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Roles of CO_2 and H_2O as oxidants in the plasma reforming of aliphatic hydrocarbons

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Abstract

Roles of CO_2 and H_2O as oxidants are discussed based on the data on the substrate conversions and the product distributions in the nonthermal plasma reforming of aliphatic hydrocarbons such as methane, propane, and neopentane from 303 K to 433 K. Only small effects of initial concentrations of hydrocarbons and types of oxidants are observed on hydrocarbon conversions, and the initial chemical interaction between hydrocarbons and the oxidants unlikely occurs. CO_2 and H_2O have shown the comparable oxidation powers in the hydrocarbon reforming. Two molar excess of CO_2 or H_2O to methane is required to oxidize methane carbon atoms to CO and CO_2, and larger amounts of CO_2 or H_2O for propane and neopentane. The different natures of CO_2 and H_2O are reflected in the synthesis gas composition as in the ordinary catalytic reforming processes at higher temperatures: higher H_2 yields and higher H_2 to CO ratios on addition of H_2O.

Keywords: Aliphatic hydrocarbons; Reforming; Nonthermal plasma; CO_2; H_2O; Mechanism

1. Introduction

It has been already reported that steam reforming of methane is the best method to produce H_2 by minimizing the amount of CO_2, compared to CO_2 reforming and partial oxidation of heavier hydrocarbons and coal [1]. CO_2 reforming is a complement of steam reforming because H_2-deficient synthesis gas is prepared in the former reaction.

However, drawbacks of the conventional processes are requirements of large scale facilities, deactivation of expensive catalysts, and short lifetimes of reactor and tubing materials caused under severe reaction conditions including high temperature, high pressure, and large process loads.

On the other hand, quick response, system compactness, and easy operations are attractive features of nonthermal plasma (NTP) because this technology can be applied to relatively small-scale operations affording hydrogen: distributed hydrogen-producing systems and fuel cell vehicles.

In NTP, partial oxidation processes are not favorable because a part of expensive H_2 is consumed in its reaction with O_2 to give water. H_2O and CO_2 are recommended as soft oxidants in NTP because their deoxygenation proceeds even at ambient temperature in the absence of O_2 [2]. Steam reforming is a highly endothermic reaction, and the high energies of excited electrons can be utilized to their utmost. In NTP media, CO_2 deoxygenation is a clean reaction giving CO as a stable product [2].

Hitherto, dielectric barrier discharge reactors have been widely applied to these reactions, and it has been shown that the following parameters affect the substrates behavior and product distribution: reactor type [3], feed gas composition [4–8] gas pressure [4], specific energy density [4,8], reaction temperature [4], energy efficiency [9], and catalyst addition [10–12]. A kinetic model has been proposed for the interaction between CH_4 and catalysts [12].

We have been exploring the potential of NTP in the processes of H_2 production [13,14], methanol reforming [15], steam reforming of methane [16,17] and higher paraffins [18], CO_2 reforming of methane [19], and synthesis gas production from H_2O–CO_2 [20].

We have already reported that aliphatic hydrocarbons are more reactive at higher reaction temperature, but that the CO_2 reactivity is temperature-independent [19]. It has been also shown that similar compositions of synthesis gas are obtained in NTP [18,19] and catalytic processes [21].

This paper discusses the roles of H_2O and CO_2 in the plasma reforming of aliphatic hydrocarbons such as methane, propane,

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and neopentane with the focus on their oxidation powers affecting substrate conversion and product distribution.

2. Experimental

2.1. Characteristics of a plasma reactor

In this research, a ferroelectric packed-bed reactor (FPR) was used as a standard reactor since FPR worked much better than silent discharge plasma reactors in producing H_2 from the small molecules [13,14]. The detailed schematic of this reactor was described in our previous publication [15].

