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Catalytic Properties of Ethylene Reactions Using Silver and Reduced Vanadium Oxide Catalysts on MEMS Chips with Micro Hot Plate

Guang-Je Guo and Jih-Mirn Jehng*

Department of Chemical Engineering, National Chung Hsing University,
No. 145, Xingda Road, South District, Taichung 40227, Taiwan

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Micro hot plate chips were fabricated using MEMS process technology as a lab-on-chip platform for catalytic reactions. Ethylene was introduced, and its reactions occurred exclusively within the temperature-controlled heating area where the catalyst was deposited, while the remaining parts of the reactor were maintained at room temperature. One micro heater design was simulated to assess heating efficiency and was subsequently fabricated. The heating zone temperature was controlled by adjusting the supplied voltage. Two catalysts, silver and reduced vanadium oxide, were coated onto MEMS chips using an ultrasonic printing machine to explore their catalytic properties in ethylene reactions. The occurrence of the reactions was investigated. Focused ion beam and scanning electron microscopy techniques were employed to characterize the morphology of the catalyst deposited on the MEMS suspension film, whereas gas chromatography was used to quantify the concentration of chemical reaction products. A Matlab program was developed to evaluate the reaction rate and gas concentration, and to compare the experimental results obtained from both batch and flow reactors.

1. Introduction

The growing interest in conducting chemical reactions within confined environments has led to the development of microreactor technology. These miniature chemical reactors, which are designed for laboratory-scale applications, offer several advantages, including reduced chemical usage and accelerated process development.[1] Moreover, they facilitate the investigation of catalyst properties in chemical reactions.

With the MEMS process technology becoming more mature, an increasing number of microreactor devices were developed. There are many choices in the materials to construct a MEMS-type microreactor. Some researchers use a polymer because of its advantages of low material cost and process easiness. For example, Whitesides and colleagues used polydimethyl siloxane to fabricate microreactors.[2,3] Several researchers use silicon wafers as base materials[4]

*Corresponding author: e-mail: jmjehng@dragon.nchu.edu.tw
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to construct their microreactors. The advantage of using silicon wafers is that it can apply a semiconductor-like process to build a MEMS structure.

Most catalyst-induced chemical reactions must occur at temperatures higher than room temperature, requiring the use of heating elements. The majority of MEMS-structured microreactors use electrical energy as the heating source and a suitable circuit to convert electrical current into heat. They also require a heat isolation structure to maintain the heating zone temperature. Micro hot plate-type heating elements are widely used in MEMS structures. Several hot plate designs have been studied in the academic world. In this paper, the leg-film type was chosen owing to its good energy efficiency and hot zone temperature uniformity. Inkjet printing[5] and ultrasonic methods are used to deposit Ag and VOx catalysts.

2. MEMS Heating Performance and Ethylene Reaction Simulations

The micro heater design target has two major goals: energy efficiency and heater uniformity in the heating area that is the catalyst reaction zone.[6] Simulation is required so that the heating performance can be estimated.

2.1 MEMS design and heating performance simulation

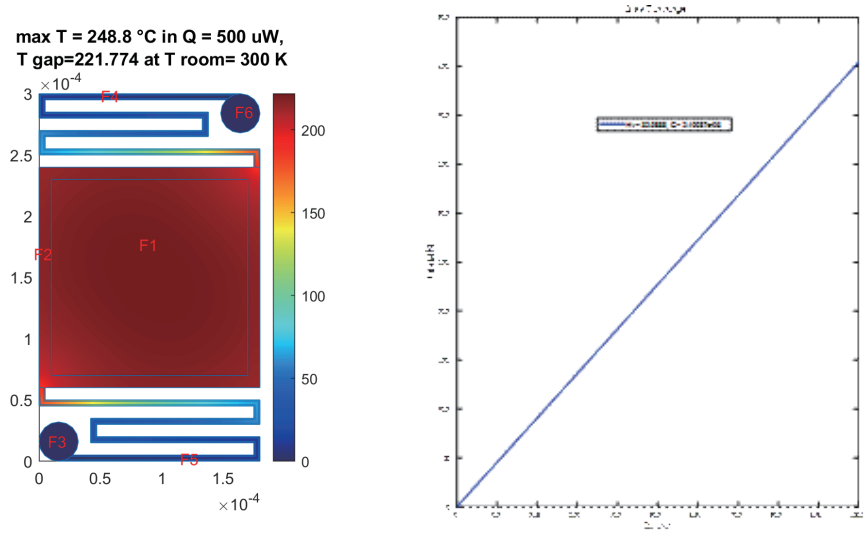
The energy efficiency and heater temperature profile are determined using Eq. (1). In the micro hot plate-type heater design, the z-direction is always small compared with the x and y-directions so that it is sufficient to use a 2D model to simulate the heating performance. A MATLAB program is built to simulate the heating performance as shown in Figs. 1 and 2, which shows that the design has good heating efficiency and uniformity in the heating zone.

