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Fabrication of microreactors for dehydrogenation of cyclohexane to benzene

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Abstract

Novel microreactors have been fabricated on silicon in order to dehydrogenate cyclohexane to benzene. There are 12 reactor chips on one single silicon wafer. The microreactor consists of three chips, which are reaction chamber, separation membrane and reactor cap. The whole dimension of the reactor is 20 mm long, 14 mm wide and 3 mm high. As for reaction chamber, 80 microchannels 50 μm wide, 400 μm deep and 8 mm long have been etched. We use silicon ⟨110⟩ wafers to obtain high-aspect-ratio microstructures. Twenty nanometer Ti is sputtered and oxidized as the adhesion layer and catalyst carrier. Twenty nanometer Pt is sputtered as the catalyst. For the separation membrane, it is 6 mm by 8 mm, with 80 folded rectangular 4 μm thick Pd foil structures 50 μm wide, 200 μm high and 6 mm long anchored on silicon. This utilizes the combination of silicon ⟨110⟩ wet etching and dry etching together. These folded Pd microstructures contribute to increase the separation area of hydrogen. The reactor cap for inlet and outlet gas pipes is made of PDMS, which is a kind of relatively new material for MEMS applications. Finally, the reaction chamber, separation membrane and reactor cap have been bonded using Polyimide with very good contact strength between chips. The microreactors have been tested using a GC with a conversion value of 18.4%.

Keywords: MEMS; Microfabrication; Microreactor; Catalyst

1. Introduction

MEMS is the next logical step in the silicon revolution. The silicon revolution began over three decades ago, with the introduction of the first integrated circuit. While electrical devices are well-established technically, the study of mechanical devices based on silicon began only a decade ago when the MEMS workshop started. The successful fabrication and operation of microsensors, microactuators and micromechanical parts by IC-based microfabrication technology enable us to produce MEMS. The three characteristic features or the three 'M's of the technology are [1]: miniaturization; multiplicity; and microelectronics.

Microreaction application of MEMS technology has represented an area of more attentions and rapidly growing interests for both research and development since the middle 1990s [2–10]. Microchemical systems could have applications in microsystems, and improving on efficiency and safety of large-scale systems [11–13]. Miniaturized reactors based on palladium micromembranes for hydrogen separation and hydrogenation/dehydrogenation still have a way to go [14], since there are still some fabrication and microscale chemical reaction that need exploring. For example, the palladium membrane and platinum reactor still have several technical issues that need to be overcome. This paper designed, fabricated and tested the prototype microreactors for dehydrogenation of cyclohexane to benzene with good inherent selectivity and reaction control.

2. Mechanism of microreactors

The mechanism of microreactors for dehydrogenation of cyclohexane to benzene can be described as [15]

$$C_6H_{12} \leftrightarrow C_6H_6 + 3H_2 \quad (1)$$

From the above function, there is an equilibrium reaction from cyclohexane to benzene and hydrogen, and conversely from benzene and hydrogen to cyclohexane when using platinum as the reaction catalyst. If benzene and hydrogen are preferred products, a micromachined palladium membrane chip can be used as the separation layer, which can separate hydrogen from cyclohexane and benzene. This will break the reaction equilibrium, and drive the conversion reaction almost totally from cyclohexane to benzene and

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hydrogen, the final required products. According to Shindo et al. [16], the hydrogen product was removed through the palladium–silver membrane, which increased the conversion from 18.9 to 99%. This drives the reaction from cyclohexane to benzene and hydrogen products beyond the equilibrium conversion.

The reaction of this kind of reactor depends on the collision number between gas molecules and catalyst wall. When the number of collisions between one molecule and catalyst-coated wall reach the order of 10^6 or higher, the reaction will occur. If the walls of the microreactor channels are close enough to reach the same order of the molecular mean free path, the molecules will be more likely to collide with the channel walls rather than collisions between each other. This is so-called Knudsen regime, where the molecule-wall collision can be described as

$$N = \frac{3}{8}\left[\frac{1}{K(w/d)}\right]\left(\frac{L}{d}\right)^2 \quad (2)$$

where N is the number of molecule-wall collisions of every molecule per unit area per unit time, $K(w/d)$ the geometric factor, L the channel length, and d the channel depth. From this principle, we can design the microreactors.

3. Design of microreactors

As shown in Fig. 1, the microreactor consists of three parts, which is reaction chamber, separation membrane and reactor cap. This is according to the above mechanism of microreaction. One inlet tube is for cyclohexane input, and two outlets are for benzene and hydrogen output. These three chips are bonded together to form the microreaction system that is the microreactor.

