HYDROGEN GENERATION BY REFORMING DIMETHYLETHER USING MICRO-CHANNEL REACTOR

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Abstract

A micro-channel reactor system composed of a reforming micro-channel reactor, a water gas shift micro-channel reactor, a selective methanation reaction micro-channel reactor, and a catalytic combustion micro-channel reactor was designed and fabricated. Each micro-channel reactor had parallel channels. Each channel width was 150 μm. The channel wall was coated by noble metal catalysts. The volume of each reactor was about 10 cm^3. The micro-channel reactor system produced 223 ccm hydrogen with CO concentration of 59 ppm by reforming 50 ccm dimethylether (DME). The reformed hydrogen produced by the micro-channel reactor system has capable to be used as a fuel for a 20W class proton exchange membrane (PEM) fuel cell.

We analyzed the performance of the micro-channel reactor. The reactor performance was estimated theoretically by channel-wall area coated with catalysts and fuel feeding rate under the reaction-controlling-condition. The reaction-controlling-condition is realized in the micro-channel reactor by making channel width narrow. Experimental performance data related to the reforming micro-channel reactor showed good correspondence with the theoretical analysis data.

RHFC System for Portable Equipment

Liquid fuels have large energy density in stable form. Liquid fuels are promising for electric power generation source for portable electronic equipments. Reformed hydrogen fuel cell (RHFC) system is one candidate of small and high efficient fuel cell system for the equipments. It is necessary to develop compact reformer in order to make RHFC system small. We selected dimethylether (DME) as a fuel because of relatively lower reforming temperature and higher energy density than

that of methanol. Noble metals were selected as catalysts because of their durability. Low temperature water gas shift reaction and selective methanation reaction of CO was selected to reduce CO whereas selective oxidation of CO is widely used. In the case of selective methanation reaction, an axially air pump is not necessary.

Micro-channel Reactor

Micro-channel reactors have parallel channels of several hundred micrometer width. Catalysts were coated on the channel surface. The micro-channel reactor for gas solid catalytic reaction has the following advantages:

1 Diffusion enhancement of source and product gas
2 Heat supply enhancement and heat removable enhancement
3 High catalyst specific area
4 Low pressure drop

We analyzed a micro-channel reactor in which channel width is W. We assumed that the first order reaction took place at the surface in the reactor, as shown in Fig.1. Diffusion flux, q_D, is modeled as follow, assuming the diffusion length to be W/2:

$$q_D = D \frac{C_b - C_s}{W/2} \quad , \tag{1}$$

where C_b is bulk source gas concentration, C_s is source gas concentration at the surface, and D is diffusion coefficient of source gas. The surface reaction rate, kC_s, is the same as the diffusion flux, q_D, therefore the following relationship is obtained:

$$q_r = kC_s = \frac{k \dfrac{2D}{W}}{k + \dfrac{2D}{W}} C_b . \tag{2}$$

The reaction-controlling-condition, k << 2D/W, is realized in the micro-channel reactor by decreasing the channel width, W, according to Eq. 2.

Next, we estimated the performance of a channel of width W, height h, and length L, under the reaction-controlling-condition, as shown in Fig. 2. Source gas of concentration C_0, feeding rate q, is supplied. The concentration in y-direction of the channel is assumed to be uniform and gas velocity u=q/Wh is assumed to be constant. The following concentration profile to x-direction in the channel is obtained, in which the source gas diffusion to the flow direction is ignored:

$$C = C_0 \exp(-\frac{2k}{Wu}x) = C_0 \exp(-\frac{2hk}{q}x) . \tag{3}$$

The source gas concentration at the outlet, C_{out}, is obtained by substituting x=L;

$$C_{out} = C_0 \exp(-\frac{2k}{wu}L) = C_0 \exp(-\frac{2hk}{q}L) = C_0 \exp(-\frac{Sk}{q}).$$ (4)

In Eq.4, the wall area, S, is 2hL. Equation 4 shows that the reaction rate constant, k, the wall area, S, and source gas supply rate, q, determine the concentration at the outlet under the reaction-controlling-condition. Next, n parallel channels with length of L/n are analyzed as shown in Fig. 3. The wall area of the n parallel channels is the same as that of the single channel. In the parallel channel case, the gas velocity is q/Whn.

$$C = C_0 \exp(-\frac{2k}{wu}x) = C_0 \exp(-\frac{2hk}{q/n}x).$$ (5)

The concentration at the outlet, C_{out}, is as follow:

$$C_{out} = C_0 \exp(-\frac{2k}{wu}\frac{L}{n}) = C_0 \exp(-\frac{2hk}{q}L) = C_0 \exp(-\frac{Sk}{q}),$$ (6)

where x=L/n is substituted in Eq. 5. Equation 6 means that the outlet concentration is independent of parallel channel number as far as surface area is the same.