FPR operated with a relatively small volume fraction of plasma that could be catalytically activated by free radicals or UV irradiation from the plasma [22]. FPR employed an ac power supply at 50 Hz in conjunction with a ferroelectric pellet layer. FPR was a coaxial type: the inner cylindrical electrode was 16.6 mm and the outer electrode was 47.3 mm in diameter, resulting in a gap distance of 15.4 mm. The $BaTiO_3$ pellets ($\varepsilon = 5000$ at room temperature) of 1 mm in diameter, were packed between the two concentric electrodes with a high ac voltage applied in the radial direction. The pellets were held by a notched and perforated Teflon plate at both ends. The effective reactor length was 127 mm. The gas streams passed through the entry tube (6.4 mm in diameter) and dispersed into the plasma zone.

When external ac voltage was applied across the high dielectric layer in a radial direction, the pellets were polarized, and an intense electric field was formed around each pellet contact point, resulting in partial discharge. The reactor was energized with 50 Hz ac at up to 10 kV rms.

2.2. Plasma chemical reforming of aliphatic hydrocarbons

Methane (CH_4), propane ($CH_3CH_2CH_3$), and neopentane [$CH_3C(CH_3)_2CH_3$] were chosen as substrate hydrocarbons in the reforming with NTP. A hydrocarbon and CO_2 balanced with N_2 in standard gas cylinders were introduced to the reactor through a Teflon tube by adjusting its concentrations and flow rates with sets of mass flow controllers and a gas mixer. All the reactions were carried out in N_2.

In the steam reforming, reactant gases were humidified with a water-bubbling type device in a thermostatic bath. The water vapor concentrations were determined by a dew point hygrometer, and its contents were controlled within the range of 0.5–2.5%.

Since all the reactions were carried out in N_2, carbonaceous materials were deposited on the inner reactor walls and on $BaTiO_3$ surface. Thus, after each run, O_2 was passed through FPR at 10 kV for 600 s to oxidatively remove the above carbon deposits.

2.3. Analysis

Plug-in power values for FPR were measured with a digital powermeter (YOKOGAWA WT 110). Applied voltages for this reactor were measured with a digital wavemeter (SONY TEKTRONIX STA 55 W). The relationship between plug-in and reactor power consumptions was determined by separately using a high-voltage amplifier 20/20B (Trek Japan, Co., Ltd.), a function generator FG-2 (Wavetek) and an oscilloscope TDS 3052 (TEKTRONIX). The ratio of reactor power consumption to plug-in power was determined as 0.1 for FPR by relating reactor and plug-in power consumptions, and hydrocarbon conversions.

The volatile byproducts were identified by GC–MS [Shimadzu QP-5050A (EI, 70 eV)-GC 17A with a capillary column of DB-1 (i.d. 0.25 mm Ø, length 60 m, width 0.25 μm]. The conversions of propane and neopentane and the yields of organic byproducts with high boiling points such as butane and 2-methylpropane were determined by GC [GL Sciences GC 353 with a capillary column of TC-1 (i.d. 0.53 mm Ø, length 30 m, width 5 μm)]. The yields of these products were too low to affect carbon balances.

H_2 and methane were quantified by GC (Shimadzu GC-14B with a packed column of Porapak Q) by using the calibration curves separately prepared.

The concentrations of CO, CO_2, methane, ethylene, and acetylene were determined on a Shimadzu GC-9A with combined columns of Porapak $Q + N$ and Molecular Sieve 13X.

As a measure of the energy density for FPR, reactor energy density (RED) will be used later (1), where power denotes the plug-in power.

$$\mathrm{RED\,(kJ/L)} = 0.1 \times \frac{\mathrm{power\,(kW)}}{\mathrm{gas\ flow\ rate\,(L/s)}} \tag{1}$$

