Operando Investigation of Intermediate Species in Non-Oxidative Methane Coupling by Non-thermal RF Plasma

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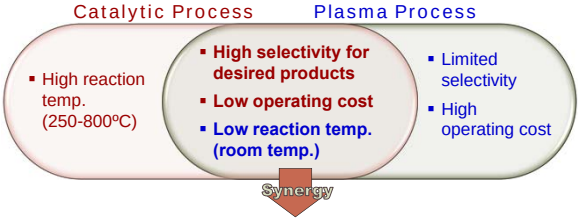
Abstract: Non-oxidative coupling of methane by low pressure RF plasma was investigated with real time monitoring tools such as Langmuir probe, and ion mass and energy spectrometer. Process parameters were systematically changed to generate various plasma conditions and thus to identify key factors affecting the methane activation. From operando analysis, it was found that effects of electron energy and ion energy on methane conversion were minimal when the electron energy of plasma is greater than methane activation energy. On the other hand, electron concentration and the residence time in plasma were strongly correlated with the degree of methane conversion. Moreover, it should be noted that the density of methanium (CH_5^+) which is a byproduct of ion-molecule reaction pathway of methyl radical formation (CH_3·), was reversely related to the extent of methane conversion due to active reactions among the methanium and C_2 product molecules. Furthermore, for tested experimental conditions in this study, the product distribution of the methane plasma reaction was more closely related with the methane conversion level than with other plasma parameters. This real time analysis results can be used to derive meaningful insights to help designing an effective synergistic plasma-catalyst system.

Direct non-OCM in RF plasma



Catalytic Plasma Process

$CH_4 + e^- \rightarrow C_2H_6, C_2H_4, C_2H_2, H_2$

1. To better understand the RF methane plasma and to study the formation of C_2 products by monitoring reaction intermediates (radicals, electrons, ions)
2. To investigate how active/key reaction intermediates interact with catalyst surfaces in plasma
3. To design optimal catalyst for plasma direct non-OCM and to come up with plasma-catalyst hybrid system

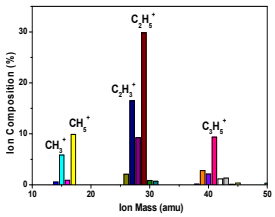
Operando Plasma Diagnostic System

Reaction Conditions

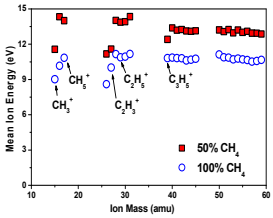
- Gas: High purity CH_4, High purity Ar
- Heater Temperature: 30-600ºC
- Flow rate: 3-30sccm
- Pressure: 40-180mTorr
- RF power: 2-90W

- ICCD: Intensity distribution of plasma
- Langmuir Probe: Electron Energy Distribution(EEDF)
- EQP: Ionic/Neutral species distribution, Cationic energy distribution, Radical detection

Properties of Ion Species During Plasma Reaction



Methane plasma ionic species distribution and composition (RF_{power}=5W, P=40mTorr, F=9sccm, $T_{electrode}$=25˚ C)



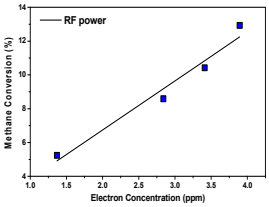
Energy level of ions in 50% CH_4/Ar and 100% CH_4 discharge

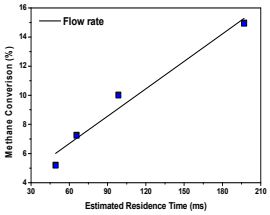
Plasma Property *vs.* Methane Conversion

Plasma reaction conditions and plasma diagnostic results at $T_{electrode}$ = 25˚ C

Varied Parameter	Fixed Parameters	Methane Conv.	Mean Electron Energy	Electron Conc.	Mean Ion Energy ($C_2H_5^+$)
50% CH_4/Ar	5W, 40mTorr, 15sccm	3.3%*	16.8eV	0.71ppm	13.9eV
100% CH_4		3.8%*	14.0eV	0.69ppm	10.9eV
10W	60mTorr, 20sccm	5.2%	14.4eV	1.37ppm	7.3eV
20W		8.6%	14.7eV	2.84ppm	11.0eV
30W		10.4%	14.0eV	3.41ppm	12.0eV
40W		12.9%	13.3eV	3.89ppm	12.6eV
5sccm	10W, 60mTorr	15.0%	13.8eV	1.44ppm	8.4eV
10sccm		10.0%	13.6eV	1.49ppm	8.2eV
15sccm		7.3%	13.7eV	1.36ppm	8.1eV
20sccm		5.2%	14.4eV	1.37ppm	7.3eV

