Microreactors for High Temperature Reactions

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Introduction

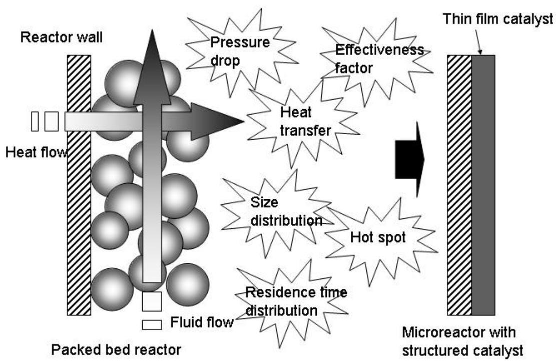
Microreactors are miniaturized reaction systems that contain one or more channels, and are typically produced by microfabrication., Their small scale leads to unique characteristics such as;

(1) rapid heat and mass transfer rates,
(2) precise temperature control
(3) large surface area per reactor volume, and
(4) laminar flow

As a result, microreactors are suitable for use in reaction systems that operate at high temperature and permit a more safe operation, especially for catalytic reactions. In this paper, applications of microreactors for use in catalytic reactions are described.

Characteristics of Microreactor for Catalytic Reaction

Fig.1 illustrates unsolved problems that exist for packed bed reactors for use in catalytic reactions. If a thin film catalyst is deposited on the reactor wall, high heat and mass transfer rates as well as a low pressure drop in the reactor could be achieved. Thus, the major goal of research on structured catalysts such as monolith-type catalyst has been to overcome problems associated with packed bed reactor [Moulijn and Stankiewicz, 2001]. When the size of channels in a reactor with structured catalysts is reduced to 100-1000 μm, it functions as a microreactor, in which transfer rates are further improved and the surface area of catalyst per reactor volume is increased. Microreactors permit reaction to take place at conditions where the catalysts are utilized most efficiently.



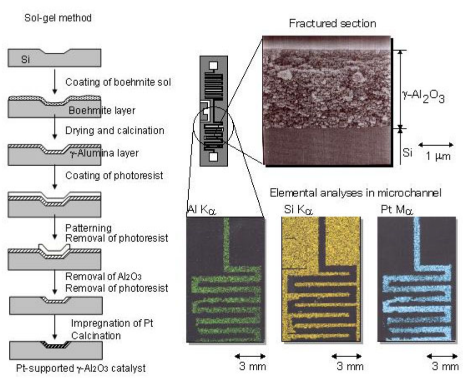


Fig.1 Microreactor with structured catalyst Fig.2 Catalyst preparation using the sol-gel method

Catalyst Preparation in Microchannel

Thin film catalysts can be formed either by physical vapor deposition and chemical vapor deposition (Tsubota et al., 2000). These dry processes are not appropriate for producing a catalyst support with a large internal surface area. Porous layers are formed by the anodic oxidation of aluminum (Rebov et al., 2001) or by a sol-gel process (Haas-Santo et al., 2001; Kusakabe et al., 2001b, 2002). Fig. 2 outlines the procedure used for preparing platinum supported γ-alumina layer in a reactor channel. A boehmite sol (γ-AlOOH) was coated on the surface of a Si substrate with reactor channels and dried in air. Using a heat-treatment at 873K, the boehmite sol was transformed to γ-alumina. The substrate surface was then coated by a photoresist, and, after patterning, all the photoresist except for the reactor channel was removed. The unprotected γ-alumina layer was dissolved in an aqueous solution of H_3PO_4. The remaining portion of the resist on the reactor channel was removed by firing in air. Finally, the γ-alumina layer was calcined after exposure to H_2PtCl_6 solution. As shown in Fig.2, alumina and platinum were homogeneously distributed in the reactor channel.

Micro Fuel Cell

A micro fuel cell system including a steam reformer for methanol has been under development for use in the compact and long-life batteries of mobile devices. As shown in Fig.3, a feed unit of methanol, water and air, a reformer, a vaporizer, a CO separator and a fuel cell with a polymer electrolyte must all be miniaturized. We previously described the fabrication of a microreactor (Kusakabe et al., 2001a, 2001b, 2002), a microevaporator, a micropump, and a micro palladium membrane (Kusakabe et al., 2001c) by using the photolithography techniques, wet etching and electrolysis as shown in Fig.4. The micro fuel cell system would be completed by integrating these elements. The adoption of a thin film palladium membrane for the removal of CO instead of catalytic oxidation can significantly improve the efficiency of a fuel cell due to the purification of

