

## Development of A Microchannel Catalytic Reactor System

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**Abstract**—The purpose of this article is to demonstrate the applicability of microreactors for use in catalytic reactions at elevated temperatures. Microchannels were fabricated on both sides of a silicon wafer by wet chemical etching after pattern transfer using a negative photoresist. The walls of the reactor channel were coated with a platinum layer, for use as a sample catalyst, by sputtering. A heating element was installed in the channel on the opposite surface of the reactor channel. The reactor channel was sealed gas-tight with a glass plate by using an anodic bonding technique. A small-scale palladium membrane was also prepared on the surface of a 50- $\mu\text{m}$  thick copper film. In the membrane preparation, a negative photoresist was spin-coated and solidified to serve as a protective film. A palladium layer was then electrodeposited on the other uncovered surface. After the protective film was removed, the resist was again spin-coated on the copper surface, and a pattern of microslits was transferred by photolithography. After development, the microslits were electrolytically etched away, resulting in the formation of a palladium membrane as an assemblage of thin layers formed in the microslits. The integration of the microreactor and the membrane is currently under way.

**Key words:** Microchannel Reactor, Microreactor, Catalytic Reactor, Photolithography, Palladium Membrane, Hydrogen Separation

### INTRODUCTION

Microreactors are composed of channels, the dimensions of which are 1-1,000  $\mu\text{m}$  in width and 1-100 cm in length [Lerou and Ng, 1996; Freemantle, 1999; Martin et al., 1999; Haswell and Skelton, 2000; Ehrfeld 2000; Ehrfeld et al., 2000; Jensen, 2001; Wörz et al., 2001]. The term “microreactors” is often used to describe differential reactors designed for testing catalytic reactions or small-scale reactors used at an early stage of scaleup. In this article, however, microreactors indicate reactors that are constructed as the final stage of process development. Although a number of studies on microreactors have been reported, many have focused on bio-related reac-

tors and analytical instruments, which are operated at temperatures below 400 K. Here, the discussion is limited to microreactors that can potentially be used at elevated temperatures.

The small scale of microreactors naturally leads to certain unique characteristics, which are shown in Fig. 1. The heat transfer rate between the reactor surface and reactants is substantial, compared to that of conventional large-scale chemical reactors. Thus, microreactors are suitable for reactions, the temperatures of which must be precisely and rapidly controlled [Löwe et al., 1999; Srinivasan et al., 1997; Quiram et al., 2000; Hsing et al., 2000; Lee et al., 2000]. Microreactors are also useful for producing small amounts of toxic or explosive chemicals [Hessel et al., 2000; Kestenbaum et al., 2000]. The point-of-use production of these compounds may minimize associated risks during transportation and storage.

The quantity of production can be increased by assembling a number of microreactors into a module, as shown in Fig. 2. Microreactors can also be utilized for the screening of catalysts, in conjunction with combinatorial chemistry. In such systems, different cat-

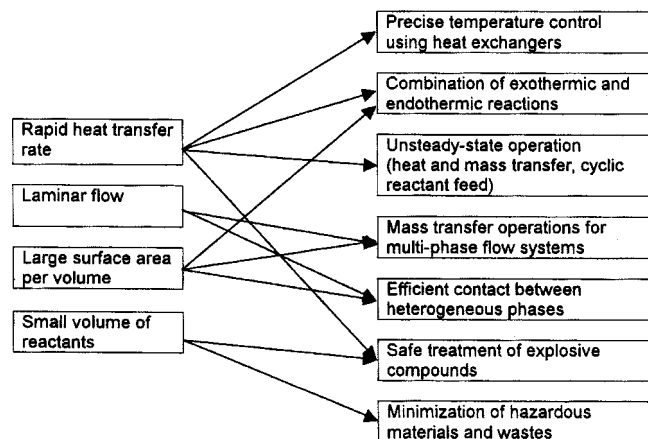


Fig. 1. Characteristics of microreactors.

