Catalytic membrane reactors based on macroporous silicon for hydrogen production

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1. Introduction

The possibility of using hydrogen as an energy carrier and its implementation in portable fuel cells has motivated a considerable research interest in the development of new and efficient hydrogen production technologies. Hydrogen storage and manipulation is however a problematic and hazardous issue. Therefore, the low-temperature on-site steam reforming of alcohols (e.g. methanol, ethanol) for hydrogen supply offers a nice solution to safety and storage issues, while providing several environmental advantages [1]. Although higher temperatures are required for ethanol steam reforming compared to that of methanol, ethanol is gaining considerable interest because it is a renewable fuel easily produced from biomass and thus, has the advantage of being CO_2 neutral. In addition, ethanol steam reforming yields more hydrogen on a molar basis:

$$C_2H_5OH+3H_2O \rightarrow 6H_2+2CO_2$$

Higher H_2 production yield and efficiency in the steam reforming reaction are achieved using an appropriate catalyst loaded in micro-structured reactors. The advantages of these catalytic wall microreactors include rapid mass and heat transport due to large surface-to-volume ratios, good structural and thermal stability and precise control of process conditions. Microreactors provide also built-in safety because large volumes are avoided. Numerous microreactors have been reported with typical channel dimensions ranging from 100 to 900 μm, e.g. conventional cordierite monoliths with channel width of ~900 μm or stainless-steel microreactors with channel diameter of ~700 μm. Here, we report on the use of macroporous silicon as a catalytic wall microreactor for H_2 generation through ethanol steam reforming. Macroporous silicon monoliths used in this work exhibits channels with a diameter and pitch distance of ~3 and 4 μm, respectively. Such breakthrough downscaling of channel dimensions and pitch distance results in a spectacular increase of inner surface area with respect to reactor volume, which provides a remarkable improvement of the specific H_2 production rate (per unit volume and feed flowrate) and opens a new route towards the miniaturization for portable applications.

2. Experimental results and discussion

Silicon micromonoliths, consisting of straight parallel channels (pores), were prepared by photo-assisted electrochemical etching of n-type wafers in 5 wt.% hydrofluoric acid (HF) solution. This is a well-established technique [3] which allows a precise control over the pore diameter and depth, while the pore distribution is lithographically defined. A macroporous membrane was formed by etching off the remaining backside silicon. Figure 1 shows SEM images of the as-prepared silicon micromonoliths with regular channels in a square arrangement (pitch=4 μm). The channels are 3.3 μm in diameter and 210 μm in length, giving an aspect ratio of about 64.

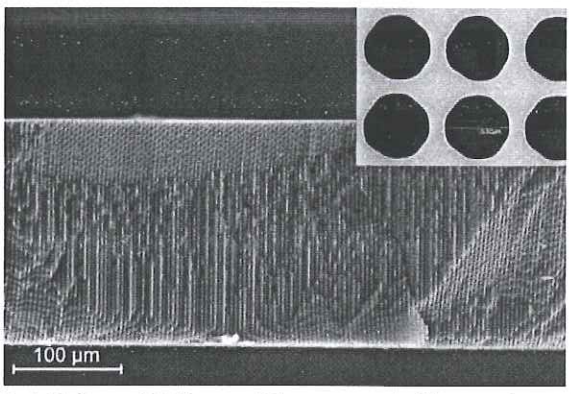

Fig. 1. A bird's-eye SEM image of the as-prepared silicon membrane. The inset is an image of the bottom side.

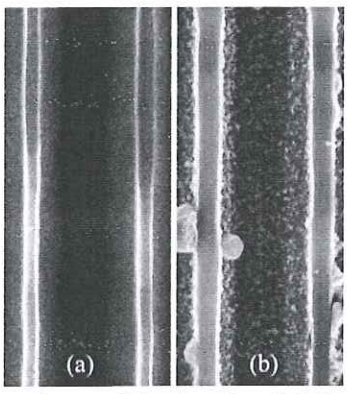

Fig. 2. SEM images of the channel walls before (a) and after (b) catalyst deposition.