The hydrocarbon [$C_nH_{2(n+1)}$] ($n = 1, 3, 5$) conversion is defined as (2). The yields of H_2 and CO_x ($x = 1$ and 2) in the steam reforming of a hydrocarbon $C_nH_{2(n+1)}$ are defined according to (3) and (4), respectively:

$$C_nH_{2(n+1)}\ \mathrm{conversion\,(mol\%)} = 100 \times \left\{1 - \frac{[C_nH_{2(n+1)}\ \mathrm{concentration\,(ppm)}]}{[\mathrm{initial}C_nH_{2(n+1)}\ \mathrm{concentration\,(ppm)}]}\right\} \tag{2}$$

$$H_2\ \mathrm{yield\,(mol\%)} = 100 \times \frac{[H_2\ \mathrm{concentration\,(ppm)}]}{[(n+1) \times \mathrm{initial}\ C_nH_{2(n+1)}\ \mathrm{concentration\,(ppm)}]} \tag{3}$$

$$CO_x\ \mathrm{yield\,(mol\%)} = 100 \times \frac{[CO_x\ \mathrm{concentration\,(ppm)}]}{[n \times \mathrm{initial}\ C_nH_{2(n+1)}\ \mathrm{concentration\,(ppm)}]} \tag{4}$$

In the CO_2 reforming of the hydrocarbons, CO yield was calculated according to (5) because the initial CO_2 concentration was equal to or higher than that of the counterpart hydrocarbon:

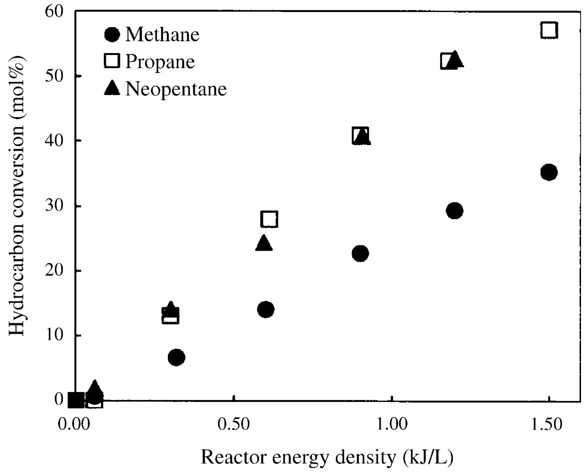

Fig. 1. Relative reactivities of methane, propane, and neopentane in the reforming with H_2O. Hydrocarbon 1.0%, H_2O 2.0%, in N_2, $Q = 0.1$ L/min.

$$\text{CO yield (mol\%)} = 100 \times \frac{[\text{CO concentration (ppm)}]}{[\text{initial CO}_2\text{ concentration (ppm)}]} \quad (5)$$

Composition of synthesis gas defined as $[H_2]/[CO]$ was calculated based on the absolute concentrations of H_2 and CO, irrespective of the oxidants.

3. Results and discussion

3.1. Chemical interaction between hydrocarbons, H_2O, and CO_2

Fig. 1 shows the conversions of methane, propane, and neopentane in the reforming with H_2O. Propane is as reactive as neopentane and methane is the least reactive. In their reforming with CO_2 as an oxidant (Fig. 2), almost the same conversions are obtained at fixed REDs for each of methane and propane as in the reforming with H_2O. Higher conversions of neopentane are obtained with CO_2 as an oxidant. The data in Table 1 show that H_2O is more reactive than CO_2 in NTP [23]. Two molecules of reactive radicals such as H and OH are generated from one molecule of H_2O, while an oxygen atom (O) is formed from one molecule of CO_2. Under our conditions, however, CO is a stable compound, and the backward reaction of CO and O is very slow [2]. The increase in the relative concentration of H_2O or CO_2 to that of the counterpart hydrocarbon decreased the hydrocarbon conversion at ambient temperature. If these oxidants chemically interact with the hydrocarbons in NTP, higher concentrations of the oxidants are expected to enhance hydrocarbon conversion. Under our conditions, high energies of energetic electrons in NTP are partitioned to the reactants in proportion to their concentrations. At lower temperatures, the substrate hydrocarbons react independent of H_2O or CO_2. In NTP at ambient temperature, the contribution of oxidative decomposition of the hydrocarbons by H_2O or CO_2 is very small.