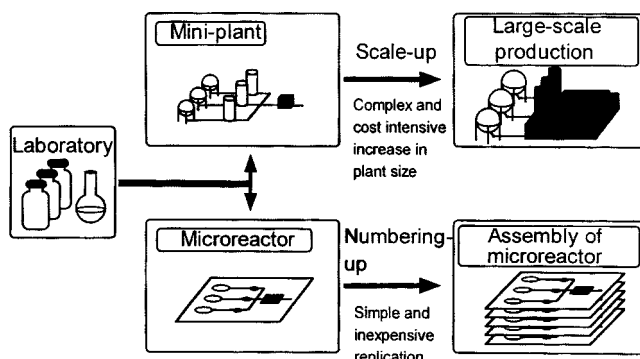
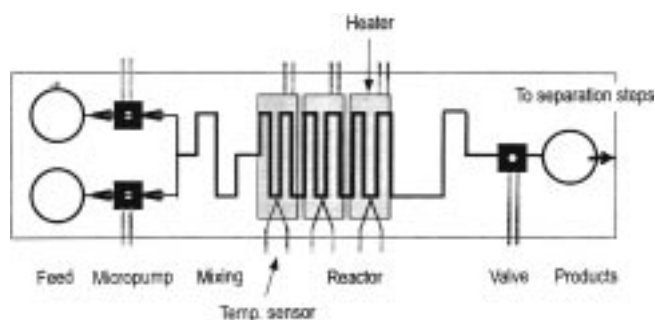


Fig. 2. Scaleup of microreactors.

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**Fig. 3. A microreactor system.**

alysts are impregnated on porous supports in microchannels. In conventional large-scale reactors, on the other hand, temperature and reaction time of the intermediate steps in a consecutive reaction can be varied only with great difficulty. Those parameters may be easily changed in microreactor systems, resulting in an increase in the yields of the intermediate products [Štěpánek et al., 1999; Liauw et al., 2000]. As shown in Fig. 3, microreactors are interfaced with other elements, such as pumps, flow control valves, pressure regulating valves heaters, coolers, temperature controllers, separation units

(membrane separators, extractors, etc.), and chemical analyzers. Further investigations of these components are also needed.

Table 1 shows some reactions that have been carried out in microreactors. Most are exothermic reactions over supported catalysts, and the formation of hot spots in the catalyst bed can be prevented because of sufficient heat removal. Microreactors are also suitable for two-phase reactions for gas-liquid and liquid-liquid systems, such as fluorination [Burns and Ramshaw, 1999; Jähnisch et al., 2000], so long as the pressure drops in the microchannels is within a permitted limit.

A wide variety of materials can be used for the fabrication of microreactors, as shown in Table 2. Plastics are suitable for use at room temperature. Metals are machinable; ceramics are highly stable against corrosion at high temperatures; and diamonds have the highest thermal conductivity. The preparation of catalysts is also a key factor for microreactors. Wires or particles can be packed in microchannels [Wilson and McCreedy, 2000; Martin et al., 1999; Tsubota et al., 2000; Losey et al., 2000]. A catalyst layer can be coated by physical vapor deposition [Cui et al., 2000; Franz et al., 2000; Kusakabe et al., 2001a] and chemical vapor deposition [Janicke et al., 2000]. These dry processes are appropriate for forming a thin film but not for producing a catalyst support layer with a wide internal