For the proposed application, the inner walls of the channels were coated with a catalyst layer containing zinc and cobalt oxides [4]. First, the channels were filled with a dimethylketone solution containing equal amounts of Zn^{2+} and Co^{2+} (0.35 M, nitrate precursors) and urea (1.4 M). After ensuring complete filling, the membrane was heated first at 348 K for 3h, then at 393 K for 15h, and finally at 673 K for 2h. Next, the catalytic layer was reduced by thermal treatment at 723 K for 1h under helium-hydrogen mixture. Two sets of H_2 generation tests were carried out with different reaction mixtures. A reaction mixture of gaseous ethanol (0.24 mL/min) and water (fed separately) diluted in He was passed at a rate of 46-82 mL/min through the membrane with ethanol:water molar ratios of 1:3 and 1:6. Another mixture (undiluted ethanol:water=1:6), was provided directly by a syringe pump at a constant rate of 0.1 mL/min. Reaction products were monitored continuously by on-line mass spectrometer.

Figure 2 shows SEM images taken from the inner walls of the pores before (a) and after (b) infiltration with a catalyst layer. As can be seen, the catalyst coating with a thickness of about 100 nm is well dispersed and adhered over the channel wall. SEM and EDX analysis revealed that the coating consists of a homogeneous fine-grained layer of intermixed ZnO and Co_3O_4 particles. The effective area of the silicon micromonoliths after assembly in stainless steel housing was 38 mm^2, which gives about $1.5x10^6$ channels. Taking into account the given pore dimensions, the specific inner surface of the channel walls is then about $3.5x10^5$ m^2/m^3. It should be noted that this value is as high as those reported in high surface area porous materials prepared by flame pyrolysis, sol-gel techniques, or supramolecular assemblies.

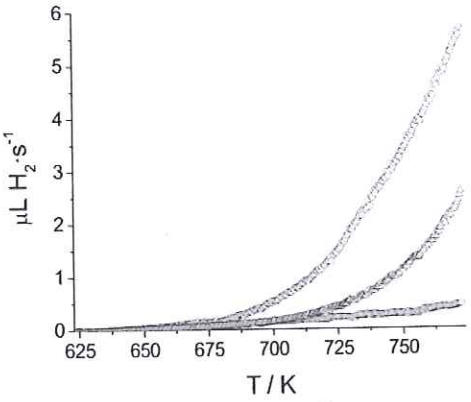

Fig. 3. Rate of hydrogen production from ethanol steam reforming at increasing temperature obtained over macroporous silicon before (□) and after loading with a catalyst film (o,Δ). 0.24 mL/min C_2H_5OH, ethanol:water=1:6 (□,o) and =1:3 (Δ).

Some results obtained from validation tests of the silicon micromonoliths against H_2 production using ethanol-water mixtures diluted in inert gas are shown in Fig. 3, were H_2 production rates are plotted versus temperature. The H_2 production rate from a blank experiment using silicon membrane without catalytic coating is much lower than that of coated microchannels. The main process occurring in the absence of catalyst is the thermal decomposition of ethanol. In contrast, when the microchannels were loaded with catalyst, the rate of H_2 production increases significantly, especially when the reaction was carried out with a feed mixture of ethanol:water =1:6 (molar). For this particular mixture, a hydrogen-rich stream composed of 71-73 vol% H_2, 23-24 vol% CO_2, and 3-5 vol% CH_4 was obtained with an ethanol conversion >90% at 773 K.

3. Conclusions

The presented results show the potential of macroporous silicon as a new and excellent micromonolithic support for catalysts in chemical microreactors. The enormous increase of the specific contact area in comparison with the conventional microreactors used enables unusually high hydrogen specific productivities even at low residence times. Moreover, further downscaling of macroporous silicon channel dimensions is also feasible: pores with diameters from 100 down to 0.5 μm and lengths up to wafer thickness (~500 μm) can easily be produced, thus providing even higher specific heat/mass transfer rates.

4. Acknowledgements

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