The whole dimension of the reactor is 20 mm long, 14 mm wide and 3 mm high. For reaction chamber, 80 microchannels are 50 μm wide, 400 μm deep and 8 mm long, with 20 nm Pt sputtered. The microchannels can increase the reaction area of catalyst. For the separation membrane, the membrane is 6 mm by 8 mm, with 80 folded rectangular 4 μm thick Pd foil structures 50 μm wide, 200 μm high and 6 mm long anchored on silicon. The folded microstructures can enlarge the separation area to increase the separation efficiency.

4. Fabrication of microreactors

4.1. Packaged microreactors

The fabrication of the microreactors for dehydrogenation of cyclohexane to benzene contains several key technologies, including bulk wet and dry micromachining, PDMS molding, and two kinds of bonding technologies, which are quite useful for any other kind of microreaction system fabrication. The final packed microreactor is shown in Fig. 2. The very top layer is PDMS cap, which works as both reactor cap and packing material. And the reaction chamber and palladium separation membrane are right beneath the PDMS cap.

4.2. Chip fabrication

First, the microchannels are etched using ⟨110⟩ silicon wafers with 2 μm SiO_2 as the mask layer. For silicon ⟨110⟩ wafers, the etching rate for 30% KOH solution at 85°C is around 2.1 μm/min. Four hundred micrometer silicon is etched away to form the microchannels. Then 20 nm Ti is deposited on microchannels by UNIFILM Sputtering System. The deposition rate is 100 nm/min. The Ti layer is oxidized by NaOH and H_2O_2 solution for a porous titanium oxide layer. This is to increase the reaction area between the gas molecules and the channel walls. The atomic percentage of oxide and titanium are 84.28 and 9.35%, respectively. After oxidation, 20 nm Pt is deposited on the titanium oxide as the reaction catalyst, where the deposition rate is 2 nm/min. The final SEM picture of reaction chamber chip is shown in Fig. 3.

The Pd separation membrane, the most difficult part to fabricate, involves wet and dry etching technologies in this research work. To fabricate the folded Pd membrane, we do the double side photolithography at the same time, then etch the silicon wafer using 30% KOH solution at 80°C. After about 200 μm double-side etching, 4 μm Pd is sputtered on the microchannel side to form the separation membrane.

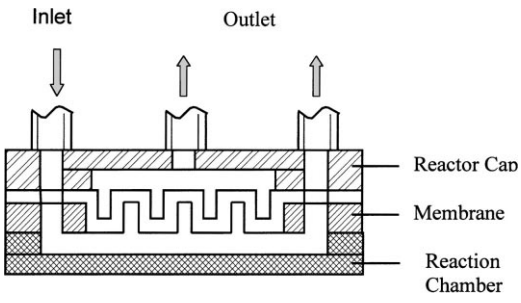

Fig. 1. Microreactor design.

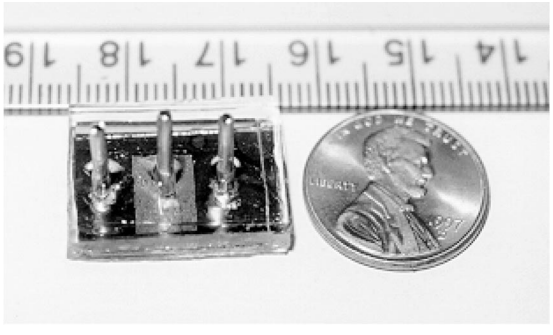

Fig. 2. Packed microreaction system.

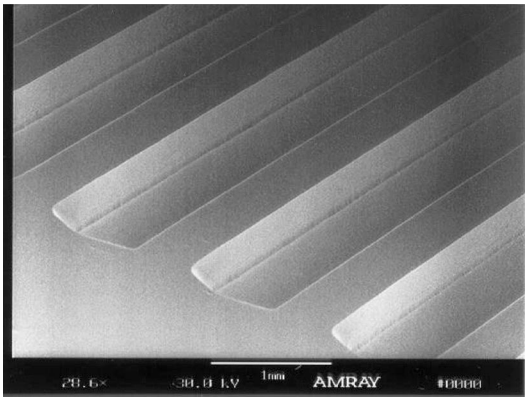

Fig. 3. SEM picture of microreactor channels.

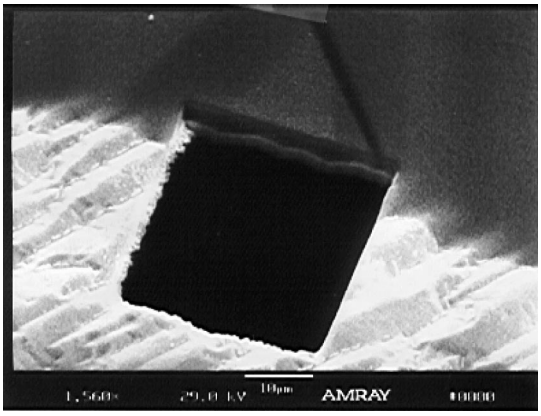

Fig. 5. SEM picture of separation membrane cut by FIB.