**Table 1. Reactions in microreactors**

Reaction	Phases	Catalyst	Properties of reaction and reactor	Reference
Fluorination of organic compounds	Gas-liquid	No	Falling liquid film reactor with rapid heat transfer, highly exothermic reaction, hazardous compounds	Chambers and Spink [1999] Chambers et al. [1999] Jähnisch et al. [2000]
Nitration of benzene	Liquid-Liquid	No	Two-phase flow in a capillary tube reactor, production of 6 ton per year	Burns and Ramshaw [1999]
Suzuki reaction (coupling)	Liquid	Solid, Pd/SiO <sub>2</sub>	Flow injection-type reactor	Fletcher et al. [1999] Greenway et al. [2000]
Dehydrogenation of cyclohexane	Gas	Solid	Sputtered Pt catalyst	Cui et al. [2000]
Dehydration of alcohols	Gas	Solid	Cyclic feeds	Wilson and McCreedy [2000]
Oxidation of H <sub>2</sub> with O <sub>2</sub>	Gas	Solid, Pt/Al <sub>2</sub> O <sub>3</sub>	Reactor with rapid heat transfer	Janicke et al. [2000]
Catalytic combn. of methane	Gas	Solid, NiO		Martin et al. [1999]
Production of HCN	Gas	Solid, Pt	CH <sub>4</sub> +NH <sub>3</sub> +(3/2)O <sub>2</sub>	Hessel et al. [2000]
Oxidn. of NH <sub>3</sub>	Gas	Solid, Pt	Rapid heat transfer	Srinivasan et al. [1997]
Partial oxidn. of CH <sub>4</sub>	Gas	Solid, Rh	Honeycomb reactor, high temperature (1463 K)	Mayer et al. [2000]
Partial oxidn. of C <sub>2</sub> H <sub>4</sub>	Gas	Solid, Ag foils	Prevention of hot spots, explosive	Kesterbaum et al. [2000]
Partial oxidn. of methylformamide	Gas	Solid	Production of isocyanate, poisonous, high conversion (higher than 95%)	Cited in Lerou and Ng [1996]

**Table 2. Materials used for the fabrication of microreactors**

Material	Heat conductivity	Temperature stability	Transparency	Workability	Cost
Plastic	×	×	△	○	◎
Glass	×	○	◎	○	○
Ceramic	△	◎	×	△	○
Silicon	○	○	×	○	○
Metal	○	○	×	○	◎
Diamond	◎	○	○	×	×

surface area. Kursawe et al. [2000] stacked alumina plates that were produced by anodic oxidation of aluminum wafers, and impregnated catalytic species in the micropores of the plates. Sadykov et al. [2000] used a monolith with thin walls as the catalyst support. Greenway et al. [2000] formed a Pd-supported silica layer by deposition of precursor slurry in microchannels.

### FABRICATION OF A MICROREACTOR

Figs. 4 and 5 show the procedure used for the microfabrication and the prepared microreactor, respectively [Tsubota et al., 2000; Kusakabe et al., 2001a]. The microreactor was constructed on a (100) Si wafer of 10 mm×40 mm. Both surfaces of the wafer were oxidized in a flow of air at 1,273 K for 6 h, and one surface was spin-coated with a negative photoresist. The resultant resist was pre-baked at 413 K for 3 min, and a pattern for a preheater, a reactor, and a thermocouple well was transferred by using a microchannel photo-

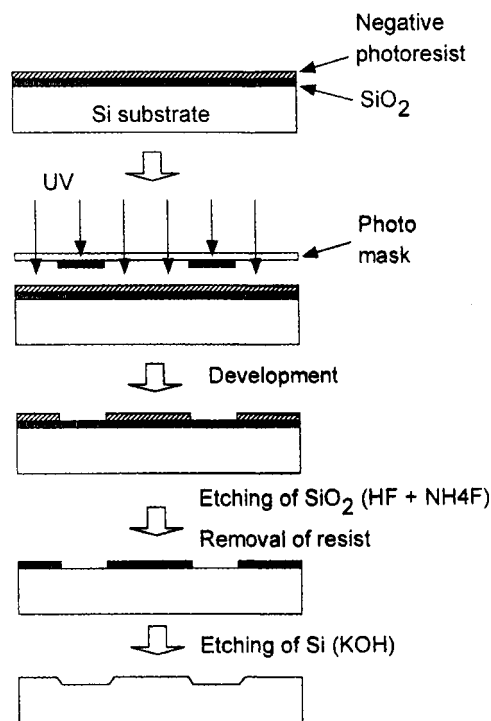


Fig. 4. Fabrication procedure for a microreactor.