2.2 Ethylene reaction mechanism

Ethylene dimerization occurs when two ethylene molecules combine to form a molecule of butene.[7,8] There are several studies about the chemical reaction mechanism, which depends on the special conditions and catalysts used.[9–11] The standard form is written as

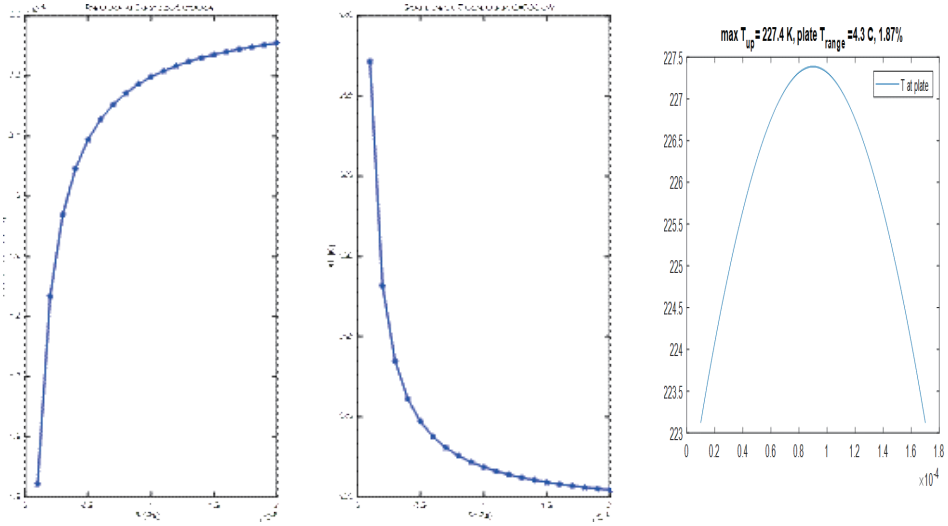
$$\begin{gathered} C_2H_4 + S^* \leftrightarrow C_2H_4 - S^*, \\ 2C_2H_4 - S^* \rightarrow 2S^* + 1 - C_4H_8 - S^*, \\ 1 - C_4H_8 - S^* \rightarrow 1 - C_4H_8 + S^*. \end{gathered} \tag{1}$$

The simulation result is shown in Fig. 3. The simulation program first simulates the reaction on the catalyst surface and then uses the result to simulate the reactor gas concentration.



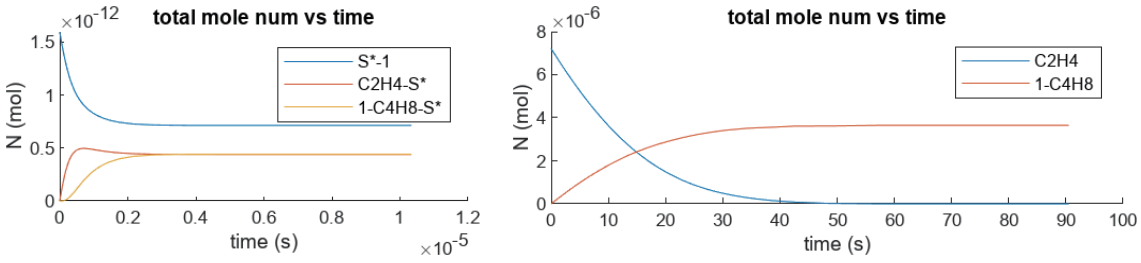
(a) (b)

Fig. 1. (Color online) Hot plate thermal simulation: (a) temperature of plate and (b) temperature vs heating power.



(a) (b) (c)

Fig. 2. (Color online) Hot plate simulation: (a) pressure vs air heat conductance, (b) pressure vs temperature increase, and (c) hot plate temperature uniformity.



(a) (b)

Fig. 3. (Color online) Ethylene reaction concentration simulation: (a) catalyst surface reaction and (b) reactor reaction.

