbon dioxide. Mitigation of CO$_2$, one of the most important greenhouse gases, is the crucial agenda in global warming issues. Meanwhile, the direct conversion of methane to C$_2$ hydrocarbons and synthesis gas has a large implication towards the utilization of natural gas in the gas-based petrochemical and liquid fuel. The CO$_2$ and CH$_4$ contents in Natuna’s, Arun’s and Terengganu’s natural gases with CH$_4$/CO$_2$ ratio 28/71, 75/15 and 80/8, respectively should be strategically utilized for the production of synthesis gas, higher hydrocarbons, liquid fuels and other important chemicals [1,2]. The potentials of non-conventional DBD plasma reactor for converting the two greenhouse gases, CH$_4$ and CO$_2$, to higher hydrocarbons and synthesis gas at low temperature and ambient pressure have also been reported [3]. A comprehensive review on recent development of plasma reactor technology for the co-generation of synthesis gas and C$_2$ hydrocarbons from methane and carbon dioxide has been reported to address the features, drawbacks, challenges, and feasibility of this technology [4].

The oxidative coupling of methane (OCM) is a promising and novel route for the conversion of natural gas to C$_2$ hydrocarbons in the presence of a basic catalyst within the temperature range of 923 to 1127 K. Recently, carbon dioxide was used to replace oxygen as an oxidant in oxidative coupling of methane by carbon dioxide (CO$_2$ OCM) to produce active oxygen species which promotes formation of...
CH\textsuperscript{3+} radicals from methane. Unlike O\textsubscript{2}, CO\textsubscript{2} does not induce gas phase radical reactions. It is thus expected that the development of active catalysts achieves high selectivity to C\textsubscript{2} hydrocarbons. From the thermodynamic studies, production of C\textsubscript{2}H\textsubscript{6} and C\textsubscript{2}H\textsubscript{4} from CH\textsubscript{4} and CO\textsubscript{2} showed low performances due to thermodynamic limitation [5,6]. Pertaining to CO\textsubscript{2} OCM reaction, various binary metal oxides have been proposed, i.e. CaO-CeO\textsubscript{2} [5], SrO-MnO\textsubscript{2} [7], and MnO\textsubscript{2}-SrCO\textsubscript{3} [8]. Almost all the catalysts achieved low methane conversion (up to 7%), high enough C\textsubscript{2} hydrocarbons selectivity (up to 85%), and low C\textsubscript{2} hydrocarbons yield (up to 4.5%). The CH\textsubscript{4} and CO\textsubscript{2} reactions over these catalysts only produce C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4} and CO without any other products such as H\textsubscript{2}, C\textsubscript{2}H\textsubscript{5}, or C\textsubscript{2}H\textsubscript{8}. In addition with respect to ternary metal oxide system, CaO-MnO/CeO\textsubscript{2} catalyst attained C\textsubscript{2} selectivity of 76.6% and C\textsubscript{2} yield of 3.7% using an optimization strategy [9].

Due to the thermodynamic constraints in obtaining high yield for the CO\textsubscript{2} OCM, further improvements are required including the exploitation of some non-conventional technologies such as plasma reactor. In this paper, a study on the effects of CH\textsubscript{4}/CO\textsubscript{2} feed ratio, total feed flow rate, and discharge voltage on performance of DBD plasma reactor without catalyst at low temperature are addressed. The effect of the process variables on the CH\textsubscript{4} conversion, selectivity and yield of C\textsubscript{2+} hydrocarbons, and H\textsubscript{2}/CO ratio are considered.

2. EXPERIMENTAL METHOD

2.1. Experimental Rig Set-up of DBD Plasma Reactor

The schematic diagram of experimental rig set-up of DBD plasma reactor is depicted in Figure 1, while Figure 2 presents the schematic diagram of high voltage generator circuit. A high voltage pulse AC generator supplies a voltage in the ranges 0 - 17 kV with a pulsed waveform at a frequency of up to 10 kHz (Atama Tech Sdn Bhd). The voltage measurement was conducted using an oscilloscope (ISO-TECH ISR 622) equipped with a high voltage probe (Atama Tech Sdn Bhd). All experimental works were conducted at fixed pulse frequency (2 kHz).

