Hydrogen Production by Methanol Steam Reforming Using Microreactor

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A microreactor technology, in which a microchannel is used as a catalytic reaction field in order to supply hydrogen to a small polymer electrolyte fuel cell (PEFC) for portable electronic devices, was described. The reduction of heat loss in the microreactor is the primary requirement for improving system efficiency, since heat release in microreactors is higher than in conventional reactors due to the increased specific surface area. Therefore, the methanol steam reforming, operated below 300 °C, is an appropriate process for the hydrogen production using the microreactor. First, the high-performance Cu/ZnO/Al2O3 catalyst for methanol reforming at low temperature was developed under the optimized preparation condition. The miniaturized methanol reformer was then developed to utilize this Cu/ZnO/Al2O3 catalyst. The length of the microchannel was determined based on one-dimensional mass and heat balance analyses. The microreactor was fabricated from silicon and glass substrates using a number of microfabrication techniques. Methanol reforming using this reactor has been demonstrated to reach the levels necessary to power a 1 W-class small PEFC system. The multilayered integrating the miniature methanol reformer with a CO remover, a catalytic combustor as a heat source for methanol reforming, vaporizers, and several necessary functional elements for hydrogen production has also been successfully fabricated. Finally, the microreactor system has been demonstrated to produce hydrogen at a rate sufficient to generate electrical power of 2.5 W.

Keywords
Hydrogen production, Methanol steam reforming, Copper catalyst, Small PEFC, Structured catalyst, Microreactor

1. Introduction

Structured catalysts and reactors for catalyst/reactor systems as a replacement for conventional fixed-bed reactors have recently attracted considerable attention1), and microreactor systems based on a microchannel as a structured catalytic reactor have generated particular interest2). The microreactor allows reactions that are difficult to realize using conventional fixed-bed reactors, and is also suitable for integration with the various additional components required for operation using microfabrication technologies. A small polymer electrolyte fuel cell (PEFC), a promising clean and high-efficiency power source for portable electronic devices, requires a reformer to produce hydrogen by the steam reforming of alcohols, hydrocarbons, or other fossil fuels3). Such reformers typically have complex structures and have proven difficult to miniaturize. In addition, methanol reforming, for example, requires temperatures of up to 300 °C.

Methanol is expected to be an appropriate fuel for the microreactor because of the feasibility of hydrogen production at low temperature4). Methanol steam reforming is an endothermic reaction, as given by Eq. (1)

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2
\]

\[
\Delta H_{\text{f}}^{\circ} = 49.5 \text{ kJ mol}^{-1}
\]

Cu/ZnO catalysts are employed in current commercial processes for methanol reforming, and can achieve reforming at relatively low temperatures of below 300 °C. Moreover, as the equilibrium concentration of CO depends on the reforming temperature, a Cu/ZnO catalyst used at low temperature has the advantage of low CO concentration (approximately 1 mol% of the produced gas), preventing deterioration of the anode. The need for only a preferential oxidation of CO (PROX) process for gas purification prior to supply to a fuel cell makes this system suitable for the realization of small reformer requiring a simple system. Cu/ZnO catalysts have been studied for use in methanol synthesis, water gas shift reaction, and methanol steam reforming5)–13). However, there were few reports on the development of the catalyst for low-temperature hydrogen production as required for miniaturized methanol reformers, and the applicability as a power source for
portable electronic devices had yet to be discussed in the early 2000’s when the authors started the research.

This article reviews the development of catalysts and microreactors for hydrogen production by methanol steam reforming on the basis of researches of the group of authors conducted from 2000 to 2008.

2. Preparation of Cu/ZnO/Al2O3 Catalyst with Superior Catalytic Performance

The Cu/ZnO/Al2O3 catalysts were prepared by coprecipitation. Al2O3 was prepared by precipitation as a third component. An aqueous solution of Na2CO3 (0.76 M, 1 M = 1 mol dm−3) was added dropwise to an aqueous solution of aluminum nitrate (1.4 M) at 60 °C under continuous stirring, and the resulting precipitate was filtered out three times, washing for 20 min between each filtering step. The precipitate was then dried for 12 h at 100 °C and calcined under air flow for 1 h at 360 °C.