Micro-channel Reactor Performance

We designed and fabricated the micro-channel reactor reforming system for DME reforming. The system was composed of the reforming micro-channel reactor, the water gas shift micro-channel reactor, the selective methanation micro-channel reactor, and the catalytic combustion micro-channel reactor. Each micro-channel reactor had parallel channels whose width was 150 μm. The channel wall was coated by noble metal catalysts. The volume of each reactor was about 10 cm^3 as shown in Fig. 4. The system had capability of 200 ccm hydrogen production. Typical source gas flow rate, produced hydrogen flow rate and CO concentration at the each reactor are shown in Fig. 5. 50 ccm DME and 400 ccm water were fed to the micro-channel reforming system, and 223 ccm hydrogen with CO concentration of 59 ppm was produced. The reformed hydrogen has capable to be used as a fuel for a 20 W class proton exchange membrane(PEM) fuel cell.

The conversion of DME in the reforming micro-channel reactor is derived from Eq. 6 as follow:

$$\chi = 1 - \frac{C_{out}}{C_0} = 1 - \exp(-\frac{Sk}{q}).$$ (7)

Experimental data is well fitted in Eq. 7 as shown in Fig. 6. The catalyst coated wall area was 150cm^2, the channel width was 150 μm, the channel height was 6.5 mm, and

parallel number was 40 in the reforming micro-channel reactor. The surface reaction rate, k, was estimated to be 0.0175 cm/s. 2D/W was estimated to be 80 cm/s. The reaction controlling condition, k << 2D/W, was effective. Figure 7 shows the exhaust gas flow rate dependence on the DME flow rate at the reforming micro-channel reactor. Hydrogen generation rate and CH_4 flow rate were increased with decrease of conversion of DME, with increase in the DME flow rate.

Conclusion

We designed and fabricated the micro-channel reactor reforming system for DME reforming composed of a reforming micro-channel reactor, a water gas shift micro-channel reactor, a selective methanation micro-channel reactor. Volume of each micro-channel reactor was about 10 cm^3. The system produced 223 ccm hydrogen with CO concentration of 59 ppm from 40 ccm DME. The reformed hydrogen has capable to be used as a fuel for a 20 W class PEM fuel cell.

According to theoretical analysis of the micro-channel reactor, the micro-channel reactor has channel design flexibility, such as channel width, channel height, channel parallel number. The theoretical analysis result of the reforming micro-channel reactor showed good correspondence with the experimental data.
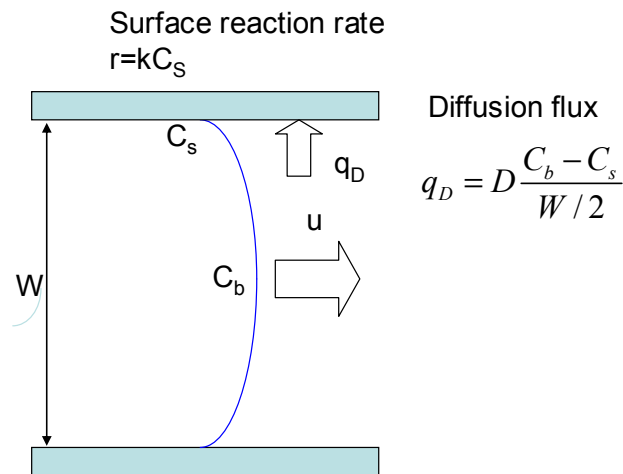
Surface reaction rate
$r = kC_S$

Diffusion flux

$$q_D = D\frac{C_b - C_s}{W/2}$$

Fig. 1 Schematic concentration profile across a channel

u=q/wh[m/s]

L[m]

W

r=kC [mol/m²/s]

C_0[mol/m³]

