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# Plasma-catalytic reforming of methane in AC microsized gliding arc discharge: Effects of input power, reactor thickness, and catalyst existence

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ABSTRACT

A new design of a microsized gliding arc discharge reactor was preliminarily investigated for the reforming of methane to various useful products. In methane reforming by the gliding arc (GA) microreactor under ambient conditions, hydrogen and acetylene were dominantly produced, with high selectivities of ~75% and ~70–90%, respectively, which were much higher than those in conventional GA reactors because of the high power density and the extremely short residence time of the GA microreactor, as compared to conventional GA reactors. Small amounts of other products (including ethylene, ethane, butadiene, and coke) were also formed. The results showed that the methane conversion strongly depended on input power and reactor thickness. A Ni-loaded porous alumina-silica catalyst, prepared by wet impregnation, was used to investigate the catalytic effect on the microreactor performance for methane reforming. A considerable enhancement of methane conversion, but not hydrogen and other product selectivities, was achieved in the combined plasma-catalytic system. Furthermore, heating the surface of the Ni-loaded catalyst brought about a significant change in product selectivity, but not methane conversion.

## 1. Introduction

Natural gas is the cleanest and environmentally safest primary fossil fuel, in terms of its lowest emission of $CO_2$. Interestingly, numerous investigations have focused on upgrading the conversion process of methane ($CH_4$), which is a main constituent in natural gas in all reserves around the world, to produce higher value-added chemicals by reforming reactions. Non-thermal plasma has reportedly been used for several chemical conversion processes, also involving either non-oxidative methane reforming [1–7], oxidative methane reforming [8–15], or hybrid plasma-catalytic methane reforming [16–29]. Due to its non-equilibrium property, non-thermal plasma, with high-energy electrons, creates principally a large number of chemically active species through electronic and ionic collision processes, and then immediately induces subsequent chemical reactions under ambient temperature and atmospheric pressure. Hence, highly stable methane molecules can potentially be converted by means of non-thermal plasma. For further development of the non-thermal plasma processing, some researchers have integrated it with the novel idea of microreactor technology [30–33]. In a microreactor, the extremely small volume and large specific surface area provide several significant process advantages, such as better heat distribution and heat transfer, precise control of a shorter residence time, a higher chance for reactant molecules to collide with electrons, and small processing amounts of reactants [30–35].

This present work focuses on studying the performance of a gliding arc discharge microreactor, based on a concept of integrating a non-thermal plasma with a microreactor technology, by using the methane reforming as a model reaction for the preliminary test. The effects of input power, reactor thickness, and nickel metal loaded on a porous alumina-silica catalyst plate on the performance of non-oxidative methane reforming were investigated. Nickel was used as the studied reforming catalyst due to its good reforming capability, as reported in several articles [18,24,36]. Moreover, the effect of heating the catalyst surface on the plasma reaction performance was also investigated.