A mixed solution of copper and zinc nitrate (total 1.8 M) at 60 °C and an aqueous solution of Na2CO3 (0.76 M) were then simultaneously added to a suspension of prepared Al2O3 in a dropwise manner under continuous stirring and at a prescribed temperature. The volumes of the solutions were adjusted such that the atomic ratio of Cu/Zn/Al was 6/3/1 (mol ratio). During precipitation, the pH of the suspension was monitored using a pH meter, and Na2CO3 solution was added at a controlled rate so as to maintain the prescribed pH. After stirring for 60 min, the precipitate was aged for 12 h at room temperature, and then filtered out five times, washing for 20 min between each filtering step. The washing temperature was 90 °C for the first wash and then 60 °C for all subsequent washes. The cake collected from the precipitate was dried for 12 h at 100 °C and calcined under air flow for 1 h at 360 °C to afford the Cu/ZnO/Al2O3 catalyst.

The effect of precipitation temperature was examined by precipitating the catalysts at 60 °C (catalyst A) and 90 °C (catalyst B) at a pH of 9.4. The effect of adding Al2O3 was examined by preparing catalysts with Al2O3 as above (catalyst C), γ-Al2O3 (JRC-ALO-6, Reference Catalyst of the Catalysis Society of Japan) at pH 9.3 and 60 °C (catalyst D, respectively), and without an additive (catalyst E). To examine the effect of pH, four catalysts with Al2O3 prepared by precipitation were prepared at pH from 8.0 to 9.2 at 60 °C (catalysts F to I).

Catalytic performance tests were carried out using a conventional fixed-bed flow reactor. The catalyst was placed in the reactor and reduced under 60 mL min⁻¹ H2 flow at 300 °C for 1 h. The catalyst bed was then cooled to 200 °C under N2 flow for 20 min, after which a mixed solution of methanol and water (steam/methanol = 2 (mol ratio)) was fed into the reactor at a gas space velocity of 100,000 h⁻¹ through a vaporizer heated to 110 °C. The catalytic performance was measured at every 25 °C step up to 300 °C. The gases produced were analyzed using a gas chromatograph with a thermal conductivity detector (TCD).

The preparation conditions and catalytic activities of the prepared catalysts are listed in Table 1. As can be seen from the table, catalyst A, prepared at 60 °C, exhibited higher catalytic activity than catalyst B (90 °C). Catalyst C, containing prepared Al2O3 (identified as boehmite by X-ray diffraction), exhibited superior catalytic activity to catalyst D (γ-Al2O3) and catalyst E (no additive), and catalyst G prepared under conditions of pH 8.8, had superior catalytic activity to any of the catalysts prepared at other pH levels.

Figure 1 shows a comparison of the catalytic performance of a commercial catalyst (MDC-3, Süd-Chemie) with that of catalyst G, which had the highest catalytic activity of any of the catalysts prepared in this study. The figure clearly shows that the Cu/ZnO/Al2O3 catalyst prepared under optimal conditions has superior catalytic activity compared to the commercial catalyst. At a given temperature, the CO selectivity of the prepared catalyst was also greater than that of the commercial catalyst. A Cu/ZnO catalyst having high catalytic activity for water gas shift reaction, in other words, reverse water gas shift reaction should be advanced. Therefore, increase of CO concentration over the optimized cata-

| Catalyst | Precipitation condition | Al2O3[g] | Methanol conversion at 250 °C [%] |
|----------|------------------------|----------|----------------------------------|
| A        | 60 9.4 (1)             |          | 68.6                             |
| B        | 90 9.4 (1)             |          | 55.7                             |
| C        | 60 9.3 (1)             |          | 78.4                             |
| D        | 60 9.3 (2)             | no additive | 67.7                             |
| E        | 60 9.3 (1)             |          | 56.9                             |
| F        | 60 9.2 (1)             |          | 82.4                             |
| G        | 60 8.8 (1)             |          | 84.3                             |
| H        | 60 8.4 (1)             |          | 78.6                             |
| I        | 60 8.0 (1)             |          | 71.4                             |

a) (1) Boehmite, (2) JRC-ALO-6.

