Steam Reforming of HC with DC Pulse Discharge

K. Iwasaki, S. Kado, and Y. Sekine

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-8656, Japan

Department of Applied Chemistry, School of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan

Abstract

By use of direct current (DC) pulse discharge, we found that the use of steam to reform hydrocarbons proceeds very efficiently and selectively under the condition of atmospheric pressure and low temperature without the use of catalyst. In the case of steam reforming of propane, the conversion was 57.2% and the hydrogen concentration in the outlet gas was 57.2% under atmospheric pressure and a low temperature.

Introduction

The fuel cell is expected to be commercialized immediately because it has high energy efficiency and produces no NOx, SOx or carbon dioxide emissions. The polymer electrolyte fuel cell (PEFC) is suited for the fuel cell electric vehicle (FCEV) and residential use due to its small size, light weight, and low operating temperature (about 363 K). One of the problems of commercializing the PEFC is the difficulty regarding hydrogen supply. Because hydrogen is gaseous fuel, its storage of hydrogen is very difficult and the energy per weight is low. The use of steam to reform gasoline, LPG or natural gas, which can be performed using the existing infrastructure, is said to be the best way to supply hydrogen. Steam reforming of hydrocarbon is shown below:

\[ \text{C}_n\text{H}_m + n\text{H}_2\text{O} \rightarrow \text{nCO} + (m/2 + n)\text{H}_2 \]

Carbon monoxide would poison the Pt electrode in the PEFC, so carbon monoxide should be removed by means of a water gas shift reaction and/or combustion. Water gas shift reaction is shown below:

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

These reactions can proceed sufficiently by use of a catalyst at about 573 K.

Steam reforming of hydrocarbon requires high temperatures (\(>1000\) K) and expensive catalysts. These high temperatures restrict the selection of material for the reactor, and energy
efficiency is low. In the fuel cell system, the cost of reforming catalyst and carbon deposition on the catalyst are serious problems. As well, the catalyst is poisoned by sulfur contained in the fuel and deactivated. Furthermore it takes 1 – 2 minutes to warm up the reactor, and the catalyst system cannot keep up with the rapid changes. These faults are fatal, especially in case of the PEFC.

Then we found that steam reforming with DC pulse discharge proceeds very efficiently and selectively under a low temperature (393 K) and atmospheric pressure without the use of catalyst. The DC pulse discharge is one of the non-equilibrium plasmas such as direct-electric barrier discharge 14,15 and radio-frequency discharge 16. A large amount of electrons are irradiated in a very short time of 10 μs. Because the irradiation time is very short, the temperature of the gas phase does not increase and useless side reactions can be suppressed, allowing steam reforming to proceed very efficiently and selectively. Moreover we can start the system immediately and can obtain the required hydrogen concentration.

Experiment
As shown in Fig. 1, a flow type reaction apparatus was used in this study. All experiments were conducted under atmospheric pressure and a 393 K temperature without the use of catalyst. Stainless steel electrodes were inserted from each end of a quartz tube of 4.0 mm inner diameter. After reactant gas was fed into the tube, negative high voltage DC power was supplied by DC power generator, and DC pulse discharge occurred in the gap of the rods. All products were analyzed using a gas chromatography equipped with FID and TCD (Shimadzu GC-14B), and the waveforms of current and voltage were observed by means of a digital signal oscilloscope (LeCroy 9340C).

Results and Discussions
Steam reforming of methane
Steam reforming of methane by means of DC pulse discharge was performed under various input energies. The mixing ratio of methane to steam was 1 : 1 (this is the stoichiometric ratio). The flow rate of feed gas was 20 cm³·min⁻¹. Pressure was 0.1 MPa, and the temperature of the gas phase was 393 K. The result of steam reforming of methane is shown in Fig. 2. Carbon monoxide was reformed with steam to carbon dioxide and hydrogen by water gas shift reaction. Then the total amount of hydrogen supplied into the PEFC was
estimated and is shown in Fig. 2. The methane conversion increased in proportion to the input energy and the hydrogen concentration in the outlet gas also increased. In this case, hydrogen concentration reached 51.7% (total amount of hydrogen: 66.7%) and the methane conversion reached 39% when the input energy was 12 W. The products were hydrogen, carbon monoxide, C2 compounds (acetylene is the main component), and a small amount of carbon dioxide. The selectivity to these products was not affected by the input energy. Other products such as hydrocarbon (C>3) were not detected. Thus it was shown that the steam reforming device, using DC pulse discharge, can easily and quickly control the amount of hydrogen formed.