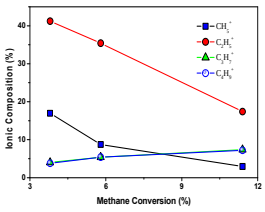
*Values are normalized with methane concentrations





Methane conversion as a function of electron concentration (left) and estimated residence time (right)

Methandium Density *vs.* Methane Conversion



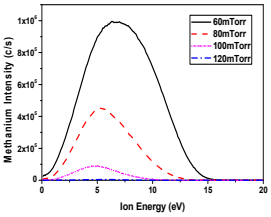
Ionic composition as a function of methane conversion for the flow rate variation results.

$CH_5^+ + C_2H_6 \rightarrow C_2H_5^+ + CH_4 + H_2$

$CH_5^+ + C_2H_4 \rightarrow C_2H_5^+ + CH_4$

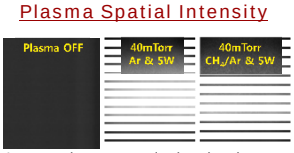
$C_2H_5^+ + C_2H_6 \rightarrow C_3H_7^+ + CH_4$

$C_2H_5^+ + C_2H_6 + CH_4 \rightarrow C_4H_9^+ + H_2 + CH_4$



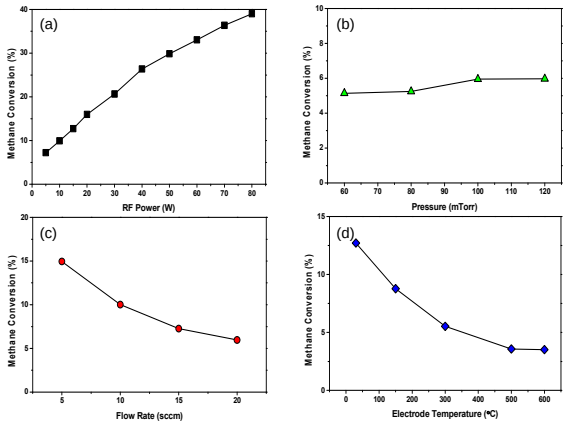
Methanium ion energy distributions for different chamber pressures.

Plasma Spatial Intensity

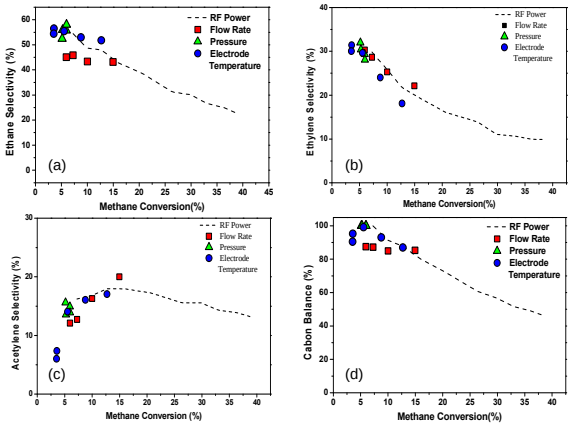


Intense plasma zone in the sheath near the bottom RF electrode

Plasma Reaction Conversion and Selectivity



Methane conversion changes with parameter variations of (a) RF power, (b) flow rate, (c) pressure, and (d) electrode temperature.



Product selectivity and carbon balance as a function of methane conversion. (a) ethane selectivity, (b) ethylene selectivity, (c) acetylene selectivity, and (d) carbon balance.

- Different process parameters were changed to selectively induce desired changes on plasma property and reaction condition. It was found that when the electron energy in plasma is sufficient to activate methane molecule, additional energy did not lead to an increased conversion. Likewise, the increase in ion energy did not improve the conversion.
- Both the electron concentration, which represents the degree of ionization, and molecule residence time in plasma were linearly correlated with the methane conversion.
- The methanium density was expected to be a quantitative representation of methyl radical formation, but the correlation between the methane conversion and ion density showed that the methanium was actively consumed through reactions with C_2 product molecules. Thus, the methyl radical density could not be measured by the methanium density.
- The reaction product distribution was not influenced by the plasma property and was mainly determined by the conversion level for the plasma conditions in this study

This research was supported by C1 Gas Refinery Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2016M3D3A1A01913257)