Table 1 Precipitation Conditions and Catalytic Activity of Cu/ZnO/Al2O3 Catalyst

| Precipitation condition Temperature [°C] | pH  | Al2O3[g] | Methanol conversion at 250 °C [%] |
|-----------------------------------------|-----|----------|----------------------------------|
|                                         |     |          |                                  |
| A                                       | 60  | 9.4      | (1)                              |
| B                                       | 90  | 9.4      | (1)                              |
| C                                       | 60  | 9.3      | (1)                              |
| D                                       | 60  | 9.3      | (2)                              |
| E                                       | 60  | 9.3      | no additive                      |
| F                                       | 60  | 9.2      | (1)                              |
| G                                       | 60  | 8.8      | (1)                              |
| H                                       | 60  | 8.4      | (1)                              |
| I                                       | 60  | 8.0      | (1)                              |

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lyst is inevitable. Nevertheless, the CO selectivity of 3 %, corresponding to the CO concentration of approximately 0.8 %, over the catalyst G at 280 °C, at which the methanol conversion reached to almost 100 %, was sufficiently low to decrease with only PROX process in a miniaturized methanol reforming system. These results show that the catalyst prepared in this study achieves methanol conversion equivalent to the commercial catalyst at about 20-25 °C lower. In the case of methanol steam reforming in a miniaturized reformer, which has larger specific surface area than a conventional reactor, operation at low temperature is particularly effective with regard to energy efficiency.

The relationship between catalyst properties and catalytic activity was examined based on the BET surface area and Cu surface area of the prepared catalysts. The Cu surface area was estimated stoichiometrically (Cu/O = 2) based on the amount of N₂O consumed to oxidize the Cu surface. As shown in Fig. 2, the catalytic activity increased with the Cu surface area, whereas the turn-over frequency (TOF) remained constant. The TOF was calculated based on methanol conversion and the Cu surface area. Therefore, the catalytic activity appears to depend on the amount of active sites related to the Cu surface area, which was enhanced by increasing the BET surface area.

Further, the results of analyses of the microscopic structure and chemical composition of catalyst G by transmission electron microscope (TEM) and energy dispersive X-ray fluorescence spectrometer (EDX) showed that the active sites of the Cu/ZnO/Al₂O₃ catalyst appear to be fine Cu species highly interdispersed with ZnO. This expectation agrees with the report (8), which describes the importance of the fine interdispersion between Cu and ZnO.

X-ray diffraction (XRD) analysis of the precipitates as precursors was carried out in order to investigate the influence of the preparation conditions on the dispersion of Cu in the final catalyst. The XRD profiles of the precursors of catalysts A and B, which were prepared at different precipitation temperatures, are shown in Fig. 3. Both precursors consist of aurichalcite ((Cu, Zn)₅(CO₃)₂(OH)₆), hydrozincite (Zn₅(CO₃)₂(OH)₆), and CuO. However, the peaks in the spectrum for the precursor of catalyst A (60 °C) are broader than those for catalyst B (90 °C). As catalyst A exhibited higher catalytic activity than catalyst B, the high dispersion of Cu in the former is probably due to the small crystallite size in the precipitate by slow formation at low temperature. Among the three crystal phases detected in the precursors, the phase related to the interdispersion of Cu and ZnO is thought to be aurichalcite, based on its chemical composition. It has been reported that Cu/ZnO catalysts prepared from aurichalcite exhibit high catalytic activity (5, 8). These results suggest that the formation of small aurichalcite crystallite through optimization of the precipitation conditions is effective for preparing Cu/ZnO/Al₂O₃ catalysts with even higher catalytic activity.

Figure 4 shows a comparison of the XRD profiles for the precursor of catalysts A, C, and F to I, which were prepared at different pH. While aurichalcite and hydrozincite were observed over a wide range of pH (8.0-9.4), malachite as a cupric component was detected only in the precursors prepared at pH 9.3 or below, and CuO as a source of cupric compounds was only observed in catalysts prepared at pH 9.2 or above. The
size of CuO and malachite crystallites was estimated from the XRD profiles. According to the results shown in Fig. 5, the minimum crystallite sizes for CuO and malachite, and hence maximum catalytic activity, are obtained at pH 8.8. It has been reported that Cu⁺² in precipitates transforms into malachite through anion exchange with copper hydroxy carbonate (Cu₂(OH)₄–₂x(CO₃)x), which replaces part of OH⁻ in amorphous Cu(OH)₂ with CO₃²⁻. When precipitation is carried out at high pH, the high concentration of OH⁻ in solution suppresses the replacement of OH⁻ in Cu(OH)₂, preventing the transformation to malachite. Hence, it is thought that crystallization of CuO proceeds by the decomposition of intermediates at high pH. In contrast, in the case of catalysts prepared at the low precipitation pH, crystallization of malachite tends to progress. As an intermediary phase between copper hydroxy carbonate and malachite, the presence of georgeite, which has identical composition with malachite but amorphous phase, has been suggested. Also, it has been evidenced that zinc can be partially substituted of copper in georgeite to form zincian-georgeite, which transforms into malachite slowly. Therefore, the precipitation of amorphous-like phase of malachite in the precursor precipitated at pH 8.8 still contains a small amount of Zn probably, and hence is thought to be responsible for further interdispersion of Cu and ZnO resulting high catalytic activity.

