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First use of macroporous silicon loaded with catalyst film for a chemical reaction: A microreformer for producing hydrogen from ethanol steam reforming

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Abstract

Macroporous silicon with millions of parallel microchannels per square centimeter can be used as a micromonolithic support for high-speed catalysis in miniaturized systems, opening a new and exciting field of research and application. We used macroporous silicon membranes with $>10^6$ parallel microchannels with a diameter of 3.3 μm and depth/width ratio >60 as microreactors for the generation of hydrogen through the steam reforming of ethanol. The microchannels walls were coated with a thin layer of Co_3O_4–ZnO catalyst by a complexation–decomposition method, resulting in a specific inner surface of 10^5–10^6 $m^2\,m^{-3}$. A constant flow of 20 $\mu L\,s^{-1}$ H_2 (0.054 $mmol\,min^{-1}$ H_2) was obtained from a liquid water–ethanol mixture at 773 K with a steam-to-carbon ratio of $S/C = 3$ and $LHSV = 2 \times 10^4\ h^{-1}$ (0.1 $mL\,min^{-1}$). The turnover frequency under these conditions was ca. 1.1 s^{-1}, based on surface Co atoms.

Keywords: Macroporous silicon; Micromonolith; Hydrogen; Ethanol; Steam reforming

1. Introduction

A major impediment to the success of fuel cells is the difficulties and hazards involved in the storage and handling of hydrogen [1]. Onsite steam reforming is an alternative to produce hydrogen from organic sources with the aid of a catalyst, with alcohols (i.e., methanol and ethanol) among the best candidates for portable applications [2]. Using alcohols for steam reforming is attractive due to their high volumetric energy density, low cost, safety, and easy transportation. Although considerable work has been done on catalytic steam reforming of methanol and ethanol for hydrogen production using conventional macroscale reactors [3–8], the use of microreactors is relatively new. Besides their compactness and light weight, the microreactor systems provide rapid mass and heat transport due to large surface area-to-volume ratios and short diffusion length, low pressure drop, and precise control of process conditions with higher product yields [9]. The improved heat transfer properties in microreactors are particularly relevant for endothermic reactions, such as the steam reforming of alcohols. Although several microreactors for onsite production of hydrogen from methanol steam reforming at 533–723 K have been reported [10–15], the higher temperatures required for ethanol steam reforming has prevented extensive work in this field [16]. Nonetheless, interest in ethanol steam reforming is growing rapidly, because ethanol is a renewable fuel readily produced from biomass (bioethanol) and yields more hydrogen on a molar basis,

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2. \qquad (1)$$

Herein we report for the first time the use of macroporous silicon membranes containing straight, parallel channels of a few micrometers in diameter for the generation of hydrogen for microdevices, and validate their capability to serve as catalyst support structures by performing steam reforming of ethanol at 698–773 K. (Silicon is stable to oxidation in the presence of steam up to 1073 K.) A new method was developed for de-

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positing a ca. 100-nm-thick layer of Co_3O_4–ZnO catalyst on the microchannel wall that is catalytically active. ZnO-supported cobalt has shown good activity and selectivity toward ethanol steam reforming at moderate temperatures in fixed-bed reactors [17,18]. Very recently, Si micromonoliths have been used as supports for zeolite films [19], but no application in a chemical reaction has been yet attempted.

2. Experimental

Macroporous silicon membranes were prepared by photo-assisted electrochemical etching [20] and subsequent opening of the pores from the back side. The substrate material was ⟨100⟩ *n*-type float-zone silicon, with a resistivity of 2–6 Ω cm. Before the electrochemical etching, the wafer surface was prestructured by lithography and tetramethylammonium hydroxide (TMAH) etching was used to create a square array of inverted pyramids. These pyramids pointed toward the bulk of the wafer and defined the positions of pore growth. The electrochemical etching was then carried out at 288 K in 5 wt% HF solution, using TritonX-100 surfactant (0.1 mmol) as a wetting agent. The structured (front) side of the wafer was in contact with the electrolyte, while the backside was illuminated through an array of LEDs with an 880-nm peak emission wavelength. A constant anodic potential of 2 V was applied. The etching current was computer-controlled and was reduced as a nonlinear function of the etching time, to compensate for the effects of limited HF diffusion in the narrow pores [20,21]. Under these conditions, about 330 min of etching time was required to achieve a pore depth of 220 μm. After the electrochemical etching, the macroporous samples were oxidized in dry O_2 at 1373 K for 30 min. The oxide layer on the backside was removed, and the remaining backside silicon was etched off in 25 wt% TMAH solution at 358 K until the pore tips were reached. Finally, the samples were dipped in 5 wt% HF to remove any oxide remaining on the pore walls and on the wafer's front side. The resulting structures were silicon membranes with pores (channels) opened at both sides and arranged in a square lattice with a periodicity of 4 μm.