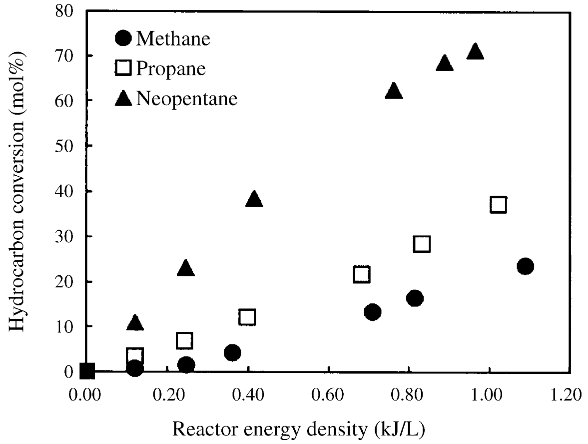

Fig. 2. Relative reactivities of methane, propane, and neopentane in the reforming with CO_2. Hydrocarbon 0.5%, CO_2 1.0%, in N_2, $Q = 0.2$ L/min.

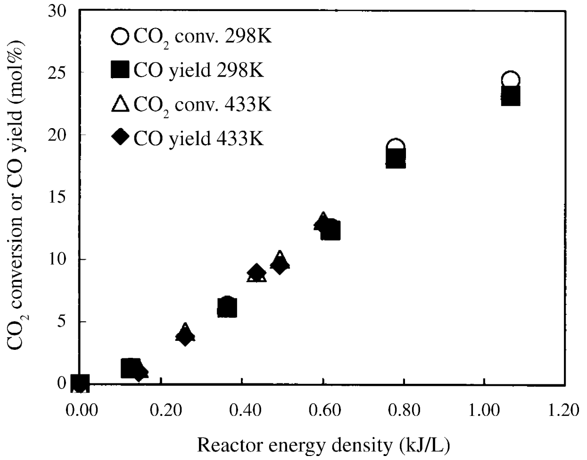

Fig. 3. Temperature effect on the CO_2 reaction behavior in NTP. CO_2 1.0%, in N_2, $Q = 0.2$ L/min.

As Fig. 3 shows, CO_2 conversion increases proportional to RED irrespective of reaction temperature in the absence of hydrocarbons. CO is quantitatively obtained from CO_2. At ambient temperature, addition of the above hydrocarbons does not affect the CO_2 reaction behavior. At 433 K, lower CO_2 conversions are obtained at higher REDs on addition of methane. It is unlikely that hydrogen atoms and H_2 in situ promote the deoxygenation of CO_2 in NTP since the C–H bonds in the

Table 1
Bond dissociation energies (BDE) of the covalent bonds in the substrates and CO

Bond	BDE (kJ mol^{-1})
H–OH	499.0
C–O	1083.9
O–CO	532.2
$H–CH_3$	438.9
$H–CH_2CH_2CH_3$	423.3
$H–CH(CH_3)_2$	399.6
$H–CH_2C(CH_3)_3$	418.8
$CH_3–CH_2CH_3$	363.4
$CH_3–C(CH_3)_3$	338.2

Ref. [23].