In summary, Cu/ZnO/Al₂O₃ catalyst capable of methanol reforming at temperatures 20-25°C lower than commercial catalysts was successfully developed. This catalyst provides enhanced energy efficiency for applications such as miniaturized reformers, which have large specific surface area.

3. Determination of Microchannel Design for Miniaturized Methanol Reformer

The length of the microchannel was determined through simulations of methanol reforming using mass and heat balance equations based on a one-dimensional model for an incompressible fluid. The rate equation of methanol steam reforming (1), as described before, for the simulation is expressed as Eq. (2)

\[ r_{SR} = \frac{\eta \rho_{cat} \delta (w + 2h + 2\delta)}{wh} k_0 \exp\left(-\frac{E_a}{RT}\right) \]

where \( r_{SR} \) is the rate of the methanol steam reforming reaction, \( \eta \) is the effectiveness factor of the catalyst, \( \rho_{cat} \) is the bulk density of the catalyst (1.6 × 10³ kg m⁻³ in this study), \( \delta \) is the thickness of the catalyst layer, and \( w \) and \( h \) are the cross-sectional width and depth of the microchannel with the catalyst layer, respectively. Hence, in Eq. (2),

\[ \rho_{cat} \delta (w + 2h + 2\delta) \]

represents the catalyst weight per unit volume of the microchannel with the catalyst layer. \( k_0 \) and \( E_a \) are the frequency factor and activation energy, which are determined by a fitting of the experimental results as described later. \( C_A, C_B, \) and \( C_C \) are the concentrations of reactant A, B, and C (in this case, methanol, water, and hydrogen). The orders of reactions in methanol, water, and hydrogen (0.26, 0.03, and −0.2, respectively) were obtained from the report of Jiang et al., according to whom the reaction rate of methanol reforming over the Cu/ZnO/Al₂O₃ catalyst can be expressed as an Arrhenius-type equation as follows.

\[ r = k_0 \exp\left(-\frac{105 \times 10^3}{RT}\right) \rho_{MeOH}^{0.26} p_{H_2O}^{0.03} p_{H_2}^{-0.2} \]

Several literatures also agree that the rate equation of methanol reforming over a Cu/ZnO/Al₂O₃ is described as an Arrhenius-type equation with a power low expression. Jiang et al. concluded that while an inhibiting effect of hydrogen was observed as shown in Eq. (3), carbon dioxide was found to have no effect. Jiang et al. also found, by referring to the reaction mechanism proposed by Takahashi et al., that carbon
monoxide has very little effect on the reaction rate, thereby suggesting the rate equation can be expressed as Eq. (3). The authors\(^{14}\) found that the concentration of carbon monoxide in the reformed gases over the high-performance Cu/ZnO/Al\(_2\)O\(_3\) catalyst used in this study also did not exceed the equilibrium concentration, which agrees that methanol reforming over the Cu/ZnO/Al\(_2\)O\(_3\) catalyst proceeds along with the mechanism proposed by Takahashi et al.\(^{26}\). Further, the authors\(^{14}\) observed no methane production over the Cu/ZnO/Al\(_2\)O\(_3\) catalyst, therefore the methanation was not considered in the present investigation.

The mass and heat balance equations are expressed as

\[
u C_{A0} \frac{dx_A}{dz} = -r_A \tag{4}
\]

\[
u p \rho c_{pm} \frac{dT}{dz} = q + h(-r_A) \Delta H_r \tag{5}
\]

where \(\nu\) is the flow rate of gases, \(C_{A0}\) is the concentration of reactant A at the inlet, \(x_A\) is the conversion of reactant A, \(z\) is the longitudinal position from the inlet, \(-r_A\) is set to equal \(r_{SR}\), \(\rho\) is the fluid density, \(c_{pm}\) is the fluid specific heat, \(q\) is the heat flux, and \(\Delta H_r\) is the heat of reaction. The boundary conditions for Eqs. (4) and (5) were defined as \(\nu = \nu_0\) and \(T = T_0\) at \(z = 0\).