![Figure 1. Schematic diagram of experimental rig set-up of DBD plasma reactor: (1). Ball valve; (2). Volumetric flow controller; (3). Check valve; (4,5). Four and three way valves; (6). DBD plasma reactor; (7). High voltage probe; (8). DC power supply; (9). High voltage generator; (10). Oscilloscope; (11). Condensor; (12). Online GC; (13). Computer for GC; (P). Pressure gage](image)

The high voltage pulse AC generator circuit as depicted in Figure 2 can be divided to two main sections: the oscillator and the power drive. The oscillator is built around a CMOS 4093 (4-nand gates) and is configured as a pulse generator (duty cycle controlled). Either on or off time may be set by using
the 150 kΩ potentiometer (high and low potentiometers). The main working frequency band can be set by proper selection of the capacitor 10 nF. The on/off time control gives a very good regulation to fine-tune the output for maximum output voltage. In fact, once the frequency was increased, the voltage was decreased, and vice versa. The power drive is built around a power switching transistor (2N3055) which is driven by a 2N2222 transistor. The power transistor receives the command signal from the oscillator that opens and closes many times per second the primary coil of the transformer, thus inducing a high voltage in the transformer secondary coil. The output voltage is dependent on the transformer type, power transistor, and power supply.

Figure 2. Schematic diagram of high voltage generator circuit

2.2. Design of Experiment (DOE)

A Central Composite Rotatable Design (CCRD) for three independent variables was employed to design the experiments [9]. The design is intended to reduce the number of experiments and to arrange the experiments with various combinations of independent variables. The ranges and levels used in the experiments are given in Table 1. The experimental design matrix resulted by the CCRD are revealed in Table 2 involves 19 sets of coded conditions expressed in natural values. The design consists of 8 cube points of two-level full factorial design, 6 star points and 5 centre points. In this paper, effect of three variables on the performances of plasma CH₄-CO₂ conversion is presented in three dimensional surface profiles. The surface profile was prepared based on the experimental results with respect to the CCRD design by utilizing Statistica software (Statsoft, Inc.). The profiles were produced in the software by implementing an empirical quadratic polynomial approach to the experimental data with reasonable determination coefficient.

Table 1. Ranges and levels of factors or independent variables used in experiments

<table>
<thead>
<tr>
<th>Factors</th>
<th>Range and levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄/CO₂ Ratio, [-]</td>
<td>-α (-1.68) -1 0 +1 +α (+1.68)</td>
</tr>
<tr>
<td>Discharge voltage, kV</td>
<td>12.6 13.4 14.6 15.8 16.6</td>
</tr>
<tr>
<td>Total feed flow rate, cm³/min</td>
<td>26.4 40 60 80 93.6</td>
</tr>
</tbody>
</table>

Note: -1 (low level value); +1 (high level value); 0 (center point); +α and -α (star points)
3. RESULTS AND DISCUSSION

3.1. Principles of DBD Plasma Reactor

The principle is based on high energy electrons. Non-thermal plasma can be defined as gas consisting of electrons, highly excited atoms and molecules, ions, radicals, photons and neutral particles in which the electrons have a much higher energy than the neutral gas particles. Non-thermal plasma is also called non-equilibrium plasma due to the significant difference of temperature or kinetic energy between the electrons and the neutral particles [3]. The gas temperature can be within the range of room temperature, while the electrons can reach temperatures of $10^4 - 10^5$ K in a dielectric-barrier discharge. The non-thermal plasma can be generated and maintained by electrical discharge [3] which is a direct way to produce non-thermal plasma by applying a high voltage to a gas space and incurring gas breakdowns. The gas breakdowns generate electrons that are accelerated by an electric field forming non-thermal plasma. The electrical discharges can be realized in several ways depending on the types of voltage applied and reactor specification.