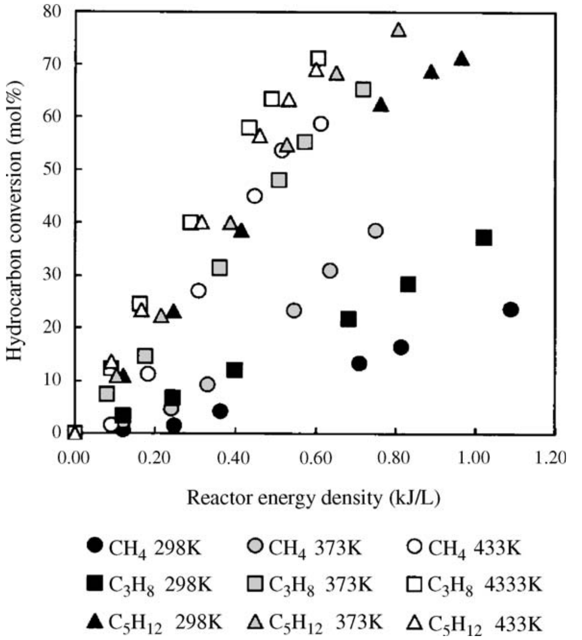

Fig. 4. Temperature effect on hydrocarbon conversion in the CO_2 reforming of the hydrocarbons. Hydrocarbon 0.5%, CO_2 1.0%, in N_2, $Q = 0.2$ L/min.

hydrocarbons are more labile than that of C–O in CO_2. CO would be oxidized back to CO_2 in the reactions with oxygen species.

The O–H bond in H_2O is also stronger than those of C–H in the hydrocarbons. Therefore, it is suggested that H_2O is less susceptible to the secondary hydrogen atom abstraction. Higher reactivities of hydrocarbons at higher temperatures (Fig. 4) are ascribed to the promotion of the hydrocarbon decomposition process induced by radicals in situ. The reforming of hydrocarbons comprises successive endothermic steps, some of which are not promoted due to the short lifetimes of energetic electrons in NTP. Therefore, thermal activation of the radicals formed from the substrate hydrocarbons, CO_2, and H_2O is effective to achieve higher conversions of hydrocarbons.

3.2. Additive effect of H_2O and CO_2 on H_2 yield

Figs. 5 and 6 show the additive effect of H_2O and CO_2 on H_2 yield, respectively. At 1.00 kJ/L at ambient temperature, comparable H_2 yields are obtained in the neopentane reforming with H_2O and CO_2 as oxidants. In the reforming of propane and methane, 1.6- and 2.5-fold higher H_2 yields are obtained with H_2O as an oxidant, respectively. In the reforming with H_2O, H_2O and hydrocarbons are competitive H_2 donors. Since neopentane has 12 hydrogen atoms per molecule, the contribution of H_2O is apparently small in H_2 formation. On the other hand, the additive effect of H_2O is observed more clearly in the reactions of methane and propane with smaller numbers of hydrogen atoms per molecule of hydrocarbon.

In the reforming with H_2O (Fig. 5), H_2 yields increase with RED, and the maximum yield for methane reforming reaches 44% due to the larger contribution of H_2 formation from H_2O. In the CO_2 reforming, the maximum H_2 yield is obtained for neopentane in 17% at ambient temperature. In the reactions of methane and neopentane, H_2 yields decrease with increases in reaction temperature. In the reactions of propane, however, maximum yields are obtained at 373 K. Compared to methane [BDE(H–CH_3) = 438.9 kJ mol^{-1}] and neopentane, {BDE[H–$CH_2C(CH_3)_3$] = 418.8 kJ mol^{-1}}, propane {BDE[H–$CH(CH_3)_2$] = 399.6 kJ mol^{-1}}is more susceptible to the hydrogen atom abstraction. The different trends of reaction temperature on the H_2 yield in the CO_2 reforming of the above hydrocarbons are ascribed to the different H-donating abilities of the hydrocarbons and hydrocarbon-dependent relative abundances of H and O atoms in situ.

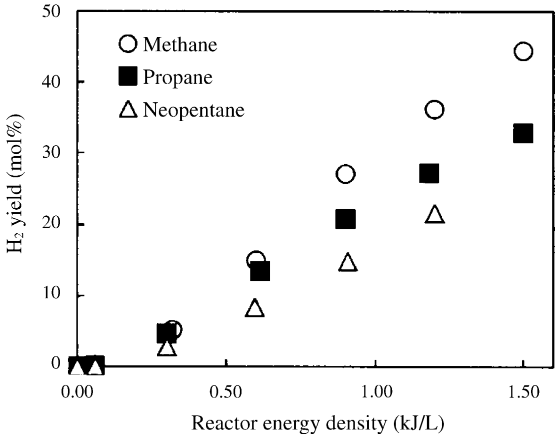

Fig. 5. Effect of hydrocarbon structure on H_2 yield in the reforming with H_2O. Hydrocarbon 1.0%, H_2O 2.0%, in N_2, $Q = 0.1$ L/min.