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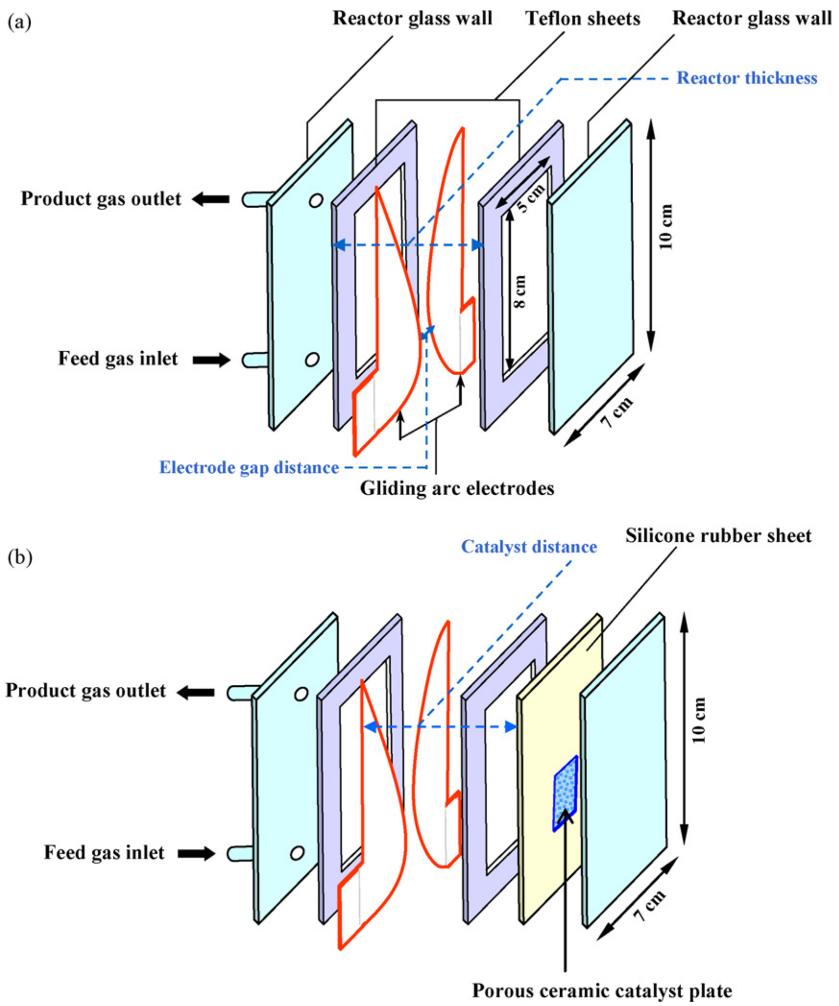

**Fig. 1.** Configuration of a gliding arc discharge microreactor (a) without a catalyst and (b) with a catalyst.

## 2. Experimental

### 2.1. Gliding arc microreactor system

The configuration of the gliding arc (GA) microreactor used in this study is illustrated in Fig. 1. The GA microreactor was made of two glass plates with a width of 7 cm, a length of 10 cm, and a thickness of 0.5 cm, and had two diverging knife-shaped electrodes fabricated from two stainless steel sheets with a thickness of 0.25 mm. These electrodes were vertically positioned inside the reactor and connected to the AC power supply. Two pre-drilled holes on the glass cover (reactor wall) served as the gas inlet and outlet. Two Teflon sheets with different thicknesses were placed between the reactor glass walls and the electrodes on both sides (see Fig. 1(a)) to create various reactor thicknesses (reactor thickness = electrode thickness + 2 × Teflon sheet thickness) and to seal the microreactor. To examine the effect of catalyst in this studied plasma microreactor system, a 2 cm × 3 cm catalyst plate was inserted into a holder made of a silicone rubber sheet, and then was packed between the reactor glass wall and the Teflon sheet on the back side of the microreactor (see Fig. 1(b)). In Fig. 1(b), the catalyst distance is defined as the distance between a silicone rubber sheet and a pair of electrodes—in other words, a right-hand-side Teflon sheet thickness. Additionally, to study the effect of catalyst surface temperature, the catalyst plate was heated to 210 °C by being externally irradiated with an infrared (IR) beam equipped with a halogen lamp (LCB50) and an IR beam heater (LCB-PS12, Inflidge Industrial Ltd.). The temperature on the surface of the catalyst plate was measured by using a thermal label indicator.

### 2.2. Catalyst preparation procedure

A porous ceramic plate with a chemical composition of 23% $SiO_2$, 75% $Al_2O_3$, and 2% others (Nikkato Corporation) was used as a catalyst support. Its Brunauer–Emmett–Teller (BET) specific surface area and specific pore volume were 2.6 $m^2/g$ and 5.9 $mm^3/g$, respectively. $Ni(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chemical Industries, Ltd.) was used as a nickel precursor. To prepare the nickel loaded on the catalyst support by using the wet impregnation method, the porous silica-alumina plate was immersed in an aqueous solution of 2.0 M $Ni(NO_3)_2 \cdot 6H_2O$ for 10 h. After that, the catalyst was dried at 110 °C for 2 h, and then calcined in air at 500 °C for 5 h. The calcined catalyst was further reduced in a $H_2$ atmosphere at 500 °C for 3 h prior to use. Both unloaded and Ni-loaded catalyst plates were used comparatively for testing the plasma reaction performance. An energy dispersive X-ray analyzer (EDX, Link ISIS, Series 300) was used to analyze the Ni content in the prepared catalyst, and it was found to be approximately 5 wt.%.