In the plasma reactor, the energetic electrons collide with molecules in the gas, resulting in excitation, ionization, electron multiplication, and the formation of atoms and metastable compounds [3,10]. When the electric field in the discharge gap is high enough to cause breakdowns in most gases, a large number of microdischarges are observed. The active atoms and metastable compounds subsequently collide with molecules, and reactions may occur. For CO$_2$ reforming of methane, it is expected that CH$_4$ and CO$_2$ participate in the reactions and be converted into higher hydrocarbons and synthesis gases. The possible reactions occurred in the CH$_4$ and CO$_2$ conversions over the DBD plasma reactor without catalyst at low temperature can be described as follows [3]:

\[
\begin{align*}
\text{CH}_4 + e & \rightarrow \text{CH}_3^* + \text{H}^+ + e \quad (1) \\
\text{CO}_2 + e & \rightarrow \text{CO} + \text{O}^* + e \quad (2) \\
\text{CH}_3^* + \text{CH}_3^* & \rightarrow \text{C}_2\text{H}_6 \quad (3) \\
\text{C}_2\text{H}_6 + e & \rightarrow \text{C}_2\text{H}_5^* + \text{H}^+ + e \quad (4) \\
\text{C}_2\text{H}_5^* + \text{CH}_3^* & \rightarrow \text{C}_3\text{H}_8 \quad (5) \\
\text{H}^+ + \text{H}^+ & \rightarrow \text{H}_2 \quad (6) \\
\text{C}_2\text{H}_6^* + e & \rightarrow \text{C}_2\text{H}_4 + \text{H}^+ + e \quad (7) \\
\text{C}_2\text{H}_4 + e & \rightarrow \text{C}_2\text{H}_5^* + \text{H}^+ + e \quad (8) \\
\text{C}_2\text{H}_5^* + e & \rightarrow \text{C}_2\text{H}_2 + \text{H}^+ + e \quad (9) \\
\text{C}_2\text{H}_5^* + \text{C}_2\text{H}_5^* & \rightarrow \text{C}_4\text{H}_{10} \quad (10) \\
\text{C}_4\text{H}_{10} + e & \rightarrow \text{C}_4\text{H}_6 + \text{H}^+ + e \quad (11) \\
\text{H}_2 + e & \rightarrow 2\text{H}^+ + e \quad (12) \\
\text{CH}_3^* + e & \rightarrow \text{CH}_2^* + \text{H}^+ + e \quad (13) \\
\text{CH}_2^* + e & \rightarrow \text{CH}^* + \text{H}^+ + e \quad (14) \\
\text{CH}^* + \text{CH}^* & \rightarrow \text{C}_2\text{H}_2 \quad (15) \\
\text{CH}_2^* + \text{CH}_2^* & \rightarrow \text{C}_2\text{H}_4 \quad (16) \\
\text{CH}^* + e & \rightarrow \text{C} + \text{H}^+ + e \quad (17)
\end{align*}
\]

In the reactions, e denotes high energy electron, while * express radical species from dissociation reaction.