The walls of the macroporous silicon channels were coated with a catalyst layer containing zinc and cobalt oxides. During the first step in the preparation procedure, the channels were completely filled with a dimethylketone solution containing equal amounts of Zn^{2+} and Co^{2+} (0.35 M, nitrate precursors), and urea (1.4 M). The precursor solution was forced to pass through the macroporous silicon channels by applying a pressure gradient with a vacuum pump and a pressure regulator set at 75 kPa. After ensuring complete air removal and complete filling of channels, the silicon membrane was heated first at 348 K for 3 h, then at 393 K for 15 h, and finally at 673 K for 2 h at 2.5 $K\,min^{-1}$. Before catalytic testing, the catalytic layer was activated by thermal treatment at 723 K for 1 h (5 $K\,min^{-1}$) under a helium-hydrogen mixture (10% H_2, 50 $mL\,min^{-1}$ total).

For catalytic testing, macroporous silicon membranes were glued with epoxy into stainless steel washers (external diameter 19 mm, internal diameter 8 mm), which were then incorporated within a stainless steel housing inside a furnace (Carbolite, accuracy ±0.1 K). Two sets of experiments were carried out with different reactions mixtures. A reaction mixture consisting of gaseous ethanol (0.24 $mL\,min^{-1}$, or 1.07×10^{-2} $mmol\,min^{-1}$) and water (fed separately) diluted in He was passed at atmospheric pressure through the silicon membrane at 46–82 STP $mL\,min^{-1}$, with $C_2H_5OH{:}H_2O$ molar ratios of 1:3 and 1:6 (steam-to-carbon ratios of 1.5 and 3 $mol\,mol^{-1}$, respectively). In addition, an undiluted mixture of $C_2H_5OH{:}H_2O = 1{:}6$ (molar ratio) was provided directly by a syringe pump (Genie Plus, Kent Scientific) at a constant rate of 0.1 $mL\,min^{-1}$. Reaction products were analyzed continuously by online mass spectrometry (Cirrus MKS) every 15 s through a capillary inlet held at 353 K. The composition values were obtained after proper calibration using a standard mixture of known composition and by parallel injection into a gas chromatograph equipped with MS 5 Å, PlotU, and Stabilwax columns (Agilent 3000A). Scanning electron microscopy (SEM) was performed with a JEOL JSM-6400 electron microscope. Microstructural characterization by high-resolution transmission electron microscopy (HRTEM) was carried out at 200 kV with a JEOL JEM-2010F electron microscope equipped with a field emission gun.

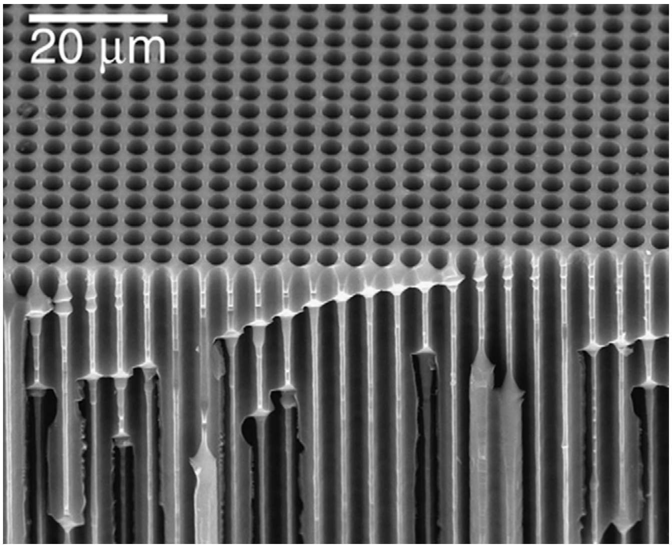


Fig. 1. SEM image of the macroporous silicon membrane as prepared showing the regular array of parallel microchannels.