The kinetic parameters of \(E_k\) and \(k_0\) in Eq. (2) were calculated by a fitting of preliminary experimental results (Table 2) for methanol conversion at various temperatures. As a result, \(E_k\) and \(k_0\) were determined to be \(114.5 \times 10^3\) J mol\(^{-1}\) and \(1.63 \times 10^{10}\) mol kg\(^{-1}\) s\(^{-1}\) Pa\(^{-0.09}\), respectively.

Next, the dimensions of the microchannel were analyzed based on the simultaneous Eqs. (4) and (5) with respect to rate Eq. (2). The effectiveness factor of catalyst was assumed to be 0.1, the catalyst layer was assumed to be 15 mm thick, and the cross-sectional width and depth of the microchannel without the catalyst layer were set at 0.6 mm and 0.4 mm, respectively. The methanol conversion and gas concentration were then calculated for a methanol flow rate of 0.013 mol h\(^{-1}\), corresponding to a liquid-based flow rate of 1.0 mL h\(^{-1}\) (stream/carbon (S/C) ratio = 2.0 mol mol\(^{-1}\)) at the inlet. At this flow rate, methanol conversion of almost 100% provides a hydrogen production rate sufficient to power a cellular phone (1 W). Therefore, \(\nu_0 = 2.3\) m s\(^{-1}\) was set as the boundary condition for Eqs. (4) and (5), and the inlet temperature was set at 280 \(^\circ\)C on the basis of catalytic activity tests\(^{14}\). For a reforming temperature of 280 \(^\circ\)C, calculations using thermodynamic data gave a fluid density and fluid specific heat of the gas composition at the inlet of 0.49 kg m\(^{-3}\) and 2.02 \times 10^3\) J kg\(^{-1}\) K\(^{-1}\), respectively. These values were used in Eq. (5). A heat flux of 1200 J m\(^{-2}\) s\(^{-1}\) was set to ensure that the microreactor temperature could be maintained at 280 \(^\circ\)C, and this value was also applied in Eq. (5).

The calculation results are shown in Figs. 6(a) and 6(b). Methanol reforming progresses in approximate proportion to the longitudinal position from the inlet at 280 \(^\circ\)C, with almost complete methanol conversion obtained 330 mm from the inlet. The microchannel of the miniaturized methanol reformer was therefore determined to be 335 mm long for this width (0.6 mm) and depth (0.4 mm).

The influence of diffusion in the catalyst layer was also considered. The average pore diameter of the high-performance Cu/ZnO/Al\(_2\)O\(_3\) catalyst, as determined from the adsorption isotherm for N\(_2\) at –196 \(^\circ\)C measured using a volumetric absorption apparatus, is 9 nm, which is smaller than one tenth of the mean free path. Thus, Knudsen diffusion dominates in the catalyst layer, and the effective diffusion coefficient can be expressed as.

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### Table 2 Pre-experimental Result of Methanol Reforming at Various Temperatures Using Microreactor

| Reaction temperature [°C] | Methanol conversion\(^{a}\) [%] |
|---------------------------|-------------------------------|
| 200                       | 16.4                          |
| 225                       | 52.3                          |
| 250                       | 100.0                         |

\(\text{a)}\) Catalyst weight: 11 mg, feed rate of methanol: \(8.9 \times 10^{-7}\) mol s\(^{-1}\), S/C: 1.2 mol mol\(^{-1}\).
Dr. T. MeA = 3.067ετ ε τ (6)

where $D_{cA}$ is the effective diffusion coefficient of reactant A, $r_e$ is the pore radius ($4.5 \times 10^{-9}$ m), $ε$ is the catalyst void ratio (0.4, also calculated from the adsorption isotherm), $τ$ is the tortuosity factor, and $M_A$ is the molecular mass of reactant A. The diffusion time of reactant A is expressed as Eq. (7).

$$t_{cata} = \frac{\delta^2}{D_{cA}}$$  (7)

Figure 7 shows the dependence of the calculated diffusion time for each reactant on the thickness of the catalyst layer under the assumption of $τ = 4$, which is a reasonable value for normal porous catalysts. For comparison, Fig. 7 also includes the results for a residence time of 0.13 s at the typical flow rate of 1.0 mL h$^{-1}$ (S/C ratio = 2.0 mol mol$^{-1}$). At the designed thickness of the catalyst layer (15 μm), the residence time, corresponding to the reaction time, would be hundreds of times longer than the diffusion time. Furthermore, as the diffusion rate of gases in the cross-sectional direction of the microchannel can be expected to be sufficiently large compared to the rate of reaction$^{27}$, diffusion limitations are considered to be negligible.