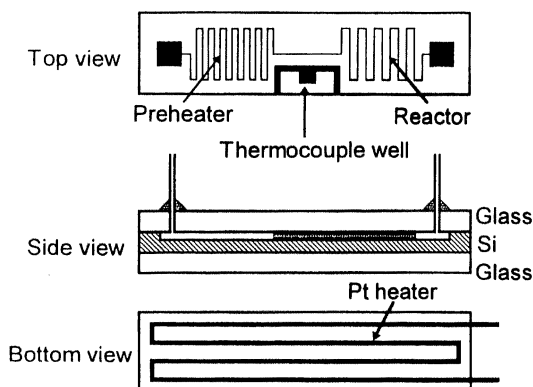


Fig. 5. A microreactor prepared.

lithography technique. A channel pattern for the heating element was then transferred to the other surface of the wafer by the same procedure. After the resist was post-baked at 413 K for 10 min, the unexposed part of the resist was removed. The  $\text{SiO}_2$  layer on the unexposed area was then removed by immersing the wafer in an HF and  $\text{NH}_4\text{F}$  buffer solution at room temperature for 10 min. After all the resist was removed, the microchannel pattern was formed by etching the wafer in a 30% KOH solution at 303 K for 2.5 h. The reactor channel was 400  $\mu\text{m}$  in upper width, 280  $\mu\text{m}$  in lower width, 100  $\mu\text{m}$  in depth and 78 mm in length. In the upstream portion of the reactor channel, a preheater section, 200  $\mu\text{m}$  in width, 100  $\mu\text{m}$  in depth and 95 mm in length, was inserted.

The surface with the reactor channel was again spin-coated with the negative photoresist. A mask with the pattern of the reactor channel (with no preheater section and no thermocouple well) was aligned to the wafer, and, by the same pattern transfer procedure, all the area except for the reactor channel was covered with the resist. The wafer surface was coated with a platinum layer by sputtering, and the resist was then lifted off. Thus, the walls of the reactor channel were coated with a layer of platinum, which functioned as a catalyst. A platinum heating wire (100  $\mu\text{m}$  in diameter and 20 cm in length) was placed in the channel, which was formed on the surface opposite to the reactor channel.

Glass plates, 1-mm in thickness, were used to cover the reactor channel, and two 300- $\mu\text{m}$  diameter holes were drilled at locations corresponding to the inlet and outlet of the reactor channel. A 300- $\mu\text{m}$  diameter stainless steel tube was inserted in each hole and was fixed in place with an inorganic adhesive. The wafer and the glass cover were then bonded by an anodic bonding technique at 673 K. The tightness of the gas seal was confirmed, since no bubbles were observed when the channel was pressurized and placed in water. The surface of the heating element was also covered with a glass plate by anodic bonding. A thermocouple, composed of 100- $\mu\text{m}$  diameter element wires, was installed in the thermocouple channel.

The hydrogenation of benzene was carried out in the reactor channel as a model reaction. The flow rates of benzene and hydrogen were controlled with mass flow controllers, and the maximum total flow rate was 1 mL/min. Concentrations at the outlet of the reactor were analyzed by means of a micro gas chromatograph with a thermal conductivity detector. The Pt catalyst was activated in hydrogen at 773 K for 3 h prior to the start of the reaction. No deactivation was observed under the reaction conditions used. The initial reaction rate constants were determined to be 0.7 and 1.4  $\text{s}^{-1}$ , respectively. Details of this reaction will be reported elsewhere [Kusakabe et al., 2001a].

### FABRICATION OF A MEMBRANE SEPARATOR

As shown in Fig. 3, the microreactor system should be composed of separation steps. Purification of the hydrogen can improve the efficiency of small-scale fuel cells with polymer electrolytes [Mex and Müller, 2000]. A number of studies have recently reported on the preparation of thin palladium-based membranes, which would be expected to separate hydrogen at high permeation rates. Fig. 6 shows the mechanism of hydrogen separation on a palladium membrane. Hydrogen is dissociated to protons on the feed side of the membrane, and the protons are then re-associated to molecular hy-

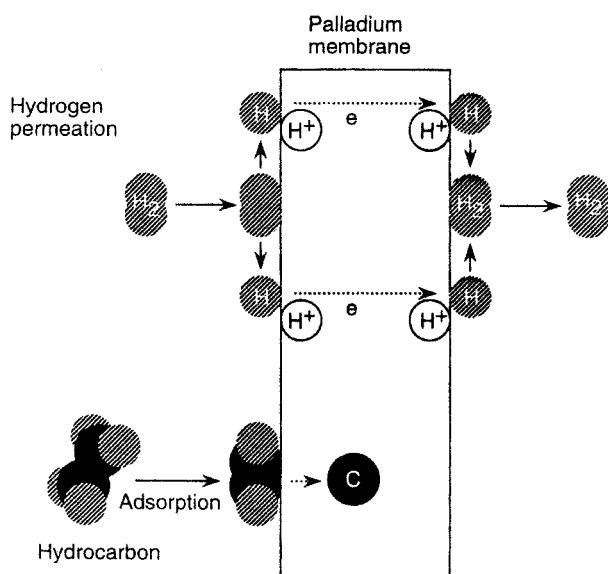


Fig. 6. Hydrogen separation through a palladium membrane.