### 2.3. Reaction testing experiments

In this work, a mixed feed gas having 5% $CH_4$ with Ar balance was introduced upward to the GA microreactor system. The flow rates of $CH_4$ and Ar were regulated by rotameters. After the composition of feed gas was invariant with time, the power unit was turned on. An AC power supply unit (Alpha Neon, M-5) was used to generate the gliding arc discharge in the microreactor from the domestic AC of 110 V and 50 Hz. The generated gliding arc discharge had a fixed frequency of 50 Hz and different input powers to the microreactor. Discharge power was measured by a power monitor (HIOKI, Type 3330). After the system reached equilibrium state (normally within 3 min after turning on the power unit), an analysis of outlet gas composition was performed at least two times. The compositions of the feed gas and the product gas streams were determined by two gas chromatographs. The first gas chromatograph (Shimadzu, GC-14B), equipped with a GS-GasPro capillary column and a flame ionization detector (FID), was used to detect $CH_4$, $C_2H_2$, $C_2H_4$, $C_2H_6$, $C_3H_8$, $C_4H_{10}$, and butadiene (1,3-$C_4H_6$). The second one (Shimadzu, GC-8A), equipped with a molecular sieve 13X packed column and a thermal conductivity detector (TCD), was used to detect $H_2$. The carbon deposit (C) formed from the reaction inside the microreactor was calculated using carbon balance. For the combined plasma-catalytic system, the experiments were repeated at least three times in order to ensure the reproducibility of the experimental data. The experimental data were averaged to assess the process performance, and the experimental error was found to be less than 5%.

### 2.4. Reaction performance assessment

The methane conversion is defined as:

$$\%\ \text{Methane conversion} = \frac{(\text{moles of methane in} - \text{moles of methane out})\ (100)}{\text{moles of methane in}} \tag{1}$$

The selectivities for hydrocarbon products are defined on the basis of the amount of C-containing products, as expressed in Eq. (2). In the case of the hydrogen product, its selectivity is calculated based on H-containing products, as expressed in Eq. (3):

$$\%\ \text{Selectivity for any hydrocarbon product} = \frac{(\text{amount of C atoms in any hydrocarbon product})\ (100)}{\Sigma(\text{amount of C atoms in the C-containing products})} \tag{2}$$

$$\%\ \text{Selectivity for hydrogen} = \frac{(\text{amount of H atoms in the hydrogen product})\ (100)}{\Sigma(\text{amount of H atoms in the H-containing products})} \tag{3}$$

## 3. Results and discussion

### 3.1. Effect of input power

The input power is technically regarded as a key parameter in operating the plasma chemical processing and in sustaining the plasma stability. To investigate the influence of input power on the non-oxidative methane reforming under the GA microreactor system, the input power was experimentally varied in the range of 4–12 W, while the feed flow rate, electrode gap distance, and reactor thickness between the reactor glass walls were kept constant. Fig. 2(a) shows the result of methane conversion as a function of input power. The methane conversion increased with increasing input power—in other words, with increasing power density, i.e. power density (J/m$^3$) = input power (J s) per feed flow rate of methane (m$^3$/s). These generated electrons have more ability to break down the strong C–H bond of methane, thereby leading to an increased methane conversion. In addition, due to the fact that the power density in this studied GA microreactor was comparatively high compared to that in a conventional GA reactor [14], the resulting methane conversion is greater in the GA microreactor, even though the discharge appearances of both GA reactor types were almost the same. For example, in the GA microreactor, a higher methane conversion of 32% was observed at a power density of 72 J/m$^3$, but in a conventional GA reactor [14], a lower methane conversion of 18% and 8% was obtained at a power density of 35 J/m$^3$ and 28 J/m$^3$ in pure methane and $CH_4$/He feed systems, respectively.