Based on the design derived above, the microchannel was arranged in a serpentine shape to minimize the size of the microreactor, which had final dimensions of $25 \times 17 \times 1.3$ mm$^3$, as described later.

These results suggested that the designed microchannel and microreactor should make the best use of the intrinsic performance of this catalyst for methanol reforming.

4. Methanol Reformer with Si-based Microreactor for Small PEFC

Figure 8 shows the cross sectional structure of the micro methanol reformer. Silicon and glass (#7740, Corning) substrates were selected as components of the microreactor. These materials have adequate thermal tolerance to handle the temperature of methanol reforming, and also allow the fabrication process to be simplified by being suitable for sandblasting for microchannel fabrication and anodic bonding at moderate temperatures for junction forming, thereby preventing possible thermal degradation of the catalyst deposited in the microchannel.

The microreactor was 25 mm long, 17 mm wide, and 1.3 mm thick, with weight of approximately 1.0 g. The microchannel formed on the Si substrate was 333 mm long, 0.6 mm wide, and 0.4 mm deep. The glass substrate, with a gas inlet and outlet of 0.5 mm in diameter, was connected to the Si substrate to complete the microchannel. The length of the microchannel was determined by mass and heat balance equations based on a one-dimensional model assuming the prescribed width and depth of the microchannel, as described earlier.

Figure 9 shows the processing flow for fabrication of the microreactor. The thin film heater and electrode was formed first by sputtering Ta-Si-O-N (heater) and Au (electrode) films onto a thin SiO$_2$ layer on one side of a Si wafer (polished on both sides) (Fig. 9(a)). Each film was then shaped respectively by photolithography (Fig. 9(b)). To prevent the thin film heater from coming into physical contact with the electrode, which could result in destruction of the films or a short circuit, an insulating layer (Ta-Si-O) was formed on the heater side of the Si substrate, leaving several areas uncoated as electrical contacts (Fig. 9(c)).

A dry-film photoresist was then fixed to the microchannel side of the Si wafer and shaped by photolithography. The serpentine microchannel was then formed by sandblasting using #400 SiC particles (Fig. 9(d)). Subsequently, the substrate was ultra-
sonicated in a hot alkaline aqueous solution to remove the dry-film photoresist. The final processed Si wafer was divided into several pieces by dicing (Fig. 9(e)). The high-performance Cu/ZnO/Al₂O₃ catalyst for methanol reforming was deposited in the microchannel by dip coating using a slurry of the catalyst (Fig. 9(g)). The slurry was prepared by adding a powder of the catalyst produced by pounding in an agate mortar to distilled water along with a small amount of hydroxyethyl cellulose to improve dispersion. After drying the catalyst layer, the dry-film photoresist was mechanically peeled from the Si substrate, and the workpiece was calcined at 350 °C. A commercial Cu/ZnO catalyst (MDC-3, Süd-Chemie) was also deposited in the microchannel by a similar procedure as a reference.

Finally, the Si substrate and glass substrate, in which the gas inlet and outlet ports were fabricated by sandblasting, were connected by anodic bonding (Fig. 9(h)). Anodic bonding was conducted at an impress voltage of 1500 V and a bonding temperature of 350 °C.

Figure 10 shows the results of SEM-EDX analyses of the microchannel. Analyses using Si-Kα and Cu-Lα beams reveal that the catalyst was selectively deposited only on the microchannel walls. Contamination of the Si surface adjacent to the microchannel with catalyst powder could introduce gaps between the Si and glass substrates during the junction process, resulting in incomplete contact and leading to gas leaks or bypassing of parts of the microchannel. Selective deposition of the catalyst layer in the microchannel is therefore very important for the fabrication of a quality microreactor. The catalyst deposition was also found to be uniform, with no exposed wall areas remaining after deposition.

Figure 11 shows the microreactor fabricated by process flow shown in Fig. 9. The size of the microreactor is suitable for use as a power source for portable electronic devices.