C_{out}

q[m³/s]

h

z y

C

S=2hL[m²]

x
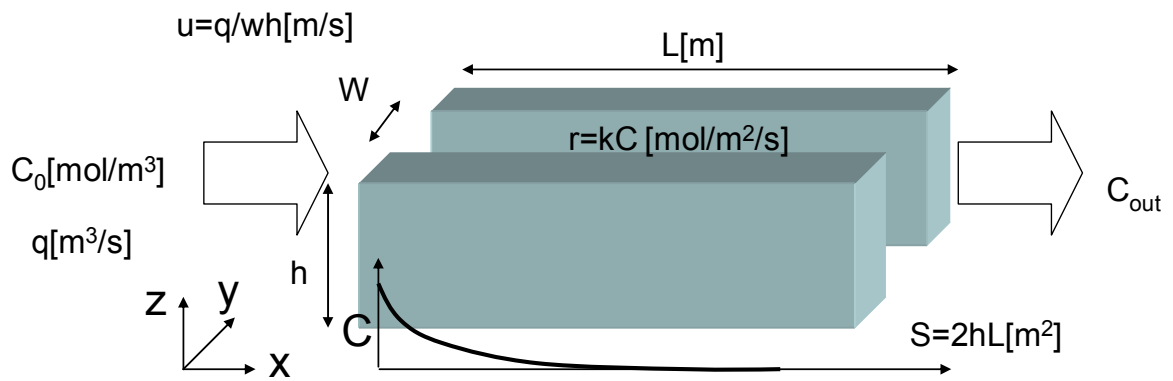
Fig.2 Schematic concentration profile along a channel

L/n

W

q/n

q

C_0

C_{out}

h
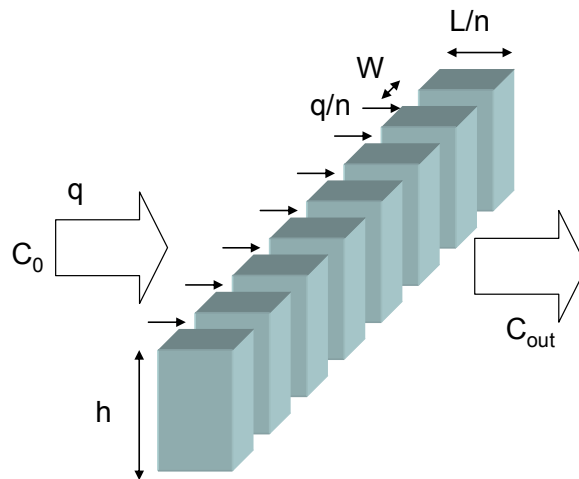
Fig.3 Schematic of n parallel channels