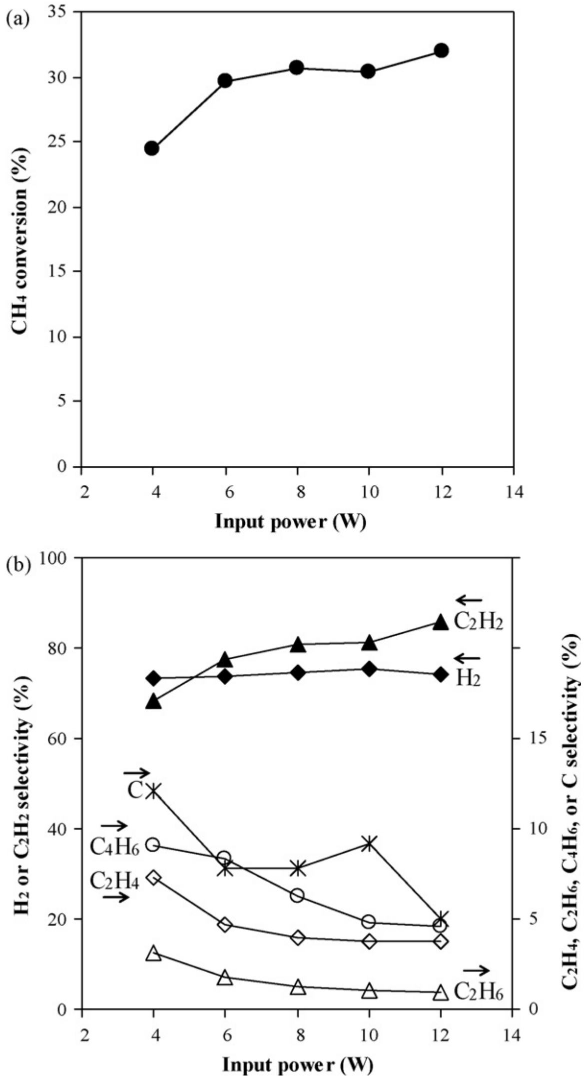

**Fig. 2.** Effect of input power on (a) methane conversion and (b) product selectivities of the non-oxidative methane reforming ($CH_4$ in feed, 5%; feed flow rate, 200 cm$^3$/min; electrode gap distance, 4 mm; and, reactor thickness, 1.25 mm).

Fig. 2(b) shows the results of product selectivities as a function of input power. All products detected in the methane reforming using the GA microreactor were $H_2$, $C_2H_2$, $C_2H_4$, $C_2H_6$, $C_4H_6$, and carbon deposit (C). An increase in input power tended to decrease the selectivities for $C_2H_4$, $C_2H_6$, and $C_4H_6$ hydrocarbons, and carbon deposit, whereas the $C_2H_2$ selectivity apparently increased, and the $H_2$ selectivity remained almost unchanged. It was observed from the product distribution that, especially at very high input power, the dominant products from the direct methane reforming under the discharge environment of the GA microreactor were $C_2H_2$ and $H_2$, with high selectivities of ~70–90% and ~75%, respectively. Interestingly, it was found that the $C_2H_2$ and $H_2$ selectivities in the GA microreactor were comparatively much higher than those in the conventional GA reactor (totaling ~20% and ~30–50% for pure methane and $CH_4$/He feed systems, respectively) [14], possibly because of its very high power density, as well as the short residence time and rapid quenching after the plasma zone due to the microsize of the reactor. Other products ($C_2H_4$, $C_2H_6$, and $C_4H_6$) were also detected, but with relatively low levels. The $C_4H_6$ product was formed only in the GA microreactor, but was not found in the conventional GA reactor [14]. These results imply that the GA microreactor can potentially be employed to produce useful $C_2H_2$ and $H_2$ products from the abundantly available methane in natural gas. Nevertheless, under the studied conditions, $C_3$ and other higher hydrocarbons, except $C_4H_6$, were not detected, suggesting that the studied GA microreactor is still not efficient in producing higher hydrocarbons from non-oxidative methane reforming. From the present results, however, further development of the GA microreactor for specified products should be of great interest.