3. Results and discussion

Macroporous silicon channels were imaged by SEM and analyzed by EDX before and after deposition of the catalyst layer. Figs. 1 and 2a show typical SEM images of the macroporous Si membrane as prepared, which has a regular distribution of channels with smooth walls. The channels are 3.3 μm in diameter and 210 μm in length, producing an aspect ratio (depth/width) of about 64. Deposition of a catalyst coating on such small channels with high aspect ratio is challenging, and classical preparation methods such as washcoating, deposition, and precipitation have proven inadequate, resulting in strong agglomeration of catalyst particles and poor dispersion. In contrast, the novel complexation–decomposition route reported in

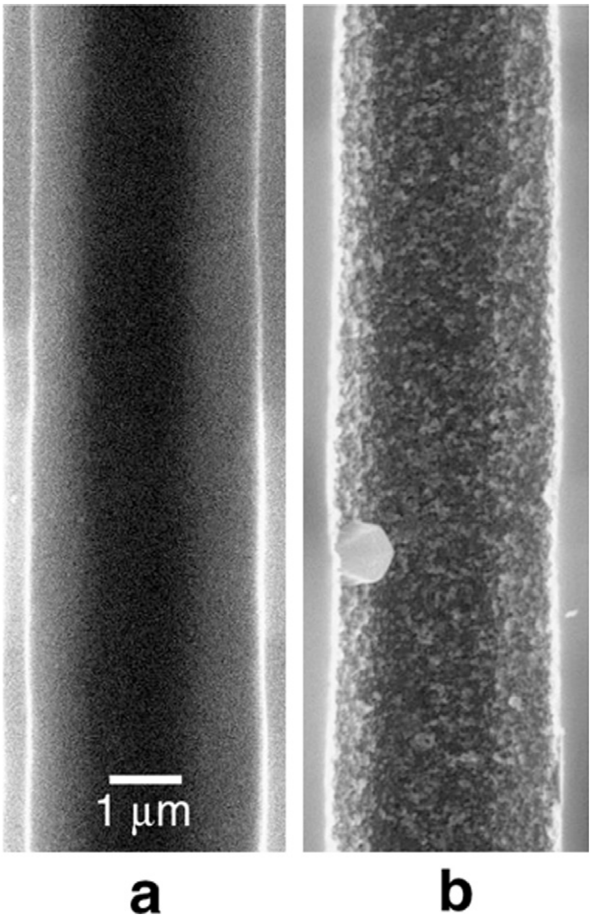


Fig. 2. SEM images of a single microchannel before (a) and after (b) catalyst deposition.

this study produced adequate results. Urea served both as a complexating agent and as a basic medium during the decomposition of complexes at increasing calcination temperature. In a separate experiment (without macroporous silicon), the presence of intermediate complexes was inferred from infrared (IR) spectroscopy. IR spectra after drying at 393 K (before decomposition) showed absorption bands at 3000–3500, 2200–2400, 1763, 1680, 1420, 1145, 1050, 1025, 825, and 775 cm^{-1}. Bands in wavenumber range 3000–3500 cm^{-1} were assigned to the stretching vibrations of hydroxyl ions. The absorption bands at 2200–2400 cm^{-1} were attributed to the existence of intercalated NH_3 species [22] and/or cyanate ion [23]. The broad band at 1420 cm^{-1} is characteristic of the CO_3^{2-} ion, whereas bands at lower wavenumbers are unspecific and may be assigned to various species, including coordinated carbonate, nitrate, and hydroxyl groups. The presence of carbonate and cyanate ions should not be surprising, because these have been known to result from the heating of urea solutions [22,23]. The band at 1763 cm^{-1} was attributed to the stretching mode of carbonyl in coordinated urea. These bands shifted (probably due to the formation of dimer and polymeric species) [23] and vanished on heating. Thermal decomposition was followed by TGA, with the main weight loss occurring at 453–533 K. After calcination at 673 K, only ZnO and Co_3O_4 were identified by FTIR as well as by XRD.

