Surface-selective infiltration of thin-film catalyst into microchannel reactors

H. Chen, L. Bednarova, R.S. Besser, W.Y. Lee *

New Jersey Center for Microchemical Systems, Department of Chemical, Biomedical, and Materials Engineering, Stevens Institute of Technology, Castle Point on Hudson, Hoboken, NJ 07030, USA

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Abstract

A thin-film Pt/Al₂O₃ catalyst was synthesized by a sol–gel synthesis method with hydrogen hexachloroplatinate hydrate and aluminum isopropoxide as precursors in a water-based solvent. The catalyst contained ~5 nm Pt particles dispersed on Al₂O₃ support, which was mostly amorphous with a specific surface area of 400–450 m²/g and a pore size distribution in the range of 2–8 nm. For uniform infiltration of the sol–gel catalyst precursor into the microchannel of Si-based reactors, a hydrophobic film was applied to the top surface of the reactors while reactive ion etched microchannel surface of the reactors remained hydrophilic. Under these surface conditions, the catalyst precursor infiltrated selectively into the microchannel without spilling over to the reactor surface. In comparison to other infiltration methods, this surface-selective approach provided an effective means of precisely controlling the amount of catalyst loaded into the reactors and keeping the reactor surface clean for subsequent sealing via anodic bonding. However, as delamination occurred preferentially at the sharp corners of the microchannel, the thickness of the catalyst layer that could be practically incorporated into the reactors was limited to ~3 µm.

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1. Introduction

Over the past decade, there has been an increasing interest in microchannel reactors with fast heat and mass transfer characteristics for applications in catalyst developments [1,2], kinetic studies [3], portable power devices [4], and on-site production of chemicals [5]. In contrast to conventional large-scale reactors, microchannel reactors have reaction volumes with cross-sectional dimensions typically in the range of micrometers to hundreds of micrometers. Despite much progress in various aspects of designing and fabricating microchannel reactors, the incorporation of a catalyst into microchannel in thin-film form remains an open research issue, when such a catalyst structure is desired for fast reactions.

Sol–gel processing is a proven thin-film deposition technique for catalyst synthesis. Haas-Santo et al. [6] have previously reported using sol–gel method to deposit SiO₂, Al₂O₃, and TiO₂ layers as catalyst support structures for metallic microchannel reactors. In comparison to other thin-film deposition techniques such as physical vapor deposition (PVD) and chemical vapor deposition (CVD), sol–gel method can easily be controlled to produce a porous structure with tunable pore size and pore volume. However, one of the challenges is to infiltrate the liquid precursor of a catalyst film into microchannels selectively and uniformly while controlling film thickness.

From an infiltration point of view, a microchannel can be defined as “open-channel” or “closed-channel” based on whether it has an opening along the length of the microchannel or only openings at the ends of the microchannel. For open-channels, a liquid catalyst precursor has been introduced by spin-coating [7], dip-coating [6,7], or micropipetting [8]. As the top surface of the reactor needs to be...
kept clean for subsequent sealing (e.g., anodic, diffusion, or compressive bonding), either a catalyst precursor must be injected precisely into the channel or the top surface has to be mechanically polished to remove the residues solidified from spilled precursor [3,9]. For closed-channels, a catalyst precursor can be infiltrated into the channel by capillary force or pressure [6,10,11]. Although this approach is easier to carry out and has no contamination issue, the uniformity of the deposited layer is difficult to control, and the evaporation of solvent in the catalyst precursor could be very slow [12].

The goal of this research was to develop a method to uniformly infiltrate sol–gel synthesized Pt/Al2O3 catalyst as an adherent thin-film on the inner surface of a silicon microchannel reactor, for preferential oxidation of CO in a reformate gas mixture, with the following objectives:

1. Synthesize the Pt/Al2O3 catalyst by sol–gel method and characterize the catalyst by surface area, pore size distribution and Pt particle size.
2. Develop and compare methods to infiltrate the catalyst precursor into open-channel and closed-channel.
3. Develop a method that can prevent surface contamination during open-channel infiltration.
4. Identify major factors that affect the adhesion of the catalyst layer to the channel surface.

We note that catalytic properties of the Pt/Al2O3 thin-film catalyst have been evaluated, and are reported elsewhere in detail [13].

2. Microchannel reactor fabrication

Single-channeled reactors were designed and fabricated on a 700 μm thick p-type silicon wafer by photolithography and deep reactive ion etching (DRIE). Two inlets, a mixing zone, a single meandering reaction channel and an outlet were etched into the silicon wafer. In this study, reactors with three different channel dimensions (length × width × depth) were used: 10 cm × 100 μm × 500 μm, 5.8 cm × 500 μm × 500 μm, and 54 cm × 150 μm × 75 μm. Vias were etched from the backside of the wafer for inlet and outlet connections [14]. The microchannel reactors were rinsed with acetone, isopropanol and deionized water, and dried in N2 flow prior to catalyst deposition steps.

