Silica Capillary with Thin Metal (Pd and Pt) Inner Wall: Application to Continuous Decomposition of Hydrogen Peroxide

Rahat Javaid, David A. Pacheco Tanaka, Hajime Kawanami, and Toshishige M. Suzuki*
National Institute for Advanced Industrial Science and Technology (AIST), Research Center for Compact Chemical Process, 4-2-1 Nigatake, Miyagino-ku, Sendai 985-8551

(Received November 5, 2008; CL-081046; E-mail: tm-suzuki@aist.go.jp)

Thin metallic (Pd and Pt) layer was coated over inner wall of silica capillary tube (i.d. ϕ 0.33 mm × 100 cm) by electroless plating. Rapid and continuous decomposition of hydrogen peroxide (H_2O_2) was achieved at room temperature simply by passing the solution through the capillary.

Chemical reactions in microchannels can provide remarkable advantages including excellent mass- and heat-transfer properties, process safety, large surface to volume ratio and enhancement of reaction rate.[1] Capillary column reactors have been applied to various organic reactions and continuous material processing, particularly by the combination with heterogeneous catalysts which have been introduced into capillaries as slurry[2] by sol–gel deposition[3] or impregnation over the interior surface.[4] Self-assembling of nanoparticles (SiO_2 and TiO_2) over capillary inner walls was successfully achieved and applied to the substrate for enzyme-immobilized microreactors.[5] Triphase hydrogenation reactions were examined by capillary column reactor modified with colloidal palladium.[6] Organic reactions were attempted by metal-supported capillary reactor coupled with electrical potential charge[7] or microwave irradiation.[8]

Electroless plating has been applied to the coating of various thin metal films over nonconductive substrates including ceramics and glasses. Thin layers of gold nanoparticles has been plated over the interior surface of silica capillary tube.[9] Electroless deposition of nickel was performed for patterning glass microchannels.[10] Since electroless plating is a versatile procedure, we have applied this technique for the coverage of capillary inner surfaces with thin layers of palladium and platinum. Due to the presence of a dense and continuous metal catalyst surface combined with a large surface to volume ratio, rapid catalytic reactions can be expected from a flow system. We attempted the catalytic decomposition of hydrogen peroxide (H_2O_2) simply by continuously feeding a solution into metal-coated capillary reactors.

Electroless plating of metals proceeds by an autocatalytic mechanism, which is initiated by activation of silica surface by seeding with palladium particles. A capillary tube made of fused silica (0.33 mm i.d., 0.45 mm o.d., 100 cm in length, 10.1 cm^2 inner surface area, GL Science, Inc.) was treated with concd HCl at 70 °C for 12 h. After washing with water and ethanol, 1% 3-trimethoxysilylpropyldiethylenetriamine dissolved in toluene was filled into the hollow space and heated at 70 °C for 18 h in order to introduce the diethylenetriamine group. Palladium nuclei as seed was immobilized onto the glass surface by the ligand substitution reaction of $[Pd(NH_3)_4]Cl_2$ with diethylenetriamine terminal, followed by the reduction of palladium with aqueous hydrazine solution.

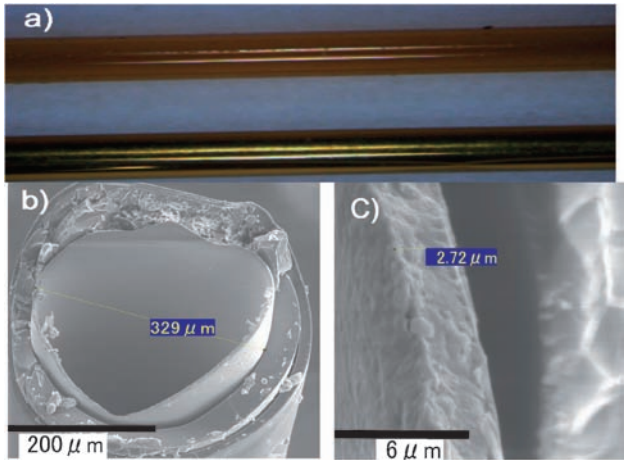

Figure 1. Optical microscope and cross-sectional SEM images of the capillary microtubes. a) silica microtube before (upper) and after palladium coating (lower), b) triphase structure of the capillary with palladium layer inside the tube, and c) thickness of the palladium layer.