3.3. Additive effect of H_2O and CO_2 on the molar ratio of H_2 to CO

Fig. 7 shows the molar ratio of H_2 to CO {[H_2]/[CO]} as functions of RED for the reforming of the hydrocarbons with H_2O. In each of them, the ratios are higher than stoichiometric

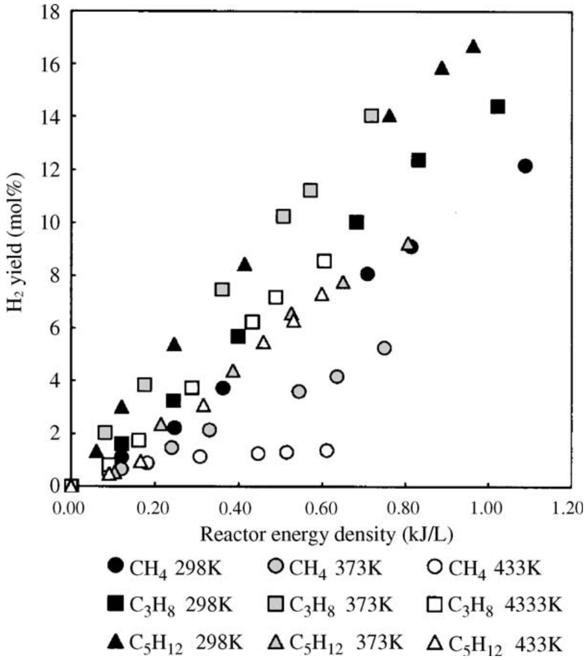

Fig. 6. Effects of hydrocarbon structure and temperature on H_2 yield in the CO_2 reforming. Hydrocarbon 0.5%, CO_2 1.0%, in N_2, $Q = 0.2$ L/min.

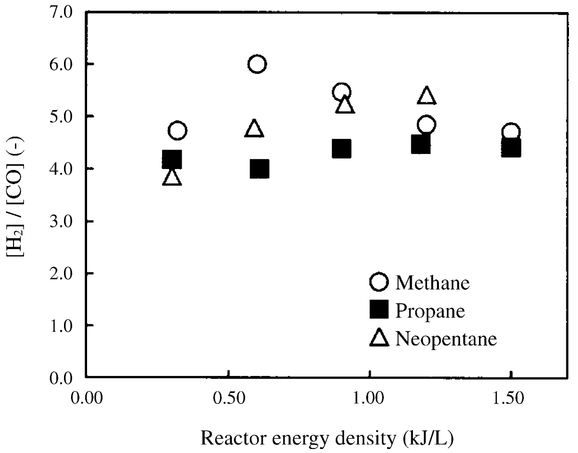

Fig. 7. Effect of hydrocarbon structure on synthesis gas composition in the reforming with H_2O. Hydrocarbon 1.0%, H_2O 2.0%, in N_2, $Q = 0.1$ L/min.

ones (3.0 for methane, 2.3 for propane, and 2.2 for neopentane, respectively). Synthesis gas composition is less affected by the RED and chemical structures of hydrocarbons compared to hydrocarbon conversion and H_2 yield.

In the CO_2 reforming of these hydrocarbons, different trends are observed (Fig. 8). In the methane reforming, $[H_2]/[CO]$ is lower than the stoichiometric ratio (1.0), but for propane and neopentane, $[H_2]/[CO]$ is higher than those stoichiometry predicts. In the case of methane, a part of hydrogen atoms and H_2 are consumed in the reactions with oxygen species. In the cases of propane and neopentane, CO formation is slower than that of H_2 due to the reactivity of CO_2 lower than the higher hydrocarbons and larger numbers of carbon atoms per hydrocarbon molecule.