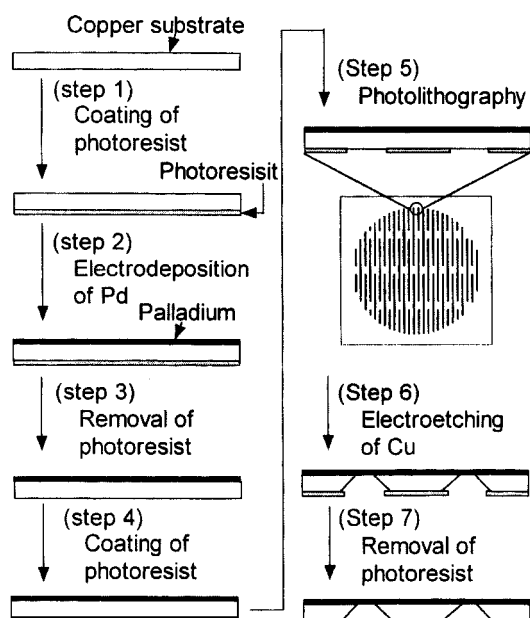


Fig. 7. Fabrication procedure for a palladium membrane.

drogen on the permeate side. Fig. 7 shows the procedure developed for the preparation of a thin, small-scale palladium membrane [Kusakabe et al., 2001b]. The substrate was a 50- $\mu\text{m}$  thick polished copper sheet (10 mm $\times$ 10 mm). One side of the substrate was spin-coated with a negative photoresist, exposed, and then baked at 413 K for 3 min and (step 1). The other side of the substrate was polished with a series of fine alumina powder (particle size=1.0 and 0.3  $\mu\text{m}$ ), after which the plate was rinsed with distilled water. A palladium layer was formed by electrodeposition on the entire uncovered surface of the copper plate, which was used as the cathode, and a platinum plate was used as the anode. The deposition of palladium was carried out at a cathode current density of 5–15 mA/cm<sup>2</sup> for 10–30 min at room temperature (step 2). The bath composition was as follows: PdCl<sub>2</sub>=19.8 g/L; citric acid=21.5 g/L; and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>=50.0

g/L. The pH was adjusted to 7 with NH<sub>4</sub>OH.

The resist on the copper surface was then removed (step 3), and the negative resist was again spin-coated on the copper surface and pre-baked at 413 K for 3 min (step 4). A mask with a pattern of microslits (100  $\mu\text{m}$  in width and 4 mm in length) drawn within a 5-mm diameter circle was aligned to the substrate, and the pattern was transferred by photolithography via contact printing (step 5). The resist was exposed, postbaked at 413 K for 10 min, and the unexposed part of the resist was removed in a developer. The uncovered copper surface was then electroetched in a 3 wt% H<sub>2</sub>SO<sub>4</sub> solution at an anodic current density of 30 mA/cm<sup>2</sup> for 210 min (step 6). The microslits, which were thus produced, exposed the palladium layer to the other side. The residual photoresist was completely removed afterward (step 7). The thickness of the deposited palladium layer was less than 10  $\mu\text{m}$ .