After seeding, electroless plating of palladium was achieved by continuously feeding (0.5 mL min^{-1}) of a plating solution (40 mL, 50 °C) composed of 0.01 M $[Pd(NH_3)_4]Cl_2$, 0.15 M sodium ethylenediaminetetraacetate, 1 M NH_3, and 0.01 M hydrazine. Peristeric pump was used for feeding of solution into capillary throughout this work. The amount of coated palladium was determined to be 39.2 mg by ICP-AES analysis of the solution out of the capillary. In the course of plating, the transparent capillary turned to a metallic color (Figure 1a). In the case of platinum, a plating solution containing 0.003 M $[Pt(NH_3)_4]Cl_2$ was used in place of $[Pd(NH_3)_4]Cl_2$ under a similar procedure except for the temperature (70 °C). The amount of platinum deposited was determined to be 23.8 mg. The shape of the metal-plated silica capillary can be flexibly changed by bending or twisting.

The cross-sectional SEM image of the palladium-coated capillary (Figure 1b) shows triple layers composed of a polyimide outer cover, the silica tube, and a thin palladium inner layer. The observed thickness of the palladium layer (2.7 μm from Figure 1c) is in rather good agreement with that calculated from the amount of deposited palladium by assuming uniform coating (3.2 μm). Similarly, the thickness of the platinum layer directly observed by SEM (1.0 μm) was well consistent with that calculated from the amount of platinum consumed by plating (1.1 μm).

The performance of the capillary was evaluated by the catalytic decomposition of H_2O_2. Efficient treatment of H_2O_2 is important since it is widely used as an oxidant in chemical

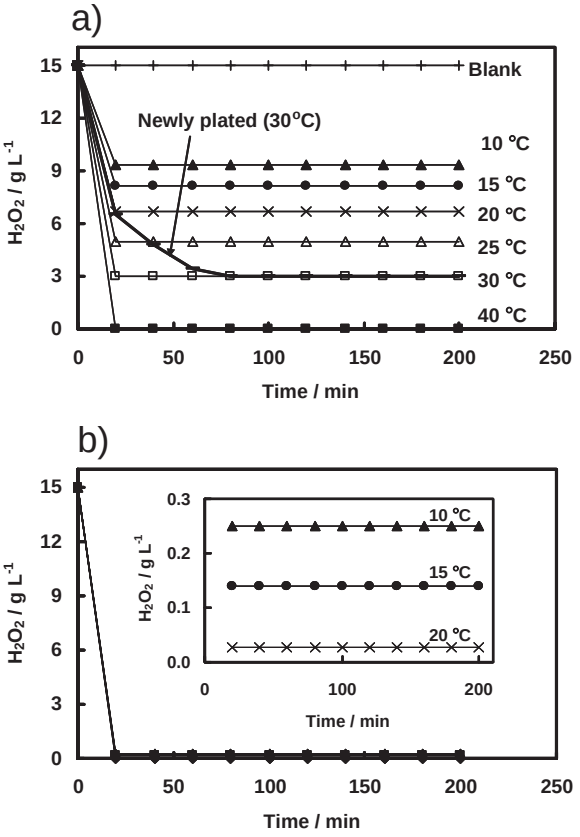

Figure 2. Concentration of H_2O_2 solution out of the capillary reactor treated at various temperatures. a) Palladium-coated capillary, b) platinum-coated capillary. Inset in Figure 2b is the magnified graph. Length of capillary was 100 cm, H_2O_2 feed was 15 g L^{-1}, and the flow rate was 0.5 cm^3 min^{-1}.

industries, bleaching of paper, sterilization, and water treatment. Platinum group metals displayed high catalytic activity for decomposition of H_2O_2.[11] However, the precedent processes by catalytic bed required high temperature or hydrogen gas supply to attain high decomposition efficiency.[11] We examined the continuous decomposition of H_2O_2 (15 g L^{-1}) by supply of the solution into capillary reactors (100 cm in length) with a flow rate of 0.5 cm^3 min^{-1}. Based on the capillary inner volume (0.08 cm^3), the residence time of reactant was less than 10 s. The concentration of H_2O_2 in each fraction was determined by $KMnO_4$ titration. During the course of reaction, leaching of either palladium or platinum did not occur.

The steady decomposition of H_2O_2 was observed within 20 min irrespective of the reactors under the fixed feed rate and temperature (Figure 2). The reaction is accompanied by an active evolution of gas ($H_2O_2 = H_2O + 0.5O_2$) in the capillary. Neither the blank silica nor palladium-seeded capillary significantly decompose H_2O_2. Obviously the platinum-coated capillary reactor gave better catalytic performance than the palladium reactor. More than 99.9% of H_2O_2 was decomposed at 20 °C by the platinum reactor, while the efficiency was low (ca. 50%) at the same temperature for the palladium reactor.