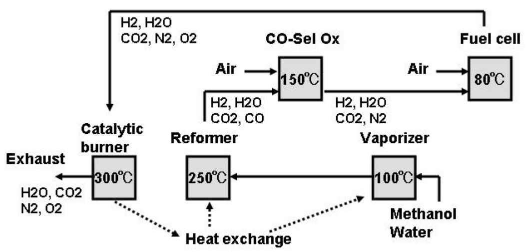


Fig.3 Hydrogen production by methanol reforming

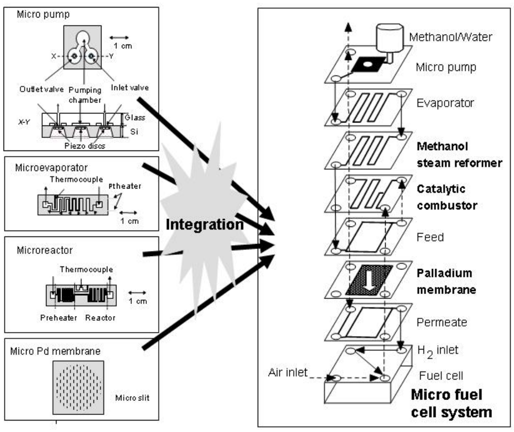


Fig.4 Micro fuel cell system

hydrogen, and reduces the volume of the micro fuel cell system. Software for computational fluid dynamics (CFD) assists in the prediction of flow behaviors necessary for designing the system. Precise temperature control in the system is also important, because the operating temperature of each elements, positioned close to each other varies from 300℃ to 80℃ as shown in Fig.3.

Catalyst Screening

Equipment for the high-throughput screening of solid catalyst with a microreactor or microarray has been proposed, and utilizes in-situ optical detection methods based on infrared (IR) thermography (Holzwarth et al., 1998), a fluorescence indicator, and resonance enhanced multiphoton ionization (REMPI) spectroscopy (Senkan et al., 1999b). Senkan et al. (1999a) carried out catalyst screening using mass spectrometry. Pt-Pd-In supported γ-alumina disk catalysts (outer diameter, 4mm) for the dehydrogenation of cyclohexane were packed in each of 20 channels in 4 part of the microreactor. The effluent gases were analyzed by withdrawing small samples from the microreactor exit using a capillary sampling probe followed by detection by on-line mass spectrometry.

The activity of the catalyst is strongly dependent on the method used for its preparation. Accordingly, total screening system should include combinatorial tools for optimizing catalyst, as shown in Fig. 5. This makes it possible to shorten the time for optimization of the catalysts, and to increase a chance for discovery of new catalysts.

Microreactor for Chemical Production

Fig. 6 summarizes some examples of representative reactions, which were examined in the investigation of the microreactors. The transport and storage of hazardous compounds can lead to safety problems. The use of small, portable production plants with microreactors, the risk of accidents can be reduced with on-site or on-demand production. Thus, a part of the large-scale chemical production systems can be shifted to small-production systems from the standpoint of safety and environment protection.

Catalytic oxidations in conventional reactors can occasionally pose a danger of open flames

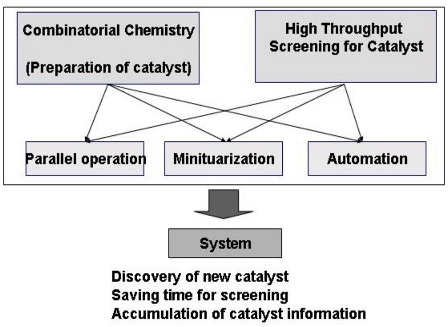


Fig.5 Catalyst screening

- Synthesis of poisonous, toxic compounds
  - Isocyanate synthesis
  - Phosgene syntheis
- Explosive reactions
  - Selective oxidation of ethene
  - Selective oxidation of 1-butane
  - Selective oxidation of isoprene
- Energy-related reactions
  - Steam reforming of methanol
  - Dehydrogenation of cyclohexane
  - Oxidation of hydrogen
- Utilization of high transport rate
  - Oxidative hydrogenation of alcohol
- Utilization of unsteady state operation

Fig.6 Reaction examples in microreactors and explosion. Microreactors can reduce this danger because of their precise temperature control and their very large surface-to-volume ratios. In addition, these reactions typically proceed very rapidly, and therefore sufficient amounts can be produced in microreactors.

It is well known that rapid periodic changes in temperature in catalytic reactions permit high conversion or high selectivity to be achieved. However, for conventional packed bed reactors, it is difficult to achieve this, because of their relatively large thermal mass. Microreactors can be easily heated up and cooled down. In addition, microreactors can be operated under unsteady state conditions by changing the temperature, pressure, and reactant composition.

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