### *3.2. Effect of reactor thickness*

The main goal of investigating the effect of reactor thickness was to determine how the microreactor configuration impacted the reaction performance under the non-thermal gliding arc discharge environment. The reactor thickness was varied by changing the thickness of the Teflon sheets from 0.2 mm to 0.5 mm, 1.0 mm, 1.5 mm, and 2.0 mm, which corresponded to the reactor thicknesses of 0.65 mm, 1.25 mm, 2.25 mm, 3.25 mm, and 4.25 mm, respectively. Fig. 3(a) shows that there was a significant increase in methane conversion (ranging from 26% to 43%) with increasing reactor thickness. A possible explanation for this is that the larger reactor thickness provides longer residence time, resulting in the promotion of the successive reaction to methane molecules, and therefore higher methane conversion. The effect of reactor thickness on the selectivities for $H_2$, $C_2H_2$, $C_2H_4$, $C_2H_6$, $C_4H_6$, and C, in terms of product distribution, is shown in Fig. 3(b). All product selectivities remained almost unchanged throughout the investigated range of reactor thickness, even though longer residence times (ranging from 0.021 s to 0.14 s) were achieved at larger reactor thicknesses (ranging from 0.65 mm to 4.25 mm). The reason is that a change in the reactor thickness in this studied GA microreactor still provided very short residence time, in the range of 0.021 s to 0.14 s, which is too short for subsequent reactions (e.g. coupling and dehydrogenation reactions). It should be noted here that the calculation of residence time is based on the gas flow rate at room temperature. This obtained result was quite similar to the effect of feed flow rate in our previous study of using the conventional GA reactor with the $CH_4$/He feed system [14], in which a longer residence time (ranging from 1.3 s to 3.8 s) at a lower feed flow rate (ranging from 150 $cm^3$/min to 50 $cm^3$/min) was found to induce the enhancement of $CH_4$ conversion (from approximately 5% to 8%), but insignificantly affected the product selectivities. Nevertheless, the most dominant product of the conventional GA reactor was $C_2H_6$ (saturated hydrocarbon) with the highest selectivity of ~40%, whereas the GA microreactor mainly yielded $C_2H_2$ (unsaturated hydrocarbon) with the highest selectivity of ~80%. This implies that the extremely short residence time in this study only influences the collision/interaction between methane molecules and electrons, and does not have much influence on the collision/interaction among products and/or the recombination of active radicals to form various products. The present results reveal that the use of a GA microreactor can significantly improve the conversion of methane and product selectivities, as compared to conventional plasma reactors.