The membrane was cut out in the shape of a disc, 5 mm in diameter, and was then sandwiched between copper gaskets with an opening 5 mm in diameter. The set of three plates was fixed in a permeation test cell so as to be gas-tight. Single-component hydrogen or nitrogen was fed to the feed side, and a sweep gas (argon) was fed to the permeate side. The pressures on the feed and permeate sides were both maintained at 101.3 kPa. The partial pressure of hydrogen and nitrogen on the permeate side was maintained at a low level. The temperature of the cell was maintained at 573–873 K. The hydrogen permeation increased with increasing temperature, and a separation factor of 120 was observed at 873 K. The hydrogen permeance is equivalent to the results reported for thin palladium membranes [Yan et al., 1994; Morooka et al., 1995]. Details of these experimental results will be reported elsewhere [Kusakabe et al., 2001b]. This hydrogen-selective membrane can be applied to the purification of the reformed gas, which is fed to polymer electrolyte fuel cells. Fig. 8 shows an example of the polymer electro-

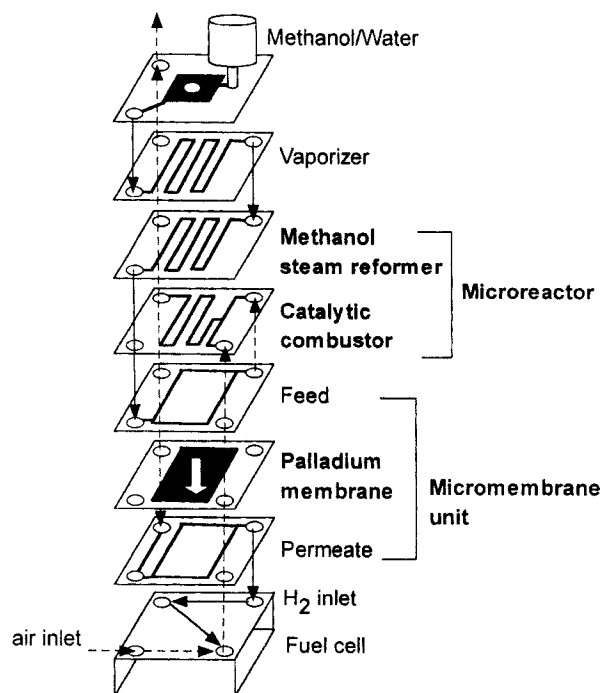


Fig. 8. Stacked frames of a small-scale fuel cell system.

lyte fuel cells combined with the hydrogen purification using a Pt membrane. Heat exchangers can be inserted if necessary.

## CONCLUSIONS

A self-heating microreactor was constructed on a (100) silicon wafer by means of photolithography, wet etching, and sputtering techniques. The reactor was successfully used in a catalytic reaction at elevated temperatures. A palladium membrane, approximately 3  $\mu\text{m}$  in thickness, was also fabricated by a combination of photolithography and electrolysis. The separation factor of hydrogen to nitrogen was 120 at 873 K. These results suggest that the construction of a microreactor combined with a small-sized membrane separator is a distinct possibility.

## ACKNOWLEDGMENTS

This study was supported by the Ministry of Education, Culture, Sports, Science and Technology, the Japan Society for the Promotion of Science (JSPS) and the New Energy and Industrial Technology Development Organization (NEDO).