Reformer

ca. 10cm³

Water gas shift
reactor

W=150μm
S=150cm²

Catalytic
combustor

Selective methanation
reactor

Fig. 4 Micro-channel reactor system

$CH_3OCH_3+3H_2O=6H_2+2CO_2$　　　　$CO+H_2O=H_2+CO_2$　　　　$CO+3H_2=CH_4+H_2O$

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  →  | Reformer |  →  | WGS |  →  | Sel. methanation |  →
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DME 50cc/min　　　　H_2: 232cc/min　　　　H_2: 244cc/min　　　　　　H_2: 223cc/min
H_2O 200cc/min　　　　CO: 3.3%　　　　　　CO: 1.6%　　　　　　　　CO: 59ppm
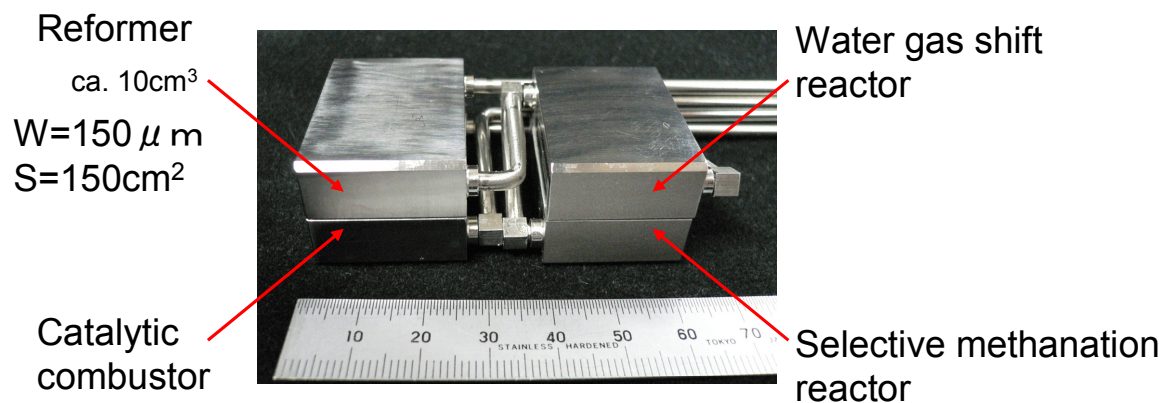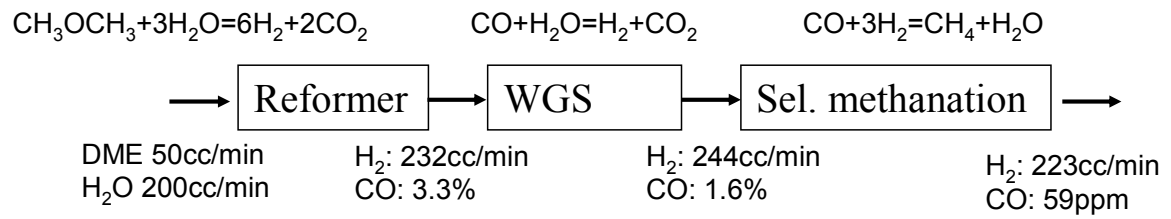
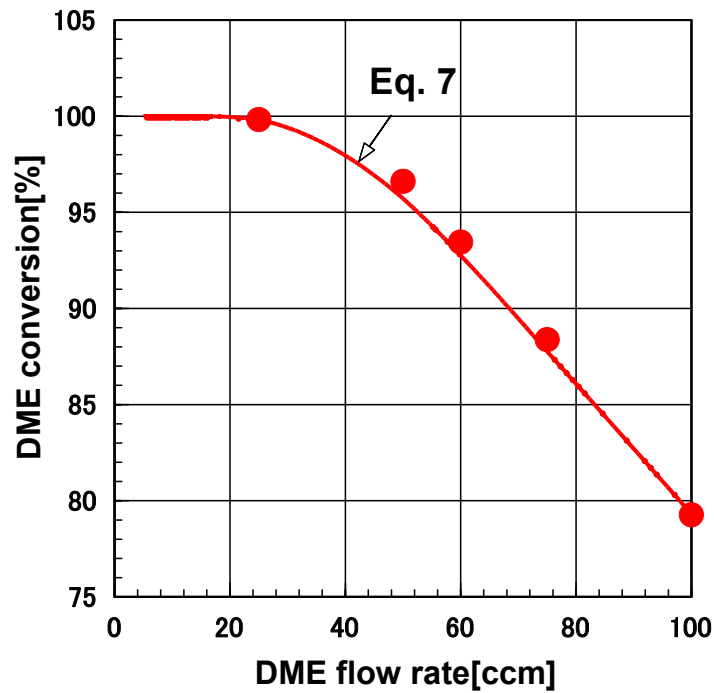Fig. 5 Performance of the micro-channel reactor system

Fig. 6 DME conversion dependence on DME flow rate at the reforming micro-channel
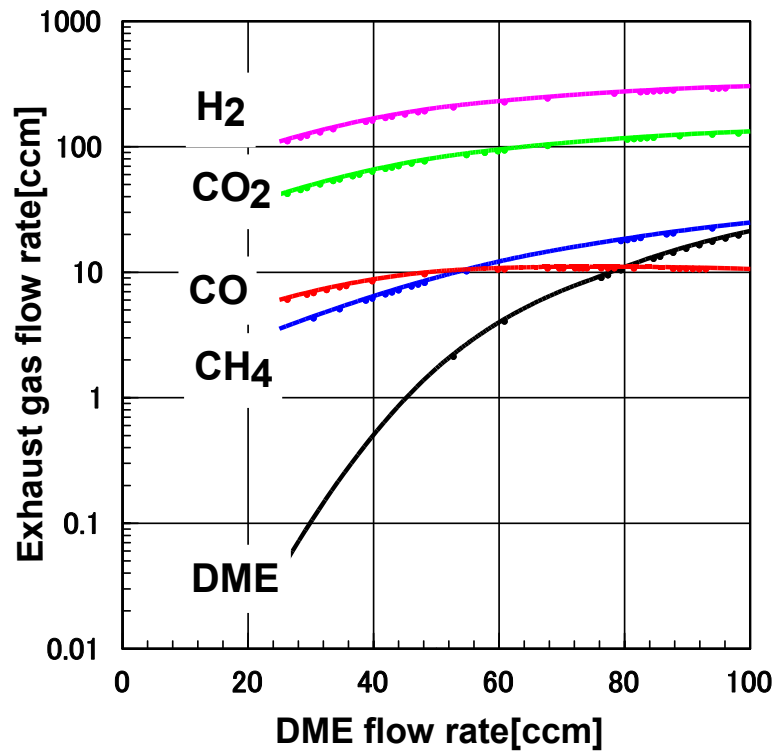reactor

Fig. 7 Exhaust gas flow rate dependence on the DME flow rate at the reforming
micro-channel reactor