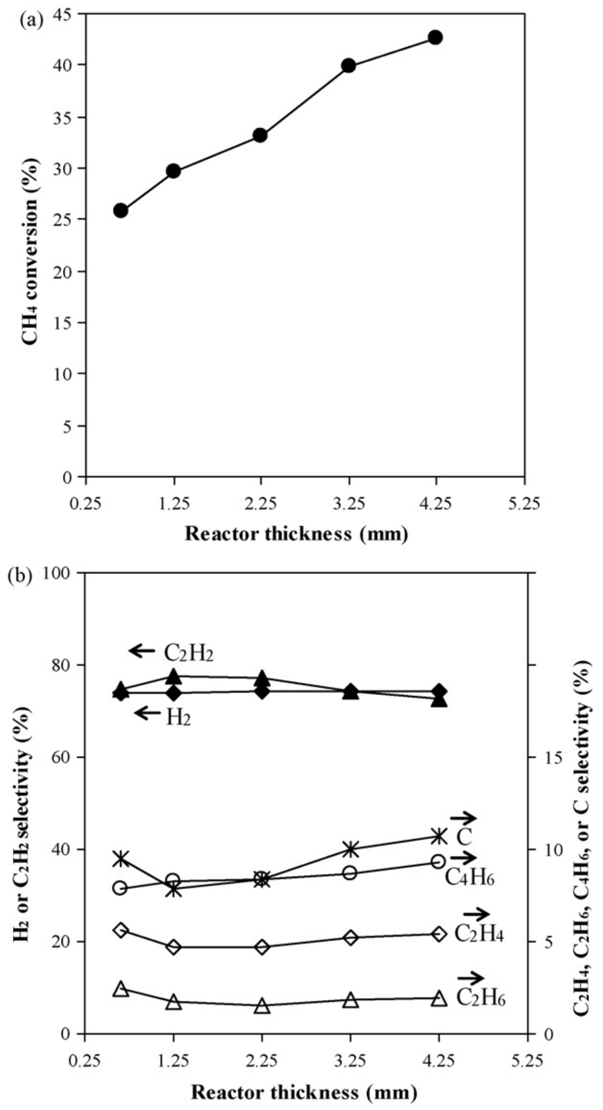

**Fig. 3.** Effect of reactor thickness on (a) methane conversion and (b) product selectivities of the non-oxidative methane reforming ($CH_4$ in feed, 5%; feed flow rate, 200 $cm^3$/min; input power, 6 W; and, electrode gap distance, 4 mm).

### *3.3. Effect of the presence of catalyst*

For the investigation of the GA microreactor, two effects (input power and reactor thickness) on the plasma reforming of methane have been already discussed above; however, the effect of using a reforming catalyst has been hypothesized to also affect the reaction performance because a microreactor has a large specific surface area. To study the combined plasma-catalytic effect on the non-oxidative reforming of methane under ambient conditions, three systems—plasma alone, plasma + unloaded catalyst, and plasma + Ni-loaded catalyst—were comparatively investigated. The catalyst support plate was placed close to the plasma zone, instead of being located inside the plasma zone, in order to avoid the disturbance of the plasma generation and the gas flow pattern. Under the studied conditions (a feed flow rate of 100 $cm^3$/min, an input power of 6 W, a frequency of 50 Hz, and an electrode gap distance of 4 mm), the temperatures at the outer wall of the plasma reactor were found to be about 125 °C, 130 °C, and 150 °C, respectively, for the three systems: plasma alone, plasma + unloaded catalyst, and plasma + Ni-loaded catalyst. In Fig. 4(a), the presence of unloaded and Ni-loaded catalysts in the plasma system leads to a positive effect in improving methane conversion, as compared with the sole plasma system. The highest methane conversion, about 50%, was found in the plasma + Ni-loaded catalyst system. It is possibly because an increase in the temperature due to heat generated by the plasma markedly influences the catalyst bed temperature and therefore enhances the catalytic activity [21,24]. Additionally, for the system of plasma + unloaded catalyst, the similar result of an increased methane conversion was also observed by Kraus et al. [18], who used the packing of a ceramic foam (92% $Al_2O_3$ and 8% $SiO_2$) in a dielectric barrier discharge (DBD) reactor for the methane decomposition. For the comparative results of the product selectivities among the three studied systems, there seems to be no marked difference in all product selectivities, especially for the hydrogen selectivity, as shown in Figs. 4(b) and (c). These results imply that the catalyst assists in enhancing methane conversion only, but not subsequent reactions. Overall, it can again be concluded that under the studied experimental conditions, the presence of the studied catalyst had a promotional effect on methane conversion, but there was no significant effect on product selectivity. The obtained results can again be explained by the fact that the GA microreactor used in this study had a very short residence time, in the range of 0.021–0.14 s, which is probably too short to promote subsequent reactions, such as coupling, dehydrogenation, and cracking reactions.