3.2. Experimental Data of DBD Plasma Reactor without Catalyst at low temperature

The experimental results of DBD plasma reactor without catalyst at low temperature are listed in Table 2. The experimental data is presented based on design of experiment (DOE) with three independent variables, CH$_4$/CO$_2$ ratio, discharge voltage, and total feed flow rate. The CCRD design is practical for addressing the effect of each independent variable as well as the interaction among the variables [9]. Gaseous hydrocarbons (C$_2$-C$_3$), hydrogen and CO are the main products in the gas phase. The CO is principally produced from the dissociation of carbon dioxide, while the light hydrocarbons and hydrogen are the primary products from methane conversion. Pertaining to the C$_2$ hydrocarbons...
products, the concentration of ethane (C₂H₆) is much higher than that of ethylene (C₂H₄), acetylene (C₂H₂) and propane (C₃H₈) in the gaseous products. The results are significantly different with the results using corona discharges [3,12] where acetylene (C₂H₂) is the primary product. Direct conversions of CH₄ and CO₂ to higher hydrocarbons and synthesis gases is promising over the DBD plasma reactor without catalyst at low temperature. In fact, the conversions using conventional catalytic fixed bed reactor at high temperature (about 850 °C) only produced C₂H₆, C₂H₄ and CO with very low CH₄ conversion, namely CO₂ OCM [9]. In other catalytic process (carbon dioxide reforming of methane), it only produced H₂ and CO at high temperature (about 850 °C) over suitable catalyst with considerable methane conversion.

Table 2. Experimental data of DBD plasma reactor without catalyst at low temperature

<table>
<thead>
<tr>
<th>CH₄/CO₂ ratio</th>
<th>Discharge voltage (kV)</th>
<th>Total feed flow rate (cm³/min)</th>
<th>X CH₄ (%</th>
<th>X CO₂ (%)</th>
<th>S C₂⁺ (%)</th>
<th>S H₂ (%)</th>
<th>S CO (%)</th>
<th>Y C₂⁺ (%)</th>
<th>Y H₂ (%)</th>
<th>Y CO (%)</th>
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Note: - X, S, Y denote conversion, selectivity and yield, respectively
- C₂⁺ comprises C₂H₄, C₂H₆, C₂H₅, C₃H₈.

3.3. Effect of Operating Conditions on CH₄ Conversion, C₂⁺ Hydrocarbons Selectivity and Yield over DBD Plasma Reactor

CH₄ conversion, C₂⁺ hydrocarbons selectivity and yield are significantly affected by discharge voltage, CH₄/CO₂ ratio and total feed flow rate as depicted in Figures 3 - 5. From Figure 3, the CH₄ conversion enhances with concentration of CO₂ in the feed. As an oxidant, CO₂ is first decomposed to CO and O⁺ by high energy electrons. The hot electrons collide with CO₂ molecules and excite them to higher energy levels to dissociate or initiate the reactions. The dissociation reaction of CO₂ generates some oxygen species. Some excited atomic species such as metastable oxygen species (O(1D)) are active species for the generation of methyl radicals from CH₄ via dissociation reaction. The dissociation of CO₂ will generate oxygen active species that assist plasma catalytic methane conversion. With co-feed of CO₂, the reaction of methane species is deeply influenced by the new reactive oxygen species so that the conversion of methane is much higher than CO₂ conversion as exhibited in Table 2. The possible mechanism is that the reactive oxygen removes H atom in methane to generate the hydrocarbons radicals [3]. The excited species will react with the hydrocarbons radicals in the plasma zone. Indeed, the co-feed CH₄ and CO₂ promote the conversion each other. The distribution of hydrocarbon products changes significantly with the CH₄/CO₂ feed ratio [10]. It is suggested that the
CH₄ concentration in the feed is an important factor for the total amount of hydrocarbons produced. Lower amount of CO₂ in the feed favours the production of C₂ hydrocarbons as revealed in Figures 4 and 5. From Table 2, the larger the CO₂ amount in the feed, the higher the CO selectivity, whereas the selectivity of all higher hydrocarbons decreased. This phenomenon is corroborated with the results of Zhang et al. [10]. The yield of gaseous hydrocarbons (C₂+) increases considerably with the CH₄/CO₂ feed ratio as exhibited in Figure 5. It is possible to control the composition of C₂ hydrocarbons and hydrogen products by adjusting the CH₄/CO₂ feed ratio. It is recommended that the range of CH₄/CO₂ feed ratio 2 – 3 should be used to get a high selectivity of C₂ hydrocarbons and hydrogen with high methane conversion. Further increasing CH₄/CO₂ ratio above 3 favours lower CH₄ conversion and coking formation. In this work, the composition of feed gas is an important factor to influence the product distribution. Obviously, more methane in the feed will produce more hydrocarbons. The drawback of DBD plasma methane conversion with pure CH₄ feed is the formation of carbon deposits on the surface of electrode. The co-feed of CO₂ can inhibit the deposition of carbon and thus sustain the operations of DBD. The coke is mainly formed via CH₄ decomposition, not CO disproportionation. The dissociation energy of CO possessing of 11.1 eV is higher than that of dissociation energy of CH₄ (x=1-4), which is lower than 5 eV [12]. The CO₂ is more difficult to be dissociated via the collisions of electrons than CH₄.