It is possible to control the synthesis gas composition by varying the ratios of initial concentrations of H_2O or CO_2 and hydrocarbon. An alternative is the reforming of a ternary mixture comprising H_2O, CO_2, and hydrocarbon since these three constituents seem to react independent of each other in NTP.

3.4. Additive effect of H_2O and CO_2 on carbon balance

Fig. 9 shows the carbon balances in the reforming of the hydrocarbons with H_2O. The slope of the dotted line is unity, and the data points on this line assure quantitative carbon balances. With a 2 molar excess of H_2O to methane, all the carbon atoms in the reacted methane are recovered as CO and CO_2. FPR can be operated continuously under these conditions without any changes in methane conversion and the yields of H_2 and CO [18]. On the other hand, only low carbon recoveries are obtained for propane and neopentane. Carbon balance can be improved by increasing the ratio of H_2O to carbon atoms in these higher hydrocarbons [18]. However, this kind of operation condition is not recommended because the process load is greatly increased: 6.0 for $[H_2O]/[\text{propane}]$ and 10 for $[H_2O]/[\text{neopentane}]$, respectively.

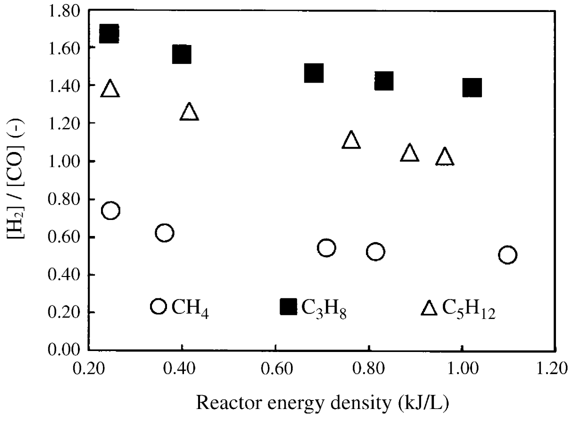

Fig. 8. Effect of hydrocarbon structure on synthesis gas composition in the CO_2 reforming. Hydrocarbon 0.5%, CO_2 1.0%, in N_2, $Q = 0.2$ L/min.

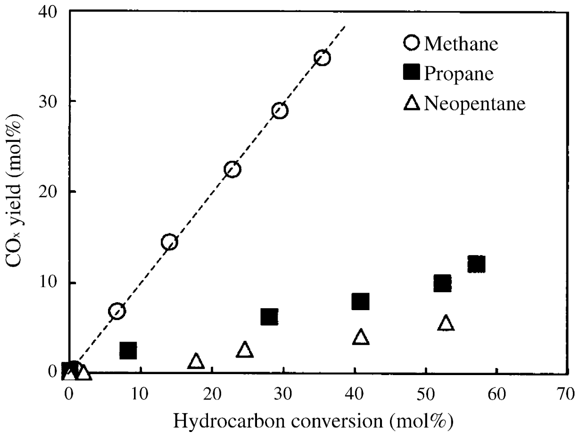

Fig. 9. Effect of hydrocarbon structure on carbon balance in the reforming with H_2O. Hydrocarbon 1.0%, H_2O 2.0%, in N_2, $Q = 0.1$ L/min.

In the CO_2 reforming of methane, fairly good carbon balances are obtained, and better carbon recoveries are obtained for propane and neopentane than the reforming with H_2O (Fig. 10). These observations are rationalized because only oxygen atoms are liberated from CO_2. The carbon atom oxidation would be promoted than in the case of H_2O as an oxidant.

From propane and neopentane, methane, and C_2 hydrocarbons are produced as byproducts other than CO_x. Nonvolatile organic compounds are also produced. In the cleaning of FPR after each run, they were oxidatively removed as CO_x.

