

Roles of CO₂ and H₂O as oxidants in the plasma reforming of aliphatic hydrocarbons

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Abstract

Roles of CO₂ and H₂O 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. CO₂ and H₂O have shown the comparable oxidation powers in the hydrocarbon reforming. Two molar excess of CO₂ or H₂O to methane is required to oxidize methane carbon atoms to CO and CO₂, and larger amounts of CO₂ or H₂O for propane and neopentane. The different natures of CO₂ and H₂O are reflected in the synthesis gas composition as in the ordinary catalytic reforming processes at higher temperatures: higher H₂ yields and higher H₂ to CO ratios on addition of H₂O.

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1. Introduction

It has been already reported that steam reforming of methane is the best method to produce H₂ by minimizing the amount of CO₂, compared to CO₂ reforming and partial oxidation of heavier hydrocarbons and coal [1]. CO₂ reforming is a complement of steam reforming because H₂-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 H₂ is consumed in its reaction with O₂ to give water. H₂O and CO₂ are recommended as soft oxidants in NTP because their deoxygenation proceeds even at

ambient temperature in the absence of O₂ [2]. Steam reforming is a highly endothermic reaction, and the high energies of excited electrons can be utilized to their utmost. In NTP media, CO₂ 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 CH₄ and catalysts [12].

We have been exploring the potential of NTP in the processes of H₂ production [13,14], methanol reforming [15], steam reforming of methane [16,17] and higher paraffins [18], CO₂ reforming of methane [19], and synthesis gas production from H₂O–CO₂ [20].

We have already reported that aliphatic hydrocarbons are more reactive at higher reaction temperature, but that the CO₂ 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 H₂O and CO₂ 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 H₂ 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 BaTiO₃ pellets ($\epsilon = 5000$ 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 (CH₄), propane (CH₃CH₂CH₃), and neopentane [CH₃C(CH₃)₂CH₃] were chosen as substrate hydrocarbons in the reforming with NTP. A hydrocarbon and CO₂ balanced with N₂ 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 N₂.

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 N₂, carbonaceous materials were deposited on the inner reactor walls and on BaTiO₃ surface. Thus, after each run, O₂ 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.

H₂ 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, CO₂, 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.

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

The hydrocarbon [C_nH_{2(n+1)}] ($n = 1, 3, 5$) conversion is defined as (2). The yields of H₂ 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:

$$\begin{aligned} & \text{C}_n\text{H}_{2(n+1)} \text{ conversion (mol\%)} \\ & = 100 \times \left\{ 1 - \frac{[\text{C}_n\text{H}_{2(n+1)} \text{ concentration (ppm)}]}{[\text{initial C}_n\text{H}_{2(n+1)} \text{ concentration (ppm)}]} \right\} \end{aligned} \quad (2)$$

$$\begin{aligned} & \text{H}_2 \text{ yield (mol\%)} \\ & = 100 \times \frac{[\text{H}_2 \text{ concentration (ppm)}]}{[(n+1) \times \text{initial C}_n\text{H}_{2(n+1)} \text{ concentration (ppm)}]} \end{aligned} \quad (3)$$

$$\begin{aligned} & \text{CO}_x \text{ yield (mol\%)} \\ & = 100 \times \frac{[\text{CO}_x \text{ concentration (ppm)}]}{[n \times \text{initial C}_n\text{H}_{2(n+1)} \text{ concentration (ppm)}]} \end{aligned} \quad (4)$$

In the CO₂ reforming of the hydrocarbons, CO yield was calculated according to (5) because the initial CO₂ concentration was equal to or higher than that of the counterpart hydrocarbon:

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