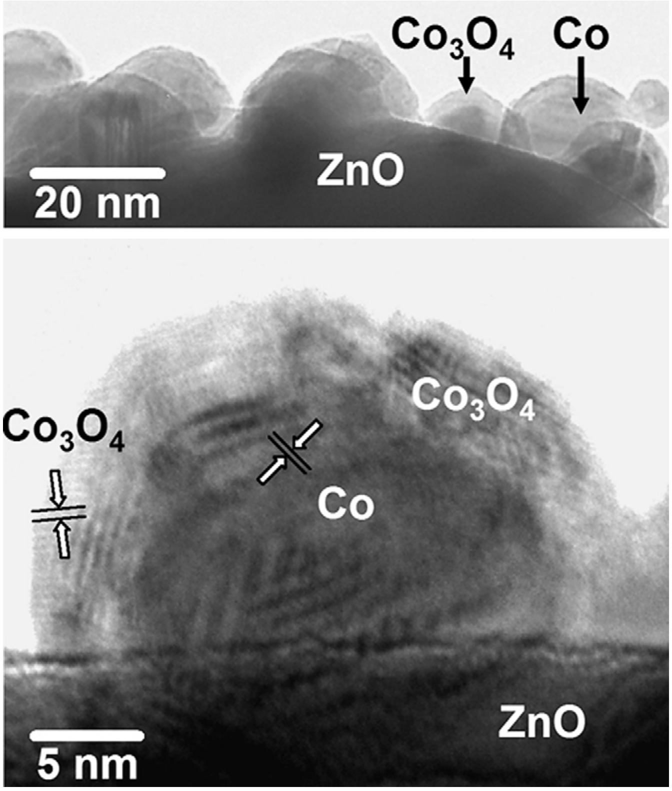


Fig. 3. Bright field and high resolution transmission electron microscopy (HRTEM) images of the catalyst film after activation.

Fig. 2b corresponds to macroporous Si after deposition of the catalyst layer by this method. The catalyst coating was about 100 nm thick and was well dispersed and adhered over the channel interior. SEM and EDX analysis revealed that the catalytic coating consisted of a homogeneous, fine-grained layer of intermixed ZnO and Co_3O_4 particles. Along with this well-dispersed layer, occasional ZnO crystallites about 1 µm in size also were present. Considering a channel diameter of 3.3 µm and a mean catalyst layer thickness of 0.1 µm, we can deduce a microchannel surface area after catalyst coating of ca. 1.3×10^6 $m^2\,m^{-3}$. After activation under H_2, Co_3O_4 was partially reduced to metallic cobalt, as determined by XRD and HRTEM. Fig. 3 shows representative low- and high-magnification TEM images of the catalyst film after activation. Lattice fringes corresponding to ZnO, metallic Co, and Co_3O_4 can be identified. Cobalt particles of ca. 10–20 nm diameter are well mixed with ZnO and partially covered by a layer of cobalt oxide. The redox pair $Co^{\delta+}/Co^0$ is an active species for ethanol steam reforming [24,25].

The effective area of the macroporous Si membranes for catalytic testing after assembly with stainless steel washers was 38 mm^2, which means about 1.5×10^6 microchannels. Taking into account the pitch distance between channels of 4.0 µm and the membrane thickness of 210 µm, this huge number of microchannels yields a total inner surface of 30 cm^2 with only ca. 10^{-3} g of total catalyst loading, and a specific inner surface, per m^3, of 3.5×10^5 m^2. This value is as high as those reported in high-surface area porous materials prepared by flame pyrolysis, sol–gel techniques, templates, or supramolecular as-

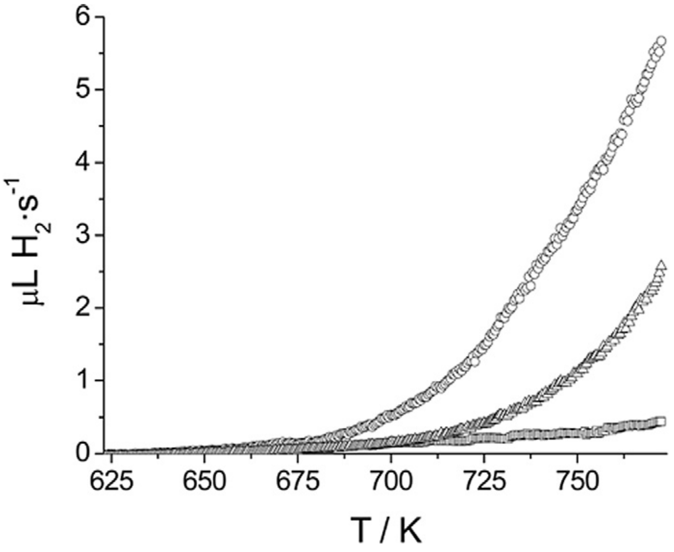


Fig. 4. Rate of hydrogen production from ethanol steam reforming at increasing temperature obtained over macroporous Si before (□) and after coating the microchannels with catalyst film (○, △). 0.24 mL min^{-1} C_2H_5OH, GHSV = 1.5–2 × 10^6 h^{-1}, S/C = 3 (□, ○), S/C = 1.5 (△).

semblies [26]; however, the regular arrangement of parallel microchannels with exactly the same dimensions and high aspect ratio makes the structure of macroporous silicon membranes unique for microreaction technology. Our catalytic tests were performed at a residence time of about 1.9–3.2 ms per microchannel and a total equivalent gas hourly space velocity (GHSV) of about 1.5–2 × 10^6 h^{-1}.