3. Experiment

3.1 Reagents

All gases (ethylene, hydrogen, nitrogen, and oxygen) were purchased from Ni-Ni Air. The ammonia vanadium was purchased from Echo Chemical Co. The nano Ag paste used was His-06 provided by Hi-Sanity Industry Co., Ltd.

3.2 Fabrication of MEMS chips

All the MEMS chips were fabricated by Rigidtech Microelectronic Corp. within a class-100 cleanroom environment to mitigate particle-induced yield losses. Lithography was carried out using a Nikon G7 stepper, while two Maxim ICP etchers were employed for material plasma dry etching processes. Dielectric film deposition was utilized by using an E-gun evaporation system sourced from Advanced System Technology Co. In the case of metal film deposition, the Visagist physical vapor deposition (PVD) tool from Cello Technology Co. was utilized.

The initial step in the fabrication of the MEMS chips entailed depositing a silicon nitride layer as the bottom electrical isolation layer on 6 inch n-type bare silicon wafers. Subsequently, stacked layers of aluminum and titanium were deposited. These metals underwent patterning through lithography and etching steps to form the bottom circuit. A 3-μm-thick polyimide (PI) film, obtained from Everlight Chemical, was then spin-coated onto the top side of the wafers. This film was subsequently patterned by lithography to expose the contact via area. The PI film functioned as a sacrificial layer and was intended to be removed during the final step of the MEMS process. A second silicon nitride layer was deposited as an electrical isolation layer for the MEMS structure. Another layer of titanium was then deposited atop the silicon nitride, which was patterned to form the heater. This heater was electrically connected to the bottom circuit through contact vias. Following the patterning of the heating wire metals, an additional silicon nitride layer was deposited, serving as a passivation layer to protect the wire metals from corrosion during chemical reactions. The leg pattern was achieved through etching, thereby eliminating undesired silicon nitride regions. Finally, the sacrificial PI layer was removed using oxygen plasma, resulting in the formation of a floating structure. A summarized representation of the entire process is shown in Fig. 4. The MEMS chips were examined by optical microscopy (OM) and scanning electron microscopy (SEM), as illustrated in Fig. 5. The MEMS chip size is $1000 \times 700\ \mu m^2$, the single pixel size from via to via is $180 \times 300\ \mu m^2$, and the heating plate area is $70 \times 140\ \mu m^2$.

3.3 Synthesis of vanadium base catalysts

To prepare vanadium base catalysts, ammonia vanadium (NH_4VO_3) and an organic acid (oxalic or tartar acid) were mixed and dissolved in DI water and then stirred for 10 min. The different split conditions used are listed in Table 1. Catalysts were coated to the heating zone area using an ultrasonic printer from SSA WET Technology Co.

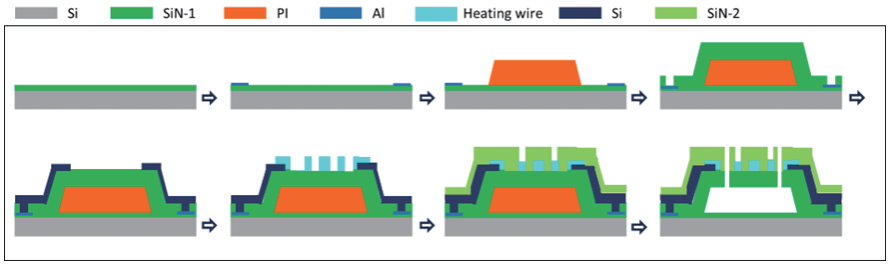
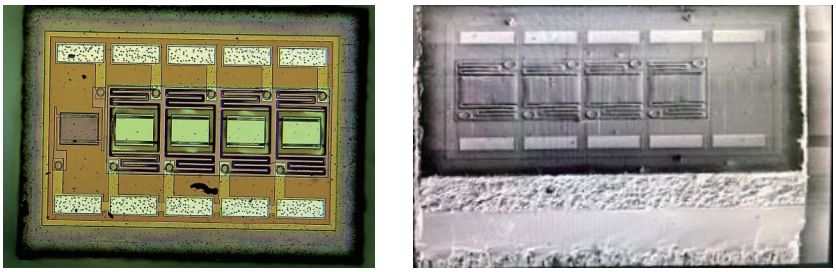


Fig. 4. (Color online) MEMS chip fabrication flow.



(a) (b)

Fig. 5. (Color online) MEMS chip pictures: (a) OM inspection and (b) SEM inspection.

