MINIMUM ENERGY REQUIREMENT FOR METHANE STEAM REFORMING IN PLASMA-CATALYST REACTOR

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1. Introduction

This paper descries advanced steam reforming of methane in plasma-catalyst hybrid reactor. Synergistic effect between non-thermal plasma (DBD) and Ni-catalyst was observed at lower reaction temperature (400°C-600°C). Methane conversion exceeded far beyond equilibrium conversion, while product selectivity tended to follow equilibrium composition at given conditions: energy cost and energy efficiency were improved by 134 MJ/kg_H_2 and 69%. According to numerical simulation of streamer propagation in pure methane, production of large number of vibrationally excited methane seems to contribute significant increase in methane conversion since vibrational species promoted dissociative chemisorption on nickel surface at lower temperature. Based on those experimental and numerical evidences, minimum energy required in plasma-catalyst hybrid reactor for methane steam reforming was estimated. The energy consumption might be reduced by one-quarter of experimental result, which also means that hybrid reactor might be able to regenerate low temperature thermal energy during low temperature plasma catalysis of methane (400°C-600°C).

2. Methane steam reforming by plasma-catalyst hybrid reactor

Experimental. Authors developed Barrier-discharge Enhanced Catalytic-bed (BEC) reactor for methane steam reforming (1-5). The wire-to-tube (I.D. 6 mm) reactor packed with 3wt%Ni/SiO_2 catalyst pellets (1.2 mm and 0.9 mm) was situated in a constant temperature bath (120°C). High voltage sine wave (76 kHz) was applied between wire and external electrodes. Methane and water-vapor mixture was fed into the reactor at various mixture ratio and flow rate. Three different conditions were investigated: (1) 3wt%Ni/SiO_2, (2) plasma and 3wt%Ni/SiO_2, and (3) plasma with SiO_2. Detailed description of reactor and experimental conditions are presented elsewhere (1).

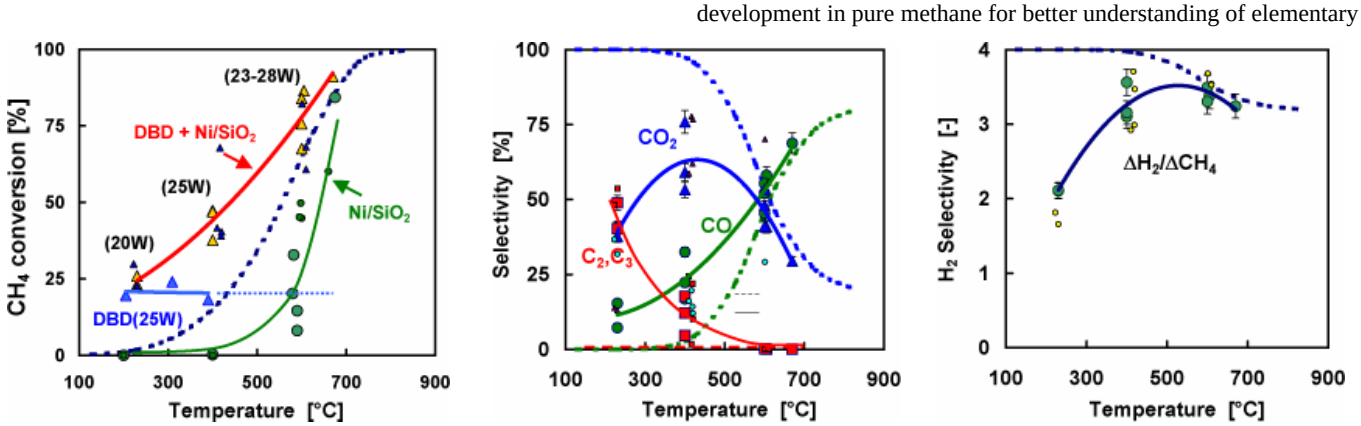
Synergistic effect between plasma and catalyst. Figure 1 (a) compares methane conversion characteristics for three different reaction systems, and (b), (c) show product selectivity. Barrier discharge is able to decompose methane at lower temperature, and 25% conversion was achieved at 200°C. However, methane conversion falls far short of equilibrium at higher temperature since methane activation by electron impact is basically independent of gas temperature (within 25°C -700°C). On the other hand, nickel catalyst does not show catalytic activity below 400°C, and methane conversion was half of the equilibrium at 600°C. If the temperature reached 700°C, methane conversion abruptly increased and attained equilibrium. We didn't observe major changes in methane conversion and product selectivity with respect to pellet diameter.