Figure 3. Effect of operating conditions on CH₄ conversion: (a) discharge voltage and total feed flow rate vs CH₄ conversion presented at CH₄/CO₂ ratio of 3; (b) discharge voltage and CH₄/CO₂ ratio vs CH₄ conversion presented at total feed flow rate of 40 cm³/min

Total feed flow rate affects the residence time within the discharge zone. Increasing the total feed flow rate reduces the conversion of methane and carbon dioxide quickly as demonstrated in Figure 3(a) [12]. In fact, increasing the total feed flow rate does not affect significantly on the C₂+ hydrocarbons and hydrogen selectivity. Fincke et al. [13] concluded that an appropriate ratio of CH₄/CO₂ in the feed, a relatively low discharge voltage, and a relatively large total feed flow rate are benefit for higher energy efficiency. Actually, the low total feed flow rate with high residence time leads to the high intimate collision among the gas molecules and high energy electrons. The high intensive collisions favour the methane and carbon dioxide conversions to C₂+ hydrocarbons.

The various kinds of electric sources were used in plasma reactor such as AC, DC, microwave, or pulse power supply operated at high voltage and high frequency AC power. Varying the discharge power/voltage affects predominantly on methane conversion and higher selectivity of higher hydrocarbons (C₂-C₅). The conversions of CH₄ and CO₂ increase with discharge voltage as exhibited in Figure 3. At high discharge power the CH₄ conversion becomes higher than that of CO₂ at higher discharge voltage since the dissociation energy of CO₂ (5.5 eV) is higher than that of CH₄ (4.5 eV) [3,14]. More plasma species are generated at higher discharge voltage. In addition to high energy electron, species such as H, OH, O radicals can attack CH₄ molecules to produce more methyl radicals. The selectivity of C₂ hydrocarbons decreases slightly with increasing the discharge voltage at fixed
frequency as revealed in Figure 4 which is corroborated with the result of Liu et al. [15] and Song et al. [16]. This means that the increased discharge power may destroy light hydrocarbons (C$_2$-C$_3$). The low discharge power is beneficial to obtain higher selectivity to light hydrocarbons (C$_2$-C$_3$), but the CH$_4$ conversion is low. Eliasson et al. [17] reported that higher discharge power is necessary for generating higher selectivity to higher hydrocarbons (C$_5$+) over DBD reactor with the presence of zeolite catalysts. Higher discharge power is suggested for efficient methane conversion. As the discharge power increases, the bulk gas temperature in the reaction zone increases.

![Figure 4. Effect of discharge voltage and CH$_4$/CO$_2$ feed ratio on C$_2$+ selectivity presented at total flow rate of 40 cm$^3$/min](image1)

![Figure 5. Effect of discharge voltage and CH$_4$/CO$_2$ feed ratio on C$_2$+ hydrocarbons yield presented at total feed flow rate of 40 cm$^3$/min](image2)