From the above obtained results, it was also hypothesized that an increase in temperature of the catalyst surface might play a significant role in improving the overall reaction performance and pathways of the combined plasma-catalytic non-oxidative methane reforming. The catalyst surface was, therefore, heated at 210 °C in order to make a comparison with cases without heating, as mentioned earlier. A controlled experiment of the sole catalyst system with heating (210 °C, without plasma) was also carried out for the sake of comparisons. The results showed that the conversion of methane was not observed in the sole catalyst system since the endothermic reaction of non-oxidative methane reforming does not thermodynamically occur at the low temperature of 210 °C, indicating that the plasma is responsible for initiating the reactions. Fig. 4(a) also shows the results of methane conversion among all the studied systems without and with heating at the catalyst surface. For the plasma + unloaded catalyst system, the methane conversion was improved when the surface of the unloaded catalyst plate was heated. In the case of the plasma + Ni-loaded catalyst system, the methane conversion remained almost unchanged with and without heating. However, only the plasma + Ni-loaded catalyst system with heating exhibited a remarkable difference in product selectivity, whereas the remaining systems gave a similar trend for all product selectivities, as shown in Figs. 4(b) and (c). The selectivities for $C_2H_4$, $C_2H_6$, and C in the plasma + Ni-loaded catalyst system with heating increased, while those for $C_2H_2$ and $C_4H_6$ decreased, compared with the other systems. Interestingly, trace amounts of saturated