We conducted some experiments in which the mixing ratio of methane to steam in the feed gas was varied. The total flow rate of the feed gas was 35 cm³/min, and the methane flow rate was 10 cm³/min. Only the steam flow rate was changed and argon was balanced. Pressure was 0.1 MPa and the temperature of the gas phase was 993 K. The results are shown in Fig. 3. The selectivity to carbon monoxide and C2 compounds was changed by the mixing ratio. The higher the partial pressure of steam was, the larger the selectivity of carbon monoxide because the amount of CH, reacted with H₂O increased. Because the methane conversion was not sharply changed, the production of hydrogen increased with the increase of the partial pressure of steam, thus indicating the need for the most efficient ratio.

In every condition, methane conversion and selectivity were independent of time on steam and no carbon deposition was observed.
Steam reforming of propane

Steam reforming of propane, which is the main component of LPG, by means of DC pulse discharge was conducted under various input energies. The mixing ratio of propane to steam was 1 : 3 (stoichiometric ratio). The flow rate of the fed gas was 21 cm³/min. Pressure was 0.1 MPa and the temperature of the gas phase was 393 K. The result is shown in Fig. 4. The propane conversion increased in proportion to the input energy, and the hydrogen concentration in outlet gas also increased. In this case, hydrogen concentration reached 57.2% (total amount of hydrogen: 75.4%) and the propane conversion reached 57.2% when the input energy was 20 W. The products were hydrogen, carbon monoxide, C2 compounds (acetylene is the main component), methane, and a small amount of carbon dioxide. The selectivity to these products was independent of the input energy. Other products such as hydrocarbon (C>4) were not detected. There was no carbon deposition.

We supposed a reaction scheme in which propane is directly dissociated into CH, fragment due to electron collisions. CH, reacted with H₂O resulting in the formation of carbon monoxide and hydrogen were formed, while CH, reacted each other to form acetylene. A small amount of CH₄ was hydrogenated, and methane and C₂ compounds except acetylene were formed. If propane dissociated, C₃H₈ → C₃H₆ → C₂H₂, C₂ compounds except acetylene, propene and propane would be formed by hydrogenation of intermediate compounds, and hydrocarbon (C>3) would be formed by coupling among intermediate. But C₂ compounds except acetylene were rarely formed and hydrocarbon (C>3) was not detected.
Steam reforming of hexane

Hexane is one of the model compounds of gasoline. Thus, steam reforming of hexane by means of DC pulse discharge was performed under various input energies. The mixing ratio of hexane, steam, and Argon was 1 : 6 : 3.5 (stoichiometric ratio). The flow rate of the feed gas was 50 cm$^3$ min$^{-1}$. Pressure was 0.1 MPa and the temperature of the gas phase was 393 K. The result is shown in Fig. 5. The hexane conversion increased in proportion to the input energy, and hydrogen concentration in the outlet gas was also increased. The products were hydrogen, carbon monoxide, C2 compounds (acetylene is the main component), methane, and a small amount of carbon dioxide. The selectivity to these products was independent of the input energy. Other products such as hydrocarbon (C3) were not detected. There was no carbon deposit. The level of selectivity was independent of reaction time.
Conclusions

We found that the steam reforming of hydrocarbon by means of DC pulse discharge proceeded efficiently and selectively, demonstrating many advantages not shared by catalytic reactions. The advantages include:

Steam reforming proceeds under the conditions of atmospheric pressure and low temperature (393 K) by use of DC pulse discharge.

Start up and response is very quick (<1.0 s).

Hydrogen can be supplied stably for long time.

The amount of methane formation is very small (selectivity < 10%).

No carbon deposition.

Free from maintenance.

DC pulse discharge system does not have the faults of the catalyst system. Thus, through the use of carbon dioxide removal technology in combination with the catalyst water gas shift reaction and combustion or the use of a membrane for hydrogen separation, a hydrogen production system employing DC pulses can be applied to practical use.

References