Based on the effect of operating variables studies, it is recommended that low total feed flow rate, high CH$_4$/CO$_2$ feed ratio and high discharge voltage are suitable for producing C$_2$+ hydrocarbons and synthesis gas. Table 3 shows the results of DBD plasma reactor at recommended conditions and their comparison with pure CH$_4$ as a feed. From the table, it is shown that CH$_4$/CO$_2$ ratio = 3 provides more promising results. However, increasing CH$_4$/CO$_2$ ratio to 4 reduces methane conversion considerably.
and leads to enhanced C₂ hydrocarbons selectivity and H₂/CO ratio slightly. It is confirmed that CO₂ as co-feed has an important role in improving CH₄ conversion by contributing oxygen active species from the CO₂. The coking formation was appeared obviously in the surface of electrode at CH₄/CO₂ ratio of 4. The significant decreasing CH₄ conversion from 21.95% to 15.23% is also reported for pure CH₄ as a feed with higher C₂⁺ hydrocarbons selectivity. The coking formation is obvious distinctly in the surface of electrode. In this case, CO₂ also helps the reduction of coking formation. It can be concluded that too high CH₄/CO₂ ratio is not suggested in the operation of DBD plasma reactor due to decrement of CH₄ conversion and coking formation reasons.

Table 3. Results of DBD plasma reactor without catalyst at potential operating conditions and comparison with that at pure CH₄ as feed.

<table>
<thead>
<tr>
<th>Process variables</th>
<th>Responses/Dependent variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄/CO₂ Ratio</td>
<td>X CH₄ (%)</td>
</tr>
<tr>
<td>3.0</td>
<td>25.38</td>
</tr>
<tr>
<td>4.0</td>
<td>21.95</td>
</tr>
<tr>
<td>Pure CH₄</td>
<td>15.23</td>
</tr>
</tbody>
</table>

3.4. Effect of DBD Plasma Conditions on H₂/CO Synthesis Gas Ratio

Figure 6 presents the effect of discharge voltage and CH₄/CO₂ feed ratio on H₂/CO synthesis gas ratio. From the figure, the H₂/CO product ratio is mainly controlled by the discharge voltage and CH₄/CO₂ feed ratio. Increasing the discharge voltage leads to an increase in the H₂/CO ratio slightly and achieves maximum at 13.5 kV. Next increasing the discharge voltage decreases the H₂/CO ratio slightly due to more CO is produced from CO₂ and CH₄ which is in agreement with the result of Song et al. [16] without catalyst. The H₂/CO ratio increases considerably with CH₄ concentration in the feed gas. This means that once CH₄ concentration in the feed gas increased more H₂ was produced and less CO in the product. It is possible to control the composition of the synthesis gas product by adjusting the molar ratio of feed gases. Zhang et al. [11] reported that lower feed flow rate and high discharge voltage is beneficial for producing synthesis gases with higher H₂/CO ratio and for obtaining high selectivity to higher hydrocarbons.

Figure 6. Effect of discharge voltage and CH₄/CO₂ feed ratio on H₂/CO synthesis gas ratio presented at total feed flow rate of 40 cm³/min

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4. Conclusions

A study on the effects of CH$_4$/CO$_2$ feed ratio, total feed flow rate, and discharge voltage on the performance of DBD plasma reactor without catalyst at low temperature were successfully addressed. The three factors in the DBD plasma reactor showed significant effects on the reactor performances, i.e. methane conversion, synthesis gas selectivity, C$_2$ hydrocarbons selectivity. A lower feed flow rate was appropriate for producing high selective C$_2$ hydrocarbons and higher H$_2$/CO ratio of synthesis gases, because of high residence time of the gases within the discharge zone. The range of CH$_4$/CO$_2$ feed ratio being 2 – 3 is suitable in the DBD reactor to obtain high selective C$_2$ hydrocarbons and hydrogen with high methane conversion. High discharge power/voltage is required to obtain high yield C$_2$ hydrocarbons. It is concluded that too high CH$_4$/CO$_2$ ratio is not suggested in the operation of DBD plasma reactor due to decrement of CH$_4$ conversion and coking formation. The application of the DBD plasma reactor is potential for the co-generation of C$_2$ hydrocarbons and synthesis gases from methane and carbon dioxide. Future development by introducing suitable catalysts is required in order to improve the C$_2$ hydrocarbons selectivity.

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