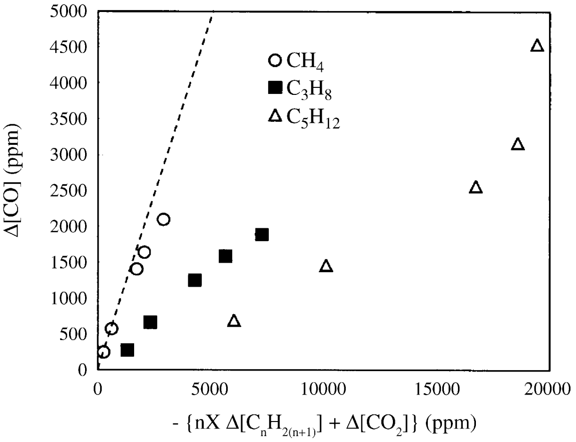

Fig. 10. Effect of hydrocarbon structure on carbon balance in the CO_2 reforming. Hydrocarbon 0.5%, CO_2 1.0%, in N_2, $Q = 0.2$ L/min.

$$SH + e^{*} \longrightarrow S\bullet + H\bullet + e \qquad (1)$$

$$CO_2 + e^{*} \longrightarrow CO + O\bullet + e \qquad (2)$$

$$H_2O + e^{*} \longrightarrow H\bullet + \bullet OH + e \qquad (3)$$

$$H\bullet + SH \longrightarrow H_2 + S\bullet \qquad (4)$$

$$O\bullet + SH \longrightarrow \bullet OH + S\bullet \qquad (5)$$

$$\bullet OH + SH \longrightarrow H_2O + S\bullet \qquad (6)$$

SH: Hydrocarbon

Fig. 11. Plausible reaction pathways for the initial conversion of the hydrocarbons, H_2O, and CO_2.

Formation of atomic carbon from CO is unlikely due to the extremely low reactivity of CO in NTP. Irrespective of oxidant types, formation of the above byproducts is ascribed to the carbon imbalances for propane and neopentane.

Our results indicate that NTP reforming process under mild conditions can be applied to methane and propane. For higher hydrocarbons such as neopentane and isooctane, higher temperatures and reforming catalysts should be required to achieve better carbon balances.

3.5. Reaction mechanism

From 303 K to 433 K, none of the hydrocarbons react without NTP. Thus, Eqs. (1)–(3) in Fig. 11 occur initially in FPR. CO_2 is a clean source of oxygen atoms, which consume hydrogen atoms and H_2 but promote the carbon atom oxidation, resulting in better carbon balance. Two active radicals are formed from H_2O, but the reaction behavior of OH has not been elucidated in this research. However, H_2 yield increases with RED in the reforming of the hydrocarbons with H_2O (Fig. 5). Its major reaction pathway should be a hydrogen atom abstraction from the hydrocarbon giving H_2O [Eq. (6)]. Further bond cleavage of O–H in OH radical produces H and O, but its contribution is expected to be small due to its low concentration in situ.

Hydrocarbons are decomposed to give hydrogen atoms and carbon radicals, which undergo further dehydrogenation and oxygenation to give CO and intermediates such as aldehydes and ketones. These organic compounds are more reactive than the parent hydrocarbons, and the final product from them is CO. In these successive processes, hydrogen and oxygen atoms from H_2O and CO_2 are involved to different degrees depending on their in situ concentrations.

4. Conclusions

In the plasma reforming of methane, propane, and neopentane with H_2O or CO_2, these oxidants affect synthesis gas composition rather than hydrocarbon conversion. As a hydrocarbon substrate in plasma reforming, methane and propane are recommended as candidates than neopentane and other higher hydrocarbons. It is possible to achieve the constant composition of synthesis gas by controlling the ratio of initial concentrations of hydrocarbon and oxidant. Some catalysts are necessary to increase the yields of H_2 and CO in plasma reforming under mild conditions.

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