It is noteworthy that the newly plated palladium reactor (Figure 2a) required an induction period prior to reaching a steady decomposition state, whereas the platinum reactor did not. From the standard electrode potential, palladium ($Pd^{II} + 2e^- = Pd^0$, 0.92 V) is more susceptible to oxidation than platinum ($Pt^{II} + 2e^- = Pt^0$, 1.19 V).[12] Presumably oxidized palladium surface is responsible for catalytic activity since such an induction period was not observed by preoxidation of the capillary with 15% H_2O_2. In addition, the catalytic activity was significantly lost when the palladium surface was reduced with 0.1 M hydrazine. Unlike palladium, the platinum reactor actively decomposed H_2O_2 after treatment with 0.1 M hydrazine, indicating that Pt^0 is the catalytically active species. Direct adsorption of H_2O_2 onto a platinum surface followed by dissociation into OH or OOH was suggested in the case of platinum metal catalyst.[13,14] The reaction was retarded by decrease of pH. This trend was more significant in the palladium-coated reactor than the platinum counterpart. Oxidized palladium surfaces are more susceptible to proton and/or anion interaction thereby access of H_2O_2 must be suppressed leading to inhibition of decomposition.[15]

The feature of the present metal-coating procedure is its simplicity and applicability to a wide range of metal catalysts by choosing desired metal as the plating solution. The capillary provides continuous catalytic layer in the interior space of a remarkably high surface area and volume ratio (1.25×10^4 m^2 m^{-3}). As the result, efficient decomposition of H_2O_2 (15 g L^{-1}) was achieved within 10 s at room temperature simply by passing the solution into the reactor.

References

1 a) K. Jähnisch, V. Hessel, H. Löwe, M. Baerns, *Angew. Chem., Int. Ed.* **2004**, *304*, 1305. b) L. Kiwi-Minsker, A. Renken, *Catal. Today* **2005**, *110*, 2. c) J. Kobayashi, Y. Mori, K. Okamoto, R. Akiyama, M. Ueno, T. Kitamori, S. Kobayashi, *Science* **2004**, *58*, 4735.

2 a) D. I. Enache, G. J. Hutchimgs, S. H. Taylor, E. H. Stitt, *Catal. Today* **2005**, *105*, 569. b) D. I. Enache, G. J. Hutchimgs, S. H. Taylor, S. Raymahasay, J. M. Winterbottom, M. D. Mantle, A. J. Sederman, L. F. Gladden, C. Chatwin, K. T. Symonds, E. H. Stitt, *Catal. Today* **2007**, *128*, 26.

3 R. Takahashi, S. Sato, T. Sodesawa, Y. Haga, K. Kobayashi, S. Watanabe, M. Ishizuka, M. Matsutani, N. Minami, *Chem. Lett.* **2006**, *35*, 1078.

4 R. Natividad, R. Kulkarni, K. Nuithitikul, S. Raymahasay, J. Wood, J. M. Winterbottom, *Chem. Eng. Sci.* **2004**, *59*, 5431.

5 H. Nakamura, X. Li, H. Wang, M. Uehara, M. Miyazaki, H. Shimizu, H. Maeda, *Chem. Eng. J.* **2004**, *101*, 261.

6 J. Kobayashi, Y. Mori, S. Kobayashi, *Adv. Synth. Catal.* **2005**, *347*, 1889.

7 C. Basheer, F. Shahitha, J. Hussain, H. K. Lee, S. Valiyaveettil, *Tetrahedron Lett.* **2004**, *45*, 7297.

8 a) P. He, S. J. Haswell, P. D. I. Fletcher, *Appl. Catal., A* **2004**, *274*, 111. b) E. Comer, M. G. Organ, *J. Am. Chem. Soc.* **2005**, *127*, 8160. c) G. Shore, S. Morin, G. Organ, *Angew. Chem., Int. Ed.* **2006**, *45*, 2761.

9 N. Takeyasu, T. Tanaka, S. Kawata, *Jpn. J. Appl. Phys.* **2005**, *44*, L1134.

10 I. Rodriguez, P. Spicar-Mihalic, C. L. Kuyper, G. S. Fiorini, D. T. Chiu, *Anal. Chim. Acta* **2003**, *496*, 205.

11 a) W. E. Armstrong, A. J. L. Toombs, U.S. Patent 5711146, **1998**. b) A. Becker, Japan Kokai 257573, **1996**.

12 A. J. Bard, L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, 2nd ed., John Wiley & Sons Inc, **2001**.

13 P. B. Balbuena, S. R. Calvo, E. J. Lamas, P. F. Salazar, J. M. Seminario, *J. Phys. Chem. B* **2006**, *110*, 17452.

14 S. Mededovic, B. R. Locke, *Appl. Catal., B* **2006**, *67*, 149.

15 V. R. Choudhary, C. Samanta, T. V. Choudhary, *J. Mol. Catal. A: Chem.* **2006**, *260*, 115.

Published on the web (Advance View) January 10, 2009; doi:10.1246/cl.2009.146