When barrier discharge and catalyst was combined, methane conversion exceeded equilibrium over the tested temperature range. The strong synergistic effect of barrier discharge and nickel catalyst was observed between 400°C and 600°C: methane conversion exceeded combined result of barrier discharge and nickel catalyst. On the other hand, catalytic reaction predominated over barrier discharge above 700°C, and synergistic effect was not observed below 200°C. Methane conversion curve for Ni/SiO_2 shifted 200°C towards lower temperature region in the presence of barrier discharge: the apparent activation temperature for nickel catalyst seemed to be lowered due to the existence of barrier discharge.

Figure 1 (b) and (c) show product selectivity obtained by BEC reactor. When the temperature was 200°C, reaction characteristics were very similar to those obtained by DBD reactor: 50% of carbonaceous products were C_2 (mainly ethane) and C_3 (propane) hydrocarbons. Product selectivity approaches equilibrium curve (dotted line) with increasing reaction temperature, and perfectly follows equilibrium curve over 600°C. It is interesting to note that methane conversion largely exceeded equilibrium value, but product selectivity follow equilibrium. This means that electron impact process plays an important role during gas phase methane activation: not only ground state methane molecule, but also excited molecule can be decomposed on nickel catalyst, leading to apparent low temperature activation of methane.

3. Radical formation by electron impact

Model. We performed numerical simulation on streamer development in pure methane for better understanding of elementary



(a) Methane conversion (b) CO, CO_2, C_2 selectivity (c) H_2 selectivity

Fig. 1 Methane conversion and product selectivity at different temperatures, showing synergistic effect of plasma and Ni catalyst on methane decomposition. (--- Equilibrium). Smaller symbols represent results obtained with 0.9 mm Ni/SiO_2 pellet.

electronic and chemical processes. We assumed that streamer was one-dimensional cylinder with 100 μm radius and 2 mm long. We simulated Anode Directed Streamer (ADS) ignited from tiny plasma spot located in front of the cathode. Basic equations were continuity equations for electron, ions, and neutral species, and Poisson's equation. 38 elementary reactions including 8 inelastic collisions were simultaneously solved. During streamer development, electric energy input and radical formation efficiency was analyzed in detail. After the termination of streamer development (~5 ns), ionic and free radical chemistry that would last for 10 ms was performed with the reaction scheme proposed by Tachibana et al (6). 16 neutral species, 4 positive ions, and 2 vibrationally excited species were considered in our model. Temperature and pressure were 300 K and 760 Torr, respectively.

Energy branching to radicals. Table 1 shows energy branching and relative radical density during streamer propagation. Excitation threshold for vibrational excitation is of the order of 0.1-0.3 eV; however, 40% of input electrical energy was consumed since rate constants are 10 times larger than that for other reactions. Vibrational population was 150 times larger than electron number density. Density of CH_3 was the highest among other methane fragments due to hydrogen abstraction reaction:

$$CH_4 + H \rightarrow CH_3 + H_2 \qquad \text{(R1)}$$

(R1) is obviously independent of electronic processes. In fact, energy branching to CH_3 is the same order as other inelastic collisions. From this point, decomposition of vibrationally excited methane poses significant importance in order to improve energy cost.

4. Minimum energy consumption in BEC reactor

In general, production of vibrational species leads to significant energy loss in many plasma processes since reactivity of vibrational species is generally low. However vibrational methane seems to increase reactivity significantly in hybrid system since it increases dissociative chemisorption on Ni surface at lower temperature. We calculated energy consumption which is necessary to decompose 1 mol of methane by electron impact, and estimated minimum energy required in methane steam reforming. Main assumptions are as follows:

1. Assume stoicheometric mixture of methane and water vapor, i.e. $CH_4 : H_2O = 1 : 2$.
2. One-third of energy spent by single streamer is utilized for methane activation.
3. Ignore reactions related to H_2O and ion lose.
4. All vibrational species react on Ni catalyst to produce hydrogen.
5. Inelastic collision by electron is independent of temperature.