Fig. 4 shows the production rate of hydrogen obtained in the catalytic tests using C_2H_5OH–H_2O mixtures diluted in inert gas at increasing temperature under different S/C ratios and GHSV values, as well as the results obtained in a blank experiment (Si membrane assembled with stainless steel washers with no catalyst coating). It is evident that the hydrogen production rate in the blank experiment was much lower than that of the Si membrane with microchannels coated with catalyst. The products obtained in the blank run were mainly H_2, CO, and CH_4 in similar amounts, indicating that the main process occurring in the absence of catalyst was the thermal decomposition of ethanol through

$$C_2H_5OH \rightarrow CH_4 + CO + H_2. \tag{2}$$

In contrast, when the microchannels of the Si membrane were loaded with catalyst, the production rate of hydrogen increased significantly, particularly when the reaction was carried out with S/C = 3. In this case, up to 5.72 μL of $H_2\ s^{-1}$ (0.015 mmol $H_2\ \text{min}^{-1}$) was obtained at 773 K. The rate of hydrogen production obtained with S/C = 1.5 (stoichiometric value for the reforming reaction [Eq. (1)]) was lower than that obtained with S/C = 3 at the same gaseous ethanol inlet rate and similar conversion. This can be explained by the distribution of products obtained in each case (Table 1). When the reaction was carried out with the stoichiometric mixture, ethanol transformed into H_2, CO_2, CO, and minor amounts of CH_4. In addition, the ratio CO/CO_2 increased with increasing temperature. This is in accordance with a reaction scheme in which first ethanol reforms into a mixture of H_2 and CO [Eq. (3)], and then CO transforms into CO_2 through the water–gas shift (WGS) reaction [Eq. (4)]:

$$C_2H_5OH + H_2O \rightarrow 4H_2 + 2CO \tag{3}$$

and

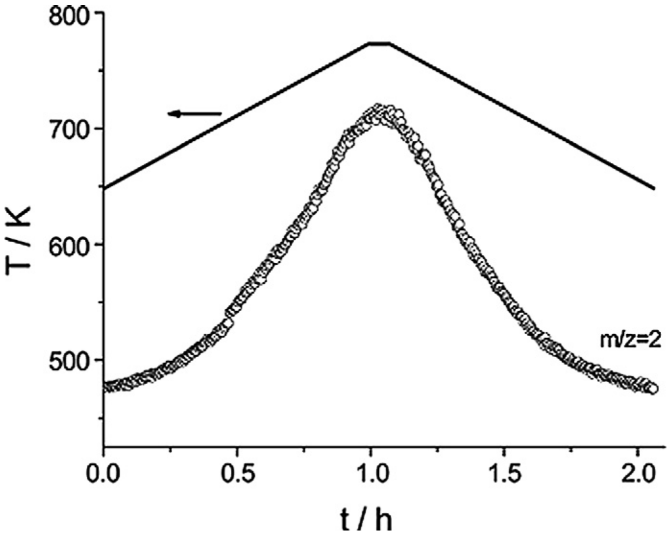
$$CO + H_2O \rightarrow CO_2 + H_2. \tag{4}$$

In this case, an increase in the reaction temperature resulted in an increase in ethanol conversion and thus also of hydrogen production (Fig. 4), along with in an increase in the relative amount of CO due to the reverse WGS reaction (Table 1), which is favored at increasing temperature [27]. In contrast, when the reaction was performed with S/C = 3, the distribution of products indicated that the steam reforming of ethanol was more selective toward the final reforming products, and a hydrogen-rich stream composed of 71–73 vol% H_2, 23–24 vol% CO_2, and 3–5 vol% CH_4 was obtained on a dry basis (Table 1). The absence of CO among the reaction products is likely due to a higher partial pressure of water, which has a strong influence on the WGS reaction [28], and methane likely was produced at low temperature from the decomposition of ethanol or acetaldehyde. The activation energy of the reaction calculated from the rates reported in Table 1 and additional experiments conducted at lower conversions (see below) is 59 ± 2 kJ mol^{-1}. Unfortunately, performing a direct comparison with reaction rates obtained in conventional fixed-bed reactors loaded with powdered ZnO-supported cobalt catalysts [17,18] is not possible, because the ethanol conversion reported is total in the temperature range used in this work.