Table 1
Vanadium base catalyst split conditions.

	Ammonia vanadium	Oxalic acid	Tartar acid	DI water
Vanadium oxalate	2.64 g	7.12 g		50 ml
Vanadium tartarate	2.64 g		7.5 g	120 ml

3.4 Ethylene reaction with catalysts

The MEMS chips were attached to four-leg-type TO-CAN substrates as shown in Fig. 6. Three pixel heating power input pads and one common ground pad were connected to electrical connecting points via wire bonding. The TO-CAN was then put into a jig and plugged into a glass vessel as shown in Fig. 7. The TOCAN pinouts were connect to a GWINSTEK PST-3202 DC power supply, which can tune the voltage across each pixel to generate the desired heat.

Several glass beads, which were all made by Shen Chiu Enterprise, were filled into the glass vessel to reduce the volume of the reactor. The vessel inlet was connected to a pipeline linked to four mass flow controllers (MFCs), which control the gas flow rate, from Protec Instruments. The outlet of the vessel was connected to a gas chromatography (GC) system from China Chromatography, which measured the gas composition.

The gas flow settings, which were controlled by the MFCs, are listed in Table 2.

(a) (b)

Fig. 6. (Color online) (a) MEMS chip on TOCAN. (b)TOCAN in jig.

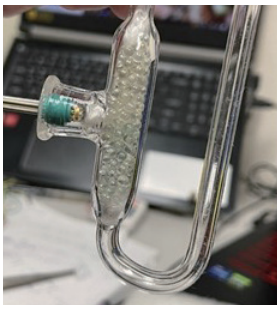


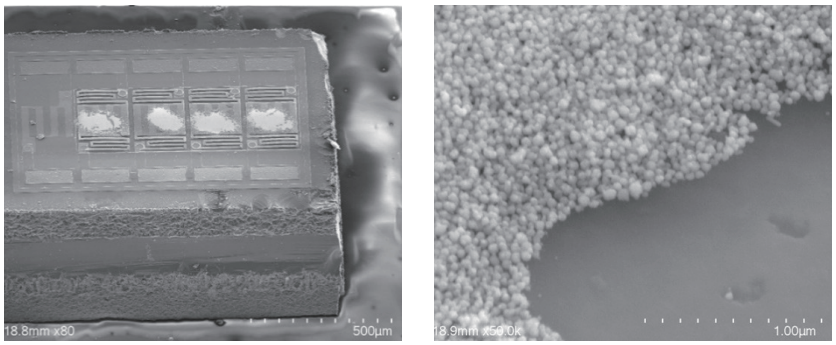
Fig. 7. (Color online) Reactor assembly.

Table 2
Gas ratio in percentage.

	Ethylene	Hydrogen	Nitrogen	Oxygen
Vanadium oxalate	5	—	—	95
Vanadium tartarate	5	—	—	95

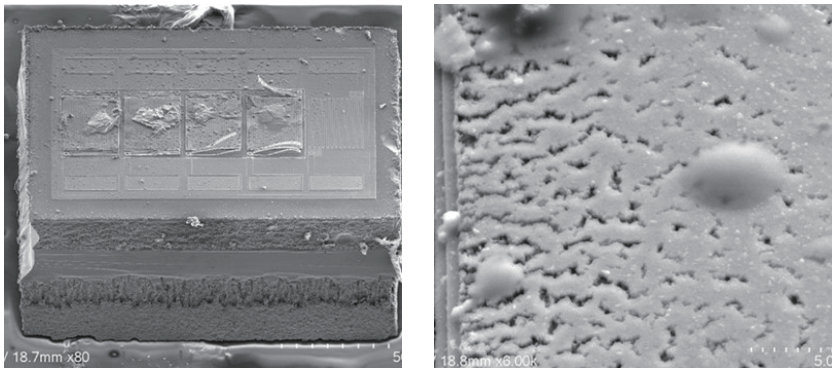
4. Results and Discussion

SEM was used to inspect the catalyst result after ultrasonic printing. The results are shown in Figs. 8–10. There were several trials conducted to measure the gas concentration change during the process, but because of the restriction of the minimum gas flow of GC, the measurement did not provide a meaningful reading owing to the very small gas concentration change during the continuous gas flow. To verify the occurrence of reactions, the MFCs were switched off for 40 min and then switched on again for the GC analysis of gas composition. The results indicated that reactions had taken place as shown in Fig. 11.