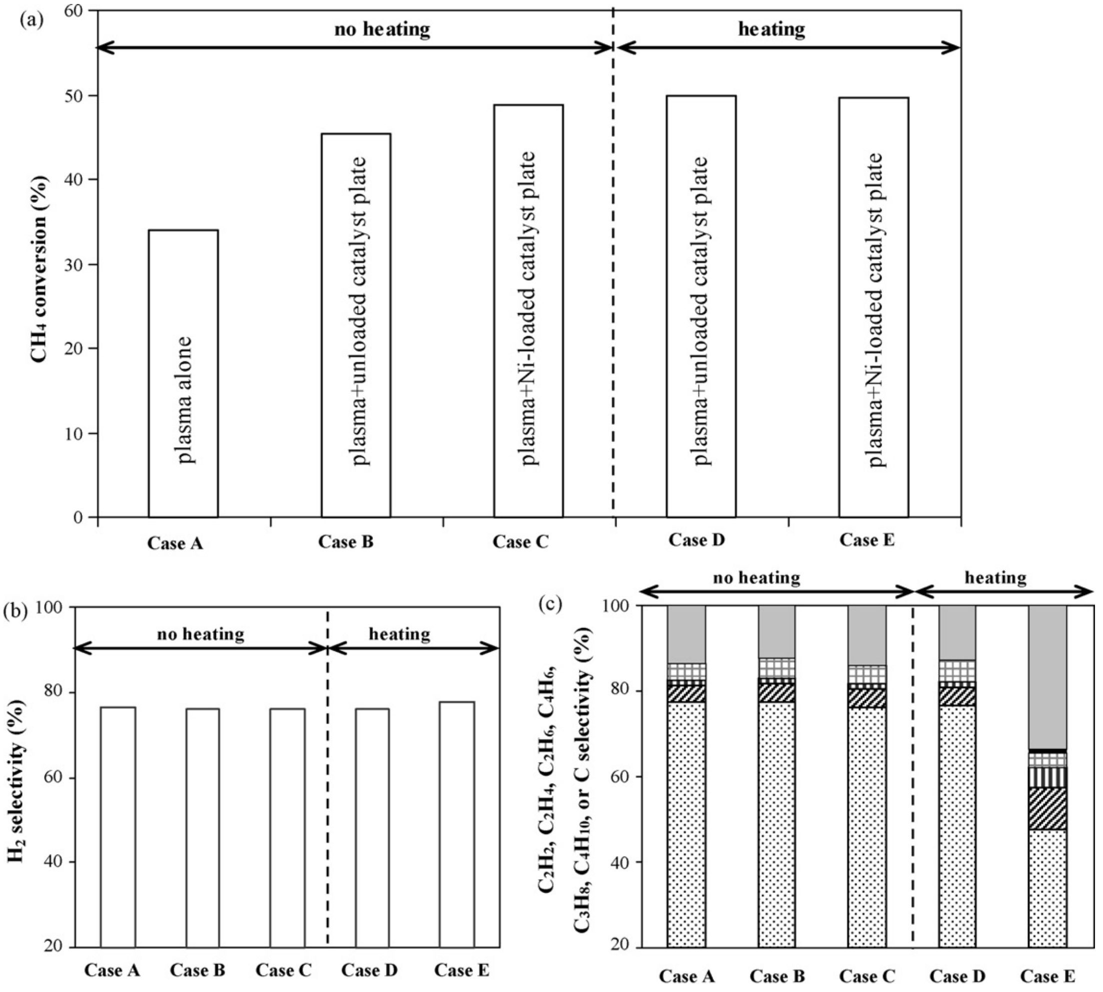

**Fig. 4.** Effect of the presence of a catalyst on (a) methane conversion, (b) $H_2$ selectivity, and (c) selectivities for (░) $C_2H_2$, (▨) $C_2H_4$, (▥) $C_2H_6$, (▦) 1,3-$C_4H_6$, (■) $C_3H_8 + C_4H_{10}$, and (▒) C of the combined catalytic-plasma non-oxidative methane reforming ($CH_4$ in feed, 5%; feed flow rate, 100 $cm^3$/min; input power, 6 W; electrode gap distance, 4 mm; and, reactor thickness, 0.95 mm).

hydrocarbons ($C_3H_8$ and $C_4H_{10}$) were found only in the plasma + Ni-loaded catalyst system with heating. Both the acetylene cracking reaction ($C_2H_2 \rightarrow 2C + H_2$) and the hydrogenation reactions of various unsaturated hydrocarbons (e.g. $C_2H_2$, $C_2H_4$, and $C_4H_6$) may potentially be activated on the nickel active sites at a temperature of 210 °C, which, in turn, may lead to a greater tendency for C, $C_2H_4$, $C_2H_6$, $C_3H_8$, and $C_4H_{10}$ formation. The results agree well with many previous studies reporting that, over nickel-based catalysts, the chemisorbed acetylene can be easily cracked to C and $H_2$, as well as be hydrogenated to $C_2H_4$ and $C_2H_6$ in a temperature range of about 150–250 °C [37–39]. The results imply that, in the case of heating, the nickel catalyst does not greatly affect the adsorption of $CH_4$ molecules, but it does play a significant role in activating the adsorption of unsaturated hydrocarbons to be converted to more saturated ones. However, the role of catalyst surface heating is still unclear and needs further investigation in order to obtain a better understanding of the plasma reforming process in the presence of catalyst.

Overall, the interaction between plasma and Ni catalyst was experimentally observed to provide only a significant enhancement of methane conversion and some product selectivities, while the $H_2$ selectivity remained unchanged. As mentioned above, the very short residence time of the GA microreactor is responsible for the limitation or the slow rates of all subsequent reactions.

## 4. Conclusions

In this GA microreactor system under the studied conditions, the dominant products of the direct non-oxidative methane reforming were $C_2H_2$ and $H_2$; whereas in the conventional GA reactor system, the primary product was $H_2$ for the pure methane feed system. However, the $H_2$ selectivity of the GA microreactor system was much higher than that of a conventional one. Input power, reactor thickness, and the presence of a Ni reforming catalyst experimentally showed important influences on the methane conversion and product selectivities. The best improvement in methane conversion was achieved in the plasma + Ni-loaded catalyst system. In addition, the product selectivities were significantly changed when the Ni-loaded catalyst plate was heated to 210 °C. Due to the high surface area-to-volume ratio of the GA microreactor configuration, the catalytic and temperature effects can be clearly observed. Therefore, the GA microreactor combined with an active catalyst has high potential for use as a new plasma chemical reactor. The sole GA microreactor should be used for the enhancement of hydrogen production from non-oxidative methane reforming reaction.

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