## REFERENCES

- Burns, J. R. and Ramshaw, C., "Development of a Microreactor for Chemical Production," *Trans IChem E*, **77**, 206 (1999).
- Chambers, R. D., Hutchinson, J. and Sandford, G., "Recent Studies at Durham on Direct Fluorination," *J. Fluorine Chem.*, **100**, 63 (1999).
- Chambers, R. D. and Spink, R. C. H., "Microreactors for Elemental Fluorine," *Chem. Commun.*, 883 (1999).
- Cui, T., Fang, J., Zheng, A., Jones, F. and Reppond, A., "Fabrication of Microreactors for Dehydrogenation of Cyclohexane to Benzene," *Sensors and Actuators B*, **71**, 228 (2000).
- Ehrfeld, W., "Microreaction Technology, Industrial Prospects," Springer, Berlin, Germany (2000).
- Ehrfeld, W., Hessel, V. and Löwe, H., "Microreactors," Wiley-VCH, Weinheim Germany (2000).
- Fletcher, P. and Haswell, S., "Downsizing Synthesis," *Chemistry in Britain*, **35**, 38 (1999).
- Franz, A. J., Ajmera, S. A., Firebaugh, S. L., Jensen, K. F. and Schmidt, M. A., "Expansion of Microreactor Capabilities through Improved Thermal Management and Catalyst Deposition," Microreaction Technology, Industrial Prospects, Ed. W. Ehrfeld, Springer, Berlin, 197 (2000).
- Freemantle, M., "Downsizing Chemistry," *Chem. Eng. News*, **22**, 27 (1999).
- Greenway, G. M., Haswell, S. J., Morgan, D. O., Skelton, V. and Styling, P., "The Use of a Novel Microreactor for High Throughput Continuous Flow Organic Synthesis," *Sensor and Actuators B*, **63**, 153 (2000).
- Hessel, V., Ehrfeld, W., Golbig, K., Hofmann, C., Jungwirth, St., Löwe, H., Richter, Th., Storz, M., Wolf, A., Wörz, O. and Breysse, J., "High Temperature HCN Generation in an Integrated Microreaction System," Microreaction Technology, Industrial Prospects, Ed. W. Ehrfeld, Springer, Berlin, 151 (2000).
- Haswell, S. J. and Skelton, V., "Chemical and Biochemical Microreactors," *Trends in Anal. Chem.*, **19**, 389 (2000).
- Hsing, I. M., Srinivasan, R., Harold, M. P., Jensen, K. F. and Schmidt, M. A., "Simulation of Micromachined Chemical Reactors for Heterogeneous Partial Oxidation Reactions," *Chem. Eng. Sci.*, **55**, 3 (2000).
- Jähnisch, K., Baerns, M., Hessel, V., Ehrfeld, W., Haverkamp, V., Löwe, H., Wille, Ch. and Guber, A., "Direct Fluorination of Toluene Using Elemental Fluorine in Gas/Liquid Microreactors," *J. Fluorine Chem.*, **105**, 117 (2000).
- Janicke, M. T., Kestenbaum, H., Hagendorf, U., Schüth, F., Fichtner, M. and Schubert, K., "The Controlled Oxidation of Hydrogen from an Explosive Mixture of Gases Using a Microstructured Reactor/Heat Exchanger and Pt/Al<sub>2</sub>O<sub>3</sub> Catalyst," *J. Catalysis*, **191**, 282 (2000).
- Jensen, K. F., "Microreaction Engineering - is small better?" *Chem. Eng. Sci.*, **56**, 293 (2001).
- Kestenbaum, H., de Oliveria, A. L., Schmidt, W., Schüth, F., Ehrfeld, W., Gebauer, K., Löwe, H. and Richter, Th., "Synthesis of Ethylene Oxide in a Microreaction System," Microreaction Technology, Industrial Prospects, Ed. W. Ehrfeld, Springer, Berlin, 207 (2000).
- Kursawe, A., Dietzsch, E., Kah, S., Hönicke, D., Fichtner, M., Schubert, K. and Wießmeier, G., "Selective Reactions in Microchannel Reactors," Microreaction Technology, Industrial Prospects, Ed. W. Ehrfeld, Springer, Berlin, 213 (2000).
- Kusakabe, K., Miyagawa, D., Gu, Y., Maeda, H. and Morooka, S., "Development of a Self-Heating Microreactor for Catalytic Reactions," *J. Chem. Eng. Japan* (2001a), **34**, 441 (2001b).
- Kusakabe, K., Takahashi, M., Maeda, H. and Morooka, S., "Preparation of Thin Palladium Membranes by a Novel Method Based on Photolithography and Electrolysis," *J. Chem. Eng. Japan* (2001b) in press.
- Lee, A., Tonkovich, Y., Fitzgerald, S. P., Zilka, J. L., LaMont, M. J., Wang, Y., VanderWiel, D. P. and Wegeng, R. S., "Microchannel Chemical Reactors for Fuel Processing Applications. II. Compact Fuel Vaporization," Microreaction Technology, Industrial Prospects, Ed. W. Ehrfeld, Springer, Berlin, 364 (2000).
- Lerou, J. J. and Ng, K. M., "Chemical Reaction Engineering: A Multi-scale Approach to a Multiobjective Task," *Chem. Eng. Sci.*, **51**, 1595 (1996).
- Liauw, M. A., Baerns, M., Broucek, R., Buyevskaya, O. V., Commenge, J.-M., Corriou, J.-P., Falk, L., Gebauer, K., Hefter, H. J., Langer, O.-U., Löwe, H., Matlosz, M., Renken, A., Rouge, A., Schenk, R., Steinfeldt, N. and Walter, St., "Periodic Operation in Microchannel Reactors," Microreaction Technology, Industrial Prospects, Ed. W. Ehrfeld, Springer, Berlin, 224 (2000).
- Losey, M. W., Schmidt, M. A. and Jensen, K. F., "A Micro Packed-Bed Reactor for Chemical Synthesis," Microreaction Technology, Industrial Prospects, Ed. W. Ehrfeld, Springer, Berlin, 277 (2000).
- Löwe, H. and Ehrfeld, W., "State-of-the-Art in Microreaction Technology: Concepts, Manufacturing and Applications," *Electrochim. Acta*, **44**, 3679 (1999).
- Martin, P. M., Matson, D. W. and Bennett, W. D., "Microfabrication Methods for Microchannel Reactors and Separation Systems," *Chem. Eng. Comm.*, **173**, 245 (1999).
- Mayer, J., Fichtner, M., Wolf, D. and Schubert, K., "A Microstructured Reactor for the Catalytic Partial Oxidation of Methane to Syngas," Microreaction Technology, Industrial Prospects, Ed. W. Ehrfeld, Springer, Berlin, 187 (2000).