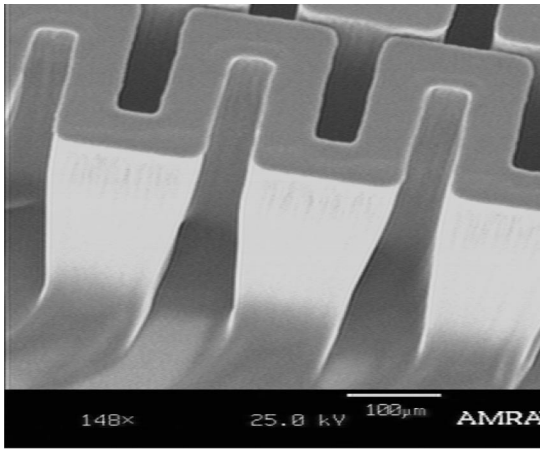

Fig. 4. Separation membrane.

After that, we use dry etching to etch away all the silicon in the window in order to get the 4 μm folded Pd separation membrane. Two recipes are used to realize the separation membrane. The etching rate at 30 sccm SF_6 with 30 sccm O_2 at 250 m Torr under the power of 300 Watts is about 0.42 μm/min. And the etching rate at 40 sccm CF4 with 4 sccm O_2 at 100 m Torr under the power of 100 W is about 0.26 μm/min. The picture of separation membrane is shown in Fig. 4.

After the chip is fabricated, focus ion beam (FIB) is used to cut the separation membrane to see the membrane, as shown in Fig. 5. The FIB power is 20 KeV, and the beam is 15 μm in diameter. From the SEM picture, we can see the Pd separation membrane easily. The roughness of the membrane is because of the KOH wet etching. To some extent, it is good for hydrogen separation because the separation area is enlarged for the folded wave membrane microstructures.

The reaction chamber and the Pd separation membrane are bonded together using Polyimide 2610. For the gas cover, an aluminum mold is fabricated by traditional machining technologies. Then PDMS is cured in the aluminum mold with the one inlet and two outlet tubes together at 110°C for half an hour. Finally, the reactor cap, the separation membrane and reaction chamber are bonded and packed together by PDMS.

5. Experiments

The reaction temperature for dehydrogenation of cyclohexane to benzene is about 200°C. Some experiments have been carried out to check PDMS stability while raising temperature. We put PDMS microstructures molded at 110°C in heating oven. The experiments indicate that PDMS microstructures are stable below 250°C.

Experiments have also been done to measure the conversion for dehydrogenation of cyclohexane to benzene. The basic experiment setup is shown in Fig. 6. The microreactors have been tested using a GC with a conversion value of 18.4%.

6. Conclusions

The prototype microreactors have been designed, fabricated and tested. Relatively large area membrane with multi high-aspect-ratio folded microstructures has been fabricated using silicon ⟨110⟩ wet and dry etching. Multi long high-aspect-ratio microchannels have been etched for chemical

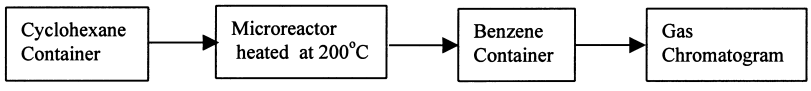

Fig. 6. Basic experiment setup.

reaction channels. PDMS and polyimide bonding with very stable chemical stability has been used for this chemical reaction device. The unique aspects of this research on microreactor for dehydrogenation of cyclohexane to benzene are as follows. (1) The three-layer microreactor design is a very effective way to realize high efficiency for thermal reaction and gas separation. (2) Ti oxidation using NaOH and H_2O_2 has been realized, which is a simple and very effective way to get the catalyst carrier compared to anodic oxidation. It is expected to achieve the higher efficiency on reaction and separation if the experimental setup is improved in the future. And the micromanufacturing technologies in this paper are suitable for the fabrication of any other kinds of microreaction systems and wholly new MEMS devices.

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Biography

Tianhong Cui received the B.S. from Nanjing University of Aeronautics and Astronautics in 1991, and PhD from Chinese Academy of Sciences in 1995. He has also served as a postdoc at Tsinghua University from 1995 to 1997, and at Electrical and Computer Engineering in University of Minnesota from 1997 to 1998. He joined National Laboratory of Metrology in Japan as a research fellow under STA fellowship from 1998 to 1999. In June 1999, he joined the faculty as a research Assistant Professor at Institute for Micromanufacturing, Louisiana Tech University. His present research interests include MEMS new fabrication technologies, novel microdevice and microsystem design and characterization, and nanotechnology.