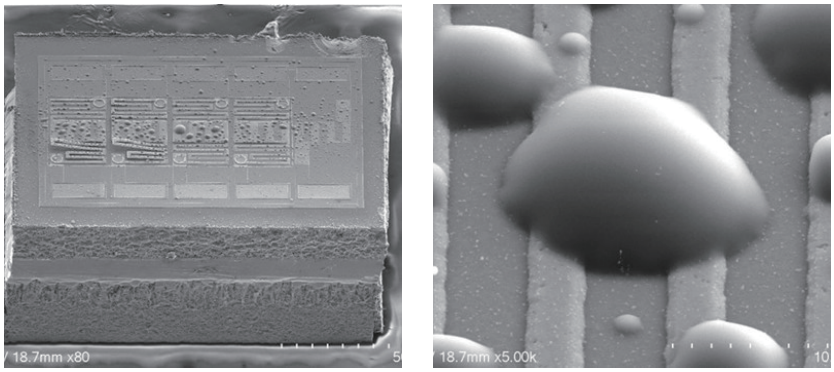
(a) (b)

Fig. 8. Nano-Ag[12,13] printing: (a) nano-Ag printing into chip and (b) nano-Ag coating.



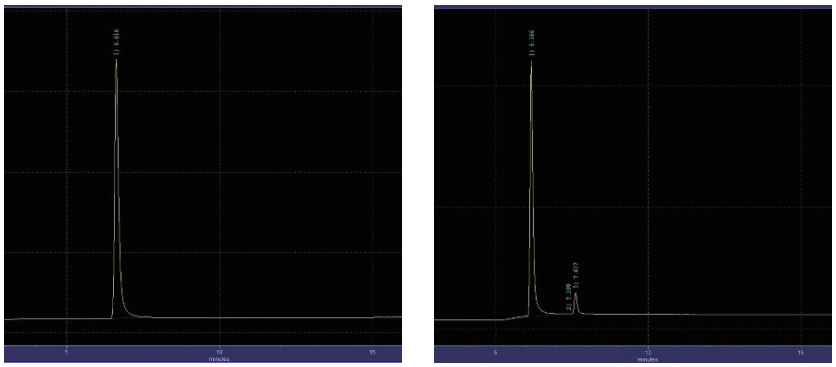
(a) (b)

Fig. 9. Vanadium oxalate: (a) catalyst printing into chip and (b) catalyst coating.



(a) (b)

Fig. 10. Vanadium tartrate: (a) catalyst printing into chip and (b) catalyst coating.



(a) (b)

Fig. 11. (Color online) GC measurement: (a) continuous flow and (b) reflow after 40 min of stoppage.

5. Conclusions and Future Work

In this paper, we presented the utilization of MEMS chips integrated with micro hot plates and catalysts to establish a microreactor environment for ethylene dimerization reactions. The thermal performance of micro hot plates and the variation in ethylene reaction concentration were simulated using MATLAB programs. Following the fabrication of the MEMS chips, the catalysts were synthesized and subsequently coated onto the hot plate area of the MEMS chips using an ultrasonic printing machine. The resulting catalyst deposition was examined through SEM techniques. Additionally, we attempted to employ a laboratory-made glass tube connected to a GC system to evaluate the chemical concentrations of ethylene reactions. However, this approach did not deliver a quantitative result owing to the inability to balance the minimum flow rate requirements of the GC system and the reaction rate of the MEMS chips.

To address these challenges, we intend to redesign the reaction environment by incorporating microfluidic channels[14,15] within the MEMS chips. Furthermore, optical inspection elements such as IR spectral sensors will be integrated to monitor changes in chemical reaction concentrations under different process conditions over the course of the reaction period.

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About the Authors

Guang-Je Guo received his B.S. degree from National Tsing Huang University, Taiwan, in 1996 and his M.S. degree from Lehigh University, U.S.A., in 2002. Since 2020, he has been a PhD student at National Chung Hsing University, Taiwan. His research interests are in MEMS, catalysts, chemical reactions, and sensors.

Jih-Mirn Jehng received his B.S. degree from Tunghai University, Taichung, Taiwan, in 1979 and his M.S. and Ph.D. degrees from Lehigh University, U.S.A., in 1987 and 1990, respectively. Since 1999, he has been a professor at National Chung Hsing University, Taiwan. His research interests are in the design and synthesis of novel heterogeneous catalysts for specific reaction applications.