- Mex, L. and Müller, J., "Miniaturised Direct Methanol Fuel Cell with a Plasma Polymerised Electrolyte Membrane," *Microreaction Technology, Industrial Prospects*, Ed. W. Ehrfeld, Springer, Berlin, 402 (2000).
- Morooka, S., Yan, S., Yokoyama, S. and Kusakabe, K., "Palladium Membrane Formed in Macropores of Support Tube by Chemical Vapor Deposition with Crossflow through a Porous Wall," *Sep. Sci. Technol.*, **30**, 2877 (1995).
- Quiram, D. J., Hsing, I.-M., Franz, A. J., Jensen, K. F. and Schmidt, M. A., "Design Issues for Membrane-based, Gas Phase Microchemical Systems," *Chem. Eng. Sci.*, **55**, 3065 (2000).
- Sadykov, V. A., Pavlova, S. N., Saputina, N. F., Zolotarskii, I. A., Pakhomov, N. A., Moroz, E. M., Kuzmin, V. A. and Kalinkin, A. V., "Oxidative Dehydrogenation of Propane over Monoliths at Short Contact Times," *Catalyst Today*, **61**, 93 (2000).
- Srinivasan, R., Hsing, I.-M., Berger, P. E., Jensen, K. F., Firebaugh, S. L., Schmidt, M. A., Harold, M. P., Lerou, J. J. and Ryley, J. F., "Micro-machined Reactors for Catalytic Partial Oxidation Reactions," *AIChE J.*, **43**, 3059 (1997).
- Štěpánek, F., Kubíček, M., Marek, M. and Adler, P. M., "Optimal Design and Operation of a Separating Microreactor," *Chem. Eng. Sci.*, **54**, 1493 (1999).
- Tsubota, T., Miyagawa, D., Kusakabe, K. and Morooka, S., "Preparation of a Catalytic Reactor Composed of a Microchannel Etched on a Silicon Wafer," *Kagaku Kogaku Ronbunshu*, **26**, 895 (2000).
- Wilson, N. G. and McCreedy, T., "On-Chip Catalysis Using a Lithographically Fabricated Glass Microreactor - the Dehydration of Alcohols Using Sulfated Zirconia," *Chem. Commun.*, 733 (2000).
- Wörz, O., Jäckel, K. P., Richter, Th. and Wolf, A., "Microreactors, a New Efficient Tool for Optimum Reactor Design," *Chem. Eng. Sci.*, **56**, 1029 (2001).
- Yan, S., Maeda, H., Kusakabe, K. and Morooka, S., "Thin Palladium Membrane Formed in Support Pores by Metal-Organic Chemical Vapor Deposition Method and Application to Hydrogen Separation," *Ind. Eng. Chem. Res.*, **33**, 616 (1994).