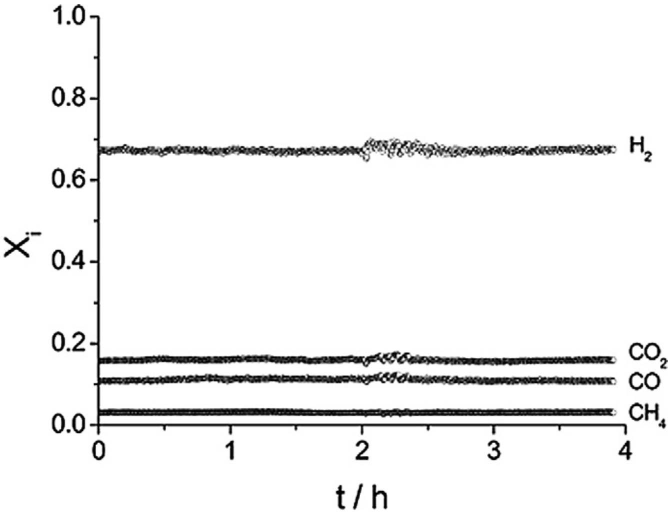
Table 1
Catalytic results obtained at atmospheric pressure with a gaseous stream containing C_2H_5OH (0.24 mL min^{-1}) and H_2O diluted in He. Standard gas-flow velocity 0.06–0.1 m s^{-1} (GHSV = 1.5–2 × 10^6 h^{-1})

C_2H_5OH:H_2O	T (K)	Activity (mol C_2H_5OH/mol Co h)	C_2H_5OH conversion (%)	Selectivity[a] (%)			
				H_2	CO_2	CO	CH_4
1:6	698	16.8	33.2	69.3	24.3	–	6.4
	723	26.4	52.2	70.1	24.9	–	5.0
	748	37.7	74.6	71.1	24.2	–	4.7
	773	45.9	90.7	73.4	23.2	–	3.4
1:3	698	16.4	32.5	70.5	23.4	6.1	–
	723	22.9	45.3	69.0	23.8	7.2	–
	748	33.6	66.5	68.1	17.5	11.6	2.8
	773	41.8	82.6	67.3	15.3	13.7	3.7

[a] Molar percentage of products (water excluded).



(a)



(b)

Fig. 5. (a) Variation of hydrogen partial pressure ($m/z = 2$) in a temperature pulse experiment. (b) Product distribution (molar fraction) obtained at 773 K. S/C = 1.5, 0.24 mL min^{-1} C_2H_5OH, GHSV = 1.5 × 10^6 h^{-1}.

We carried out several experiments to evaluate the response and stability of the microreformer. We applied temperature pulses under steady-state conditions, and found that the generation of hydrogen was completely reversible at each temperature (Fig. 5a). Further, we detected no significant variations in product distribution during stability tests conducted at different temperatures (Fig. 5b). A micro-fuel cell capable of running a portable device of several watts requires a hydrogen flow of several mL min^{-1}. This can be achieved with our microreformer by increasing the amount of ethanol in the reactant mixture. When a C_2H_5OH:H_2O = 1:6 molar mixture was supplied directly from a syringe pump (total liquid flow, 0.1 mL min^{-1}; LHSV = 2 × 10^4 h^{-1}), up to 1.2 mL min^{-1} H_2 (0.054 mmol H_2 min^{-1}) was obtained at 773 K. In this case, the overall ethanol conversion was low (ca. 1.5%), but higher values could be readily obtained by stacking several Si membranes. (The macroporous Si membrane is only 0.21 mm thick.) A turnover frequency (TOF; number of hydrogen molecules produced per surface cobalt per s) was estimated using the Co particle size determined by TEM. At 773 K, the TOF was ca. 1.1 s^{-1}.

4. Conclusion

Macroporous silicon is envisioned as a new and excellent micromonolithic support for catalysts in chemical microreactors. In this work, we have demonstrated the high efficiency of macroporous silicon membranes for producing hydrogen from ethanol steam reforming at moderate temperature after coating the microchannels with a thin layer of an appropriate catalyst (Co_3O_4–ZnO) by a novel complexation–decomposition route. High and stable selectivity toward the reforming products, H_2 and CO_2, with >73 vol% H_2 was attained at 773 K and S/C = 3 at contact times of <5 ms per channel. Micro-fuel cells, which are expected to be involved in the energy supply for portable electronic devices in the future, may benefit from the microtechnology derived from macroporous silicon-based microreformers that generate hydrogen.

Acknowledgments

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