The test system for methanol reforming using the microreactor was as follows. The microreactor was fastened to a stainless steel (SUS304) holder with flow channels. The gap between the gas ports of the microreactor and holder was sealed with a rubber gasket. The microreactor was heated by applying direct current to the thin film heater, and the temperature of the microreactor was measured by a thermocouple fixed to the glass substrate on the microchannel side. Prior to methanol reforming, the catalyst was reduced under H₂ flow at 250 °C for 20 min, followed by purging with N₂. A methanol aqueous solution (steam/methanol ratio, i.e., S/C ratio = 2.0 mol mol⁻¹) was then fed to the microreactor by a micro feeder through a vaporizer composed of a dummy microreactor without a catalyst layer. The performance of the microreactor was evaluated for a liquid-based feed rate of 0.25 to 3.2 mL h⁻¹. After separation of the liquid components (methanol and water) by a cold trap set in an ice-water bath, the flow...
rate of the produced gas was measured by a soap film flow meter, and the reformate was analyzed using a micro gas chromatograph with a TCD.

Figure 12 shows the methanol conversion and hydrogen production rates using the microreactor with the high-performance Cu/ZnO/Al₂O₃ catalyst in comparison to the results using the same reactor with a commercial catalyst measured at a microreactor temperature of 280°C. Methanol conversion decreased with increasing feed rate of the reactant, whereas the hydrogen production rate increased.

The microreactor requires several watts of electrical power for heating to the operating temperature of 280°C without thermal insulation, exceeding the predicted power generated by the microreactor system. Although the thermal efficiency of this microreactor system cannot be discussed based on this experimental results, it is anticipated that housing in a suitable vacuum package will achieve methanol reforming with sufficiently low heat loss. The construction of a vacuum package is thus considered essential to improving the thermal efficiency of the proposed system. Combination with catalytic combustion as a heat source by consumption of methanol or recycled hydrogen from the anode side of a PEFC may allow further improvements in thermal efficiency to be realized, as described later.

Nevertheless, the obtained results demonstrate that a microreactor based on the Cu/ZnO/Al₂O₃ catalyst is capable of hydrogen production rates exceeding 0.05 mol h⁻¹ at a reactant feed rate of 1.6 mL h⁻¹. The resulting hydrogen production rate, which was larger than that obtained by using of a commercial Cu/ZnO catalyst, suggested a capability for driving a 1 W-class small PEFC.

Further, a small PEFC system containing microreactors produced with microfabrication technologies was developed. The proposed power generation system consists of three microreactors, namely a vaporizer, a methanol reformer with the high-performance Cu/ZnO/Al₂O₃ catalyst, and a CO remover with a commercial Pt/Al₂O₃ catalyst, as well as a single PEFC approximately the same size as one microreactor. In the attempt of the electrical power generation from
of approximately 100 mW cm$^{-2}$, which was nearly equivalent to that observed with pure hydrogen, suggests the feasibility of the proposed system as a power source in portable electrical device applications.

5. **Multi-layered Microreactor System with Methanol Reformer for Small PEFC**

A multi-layered microreactor system with a methanol reformer to supply hydrogen for a small PEFC to be used as a power source for portable electronic devices was developed$^{17}$. The microreactor consists of four units (a methanol reformer with catalytic combustor, a CO remover, and two vaporizers), and was designed using thermal simulations to establish the appropriate temperature distribution for each reaction, as shown in Fig. 13.

The microreactor was constructed from thirteen microchanneled glass plates stacked with anodic bonding and placed in a vacuum package for thermal isolation. The prototype miniature reactor system has dimensions of 22 mm long, 21 mm wide, 10.7 mm height. The appropriate catalyst for each reaction, namely the high-performance Cu/ZnO/Al$_2$O$_3$ catalyst for methanol reforming, a Pt/Al$_2$O$_3$ catalyst prepared by the impregnation method for catalytic combustion of methanol, and a commercial PROX catalyst for CO removal, was deposited on the microchannel of each reactor. When the microreactor was heated by applying voltage to a thin film heater attached to one side of the reformer, the temperature distribution observed for each unit approximated the simulated results. Further, methanol reforming was achieved in the microreactor using heat supplied from the internal catalytic combustor. The reforming temperature of the microreactor could be maintained at 280 $^\circ$C without a supply of electrical power. A hydrogen production rate sufficient to generate 2.5 W of electrical power was obtained. Rapid start-up of methanol reforming using the Cu/ZnO/Al$_2$O$_3$ catalyst has also been shown to be feasible under an oxidative atmosphere, for which the durability of the catalyst can be improved by the addition of iron to the catalyst composition$^{28}$. In addition, in order to achieve long-lasting activity for methanol reforming, the performance of Pd/ZnO catalysts prepared using various procedure and conditions, as well as modification with Si, was investigated$^{29}$.