When external field strength is 200 Td, a single streamer spends 0.150 μJ electrical energy during propagation, and vibrationally excited methane in streamer, on space average, is populated by 1000ppm. Assume those vibrational methane is able to fully decompose if Ni catalyst is present, then 0.85×10^{-13} mol of methane is supposed to decompose to produce hydrogen, which corresponds to 0.757 μJ of heating value. That is,

$N_{methane} = 2.55 \times 10^{-9}$ mol $\times$ 0.001 $\times$ (1/3) = 8.5×10^{-13} mol
Heating value for $N_{methane}$: 890 kJ/mol $\times$ 8.5×10^{-13} [mol] = 0.757 μJ
Heating value for $N_{hydrogen}$ (= $4N_{methane}$): 0.757 $\times$ (1144/890) = 0.973 μJ
Energy absorbed by steam reforming: 0.973-0.757 = 0.216 μJ

About 70% of endothermic reaction enthalpy (0.15 μJ/0.216 μJ =0.7) must be supplied through electronic process, while 30% is from low temperature thermal energy source. This relation is schematically expressed in Fig. 2. Although current plasma-catalyst hybrid reactor spends 744 kJ of electrical energy per 1 mol of methane, it might be minimized by 176 kJ if ion current and any other loses could be neglected.

5. Concluding remarks

The result does not necessarily mean that plasma fuels processing must be combined with catalyst. The point is that plasma processing, in principle, accompanies considerable energy loses during inelastic electron impact process. Even though 50% of electrical energy is utilized by radical production, minimum energy requirement incredibly amounts to 6000 kJ per 1 mol of methane without help of vibrational methane since population of those radical is very small (3×10^{-14} mol in a single streamer). Authors strongly recommend plasma hybrid system which promotes decomposition of vibrational species or chain reactions in a given condition.

References

(1) T Nozaki, Catalysis Today, in print (2003).
(2) T Nozaki et al, Part 2, Catalysis Today, in print (2003).
(3) H H Kim et al., IEEE Trans. Ind. Appl., **35**(6) (1999) 1306-1310.
(4) A Ogata et al., IEEE Trans. Ind. Appl., **37**(4), (2001) 959-964.
(5) H Kabashima et al., IEEE Trans. Ind. Appl., **39**(2) (2003) 340-345.
(6) K Tachibana et al., J Phys D: Appl Phys **17** (1984) 1727-1742.

Table 1. Electric processes and energy branching (200 Td, 300 K-760 Torr, $N_e \approx 10^{14}$ cc^{-1}, 1 μs)

$CH_4 + e \rightarrow$	ε_i [eV]	Density	Energy branch %
$CH_4(\nu 24) + e$	0.162	$150N_e$	11.9
$CH_4(\nu 13) + e$	0.361		24.5
$CH_3 + H + e$	9.0	$10N_e$	17.0
$CH_2 + H_2 + e$	10.0		13.2
$CH + H_2 + H + e$	11.0	N_e	10.8
$C + 2H_2 + e$	12.0		9.3
$CH_4^+ + e + e$	12.6	N_e	9.4
$CH_3^+ + H + e + e$	14.3		4.0

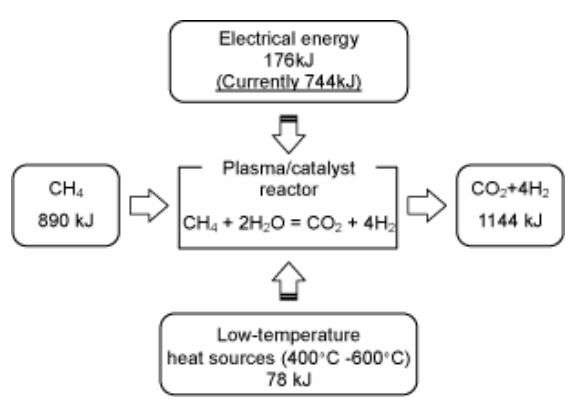


Figure 2. Schematic representation of energy balance