6. **Conclusion**

In this article, the development of catalysts and micro reactors for methanol steam reforming was described on the basis of researches of the group of authors. A structured catalytic reactor based on a microreactor is an attractive approach to miniaturizing PEFC. The structure of reactor and the catalyst layer have a strong influence on the performance of the reaction, in addition to the performance of the catalyst itself. It is therefore necessary to clarify the reaction behavior in order to optimize the performance of the structured catalytic reactor. Although the catalyst is the primary elemental technology, the catalyst and reactor should be design and optimized as a system to achieve the highest efficiency for this technology$^{28}$.

**Nomenclatures**

- $c_p$: fluid specific heat [J kg$^{-1}$ K$^{-1}$]
- $c_A$: concentration of reactant A [mol m$^{-3}$]
- $C_{A0}$: concentration of reactant A at the inlet of the reactor [mol m$^{-3}$]
- $D_{Ae}$: effective diffusion coefficient of reactant A [m$^2$ s$^{-1}$]
- $E_a$: activation energy [J mol$^{-1}$]
- $h$: cross-sectional depth of the microchannel [m]
- $\Delta H_{Re}$: standard heat of reaction [J mol$^{-1}$]
- $\Delta H_i$: heat of reaction [J mol$^{-1}$]
- $k_o$: frequency factor in the case of applying rate Eq. (2) [mol kg$^{-1}$ s$^{-1}$ Pa$^{-0.09}$]
- $M_A$: molecular mass of reactant A [kg mol$^{-1}$]
- $P_A$: partial pressure of reactant A [Pa]
- $q$: heat flux [J m$^{-2}$ s$^{-1}$]
- $r$: rate of reaction [mol s$^{-1}$ m$^{-3}$]
- $r_A$: rate of reaction of reactant A [mol s$^{-1}$ m$^{-3}$]
- $r_w$: pore radius [m]
- $r_{Re}$: rate of methanol steam reforming reaction [mol s$^{-1}$ m$^{-3}$]
- $R$: gas constant = 8.314 J mol$^{-1}$ K$^{-1}$
- $t$: time [s]
- $t_{diff}$: diffusion time in the catalyst layer of reactant A [s]
- $T$: temperature [K]
- $T_0$: temperature at the inlet of the reactor [K]
- $u_0$: flow rate of gases [m s$^{-1}$]
- $w$: cross-sectional width of the microchannel [m]
- $x_i$: position in j axis [m]
- $z$: longitudinal position from the inlet of the reactor [m]
- $\vartheta$: thickness of the catalyst layer [m]
- $\varepsilon$: catalyst void ratio [-]

**Greek symbols**

- $\delta$: catalyst void ratio [-]
η : effectiveness factor of catalyst [-]
μ : coefficient of viscosity [Pa s]
ρ : fluid density [kg m⁻³]
ρₜ : bulk density of the catalyst layer [kg m⁻³]
τ : tortuosity factor [-]

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要 旨
マイクロリアクターを用いたメタノールの水蒸気改質による水素製造

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小型電子機器のための新しい電源として期待されている小型の固体高分子形燃料電池（PEFC）のために、微小流路（マイクロチャンネル）上で反応が進行するマイクロリアクターの開発が必要である。マイクロリアクターは、反応器の体積あたりの表面積が大きく、伝熱効果が大きいため、反応速度が速いため、同時に放熱も容易であることから、従来の反応器と比較して熱の有効利用が特に重要となる。このことから、300℃以下の低温で水素製造が可能であるメタノールの水蒸気改質のために、最適化した条件で高性能なCu/ZnO/Al₂O₃触媒が開発された。特に、このCu/ZnO/Al₂O₃触媒をマイクロリアクターにプレート化したマイクロリアクターを設計するために、1次元モデルに基づいて現実の基板や深さを仮定する物質・熱収支式の解析結果からチャンネルの長さが決定される。なお、水素の製造コストを考慮して、ソーダクライアチュラ系の触媒を用いたリアクター系の開発を進めている。

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