3. Catalyst synthesis and characterization

An aluminum hydroxide sol was prepared by following the procedure developed by Yoldas [15]. The preparation was carried out in a glovebox filled with N2. Magnetically stirred deionized water was heated up to 85 °C in a round bottom flask. Aluminum isopropoxide (AIP, Aldrich, >99.99%) was added to the water to initiate hydrolysis. The mixture was kept open at 85 °C for 45 min to remove isopropanol, which was a byproduct of the hydrolysis. After nitric acid (Aldrich, 70%) was added to peptize hydroxide precipitates, the sol became clear. The mixture was stirred at 90 °C for 24 h. The overall molar ratios of AIP:H2O:HNO3 used for the sol preparation were: 1:113:0.2. The sol contained ~100 nm long aluminum hydroxide (i.e., boehmite) platelets with the ζ-potential of +25 mV at this preparation stage, as measured by dynamic laser scattering (90Plus, Brookhaven Instruments Corp.). These numbers were in agreement with the previous findings of other investigators [16,17].

The incorporation of Pt into the aluminum hydroxide sol was similar to the procedure reported by Manasilp [18]. Hydrogen hexachloroplatinate(IV) hydrate (Aldrich, >99.9%) was dissolved in 1.3 butanediol (0.02 g of Pt in 1 mL of the solution). The Pt solution was added to the sol under stirring to obtain a Pt loading of 2 wt.% in the final catalyst structure. The mixture was a stable colloidal suspension, and did not exhibit significant sedimentation or gelation over one month. This mixture was used as the precursor for catalyst synthesis experiments. The catalyst precursor was dried at 80 °C for 12 h and calcined at 500 °C for 2 h in air, followed by reduction in H2 at 450 °C for 4 h. Using this synthesis procedure, the catalyst was prepared in both powder and thin-film forms. We will describe our thin-film preparation procedures in the following sections. The powder form was initially used for ease of characterization for surface area and porosity measurements.

The Pt/Al2O3 catalyst powder was characterized by N2 physisorption with a Quantachrome Autosorb-1 system. Before each measurement, the catalyst sample was degassed at 300 °C for 12 h. The measured values of specific surface area using the BET method were in the range of 400–450 m²/g. The density of the porous structure was calculated to be ~1.1 g/cm³ and the porosity was about 70% based on the specific pore volume measurement. There were no pores in the diameter range below 2 nm in the structure as

![Fig. 1. Typical BJH mesopore size distribution of the Al2O3 support.](image-url)
indicated from the t-plot method. A typical mesopore size distribution was obtained by analyzing the desorption curve using the BJH method (Fig. 1). The diameter of most pores was in the range of 2–8 nm, which was close to the lower limit of the size range defined as mesopores (2–50 nm).

From transmission electron microscopy (TEM) observations, Pt metal particles appeared evenly distributed on the Al₂O₃ support, as shown in Fig. 2(A). The diameter of the Pt particles was in the range of 2–10 nm with the mean diameter calculated to be 5.7 nm from the particle size distribution analysis shown in Fig. 2(B). The catalyst powder before and after the reduction step was examined on a Siemens D5000 X-ray diffractometer (XRD). Broad XRD peaks for the metallic Pt phase observed for both samples showed the presence of Pt metal particles. The particle size of Pt calculated from the XRD patterns using the Scherrer formula [19] was 11 nm for both samples. This result was consistent with the TEM measurements, considering that the XRD method is known to be more sensitive towards larger crystallites [19]. The XRD pattern of the Al₂O₃ support showed very low peaks of γ-Al₂O₃, indicating that the Al₂O₃ support was mostly amorphous with a small amount of the γ phase.

The dispersion of Pt measured by CO chemisorption on a Quantachrome ChemBET 3000 system was about 22%, and that calculated from TEM measurement was about 24%. These chemisorption and TEM results indicated that nearly all atoms at the surface of the Pt particles had been able to adsorb CO. Therefore, we concluded that most of the Pt particles were not encapsulated by the Al₂O₃ matrix during this “one-step” synthesis procedure and their surface atoms were accessible to the gas.

4. Closed-channel infiltration

The catalyst was prepared in a thin-film form by infiltrating the catalyst precursor into the silicon microchannel reactors and by subsequent drying, calcination and reduction. Both closed-channel and open-channel infiltration experiments were carried out using the procedures outlined in Fig. 3. As shown in Fig. 3(A), the catalyst precursor was infiltrated into the closed-channel reactor through the reactor outlet, after the reactor was permanently sealed with a Pyrex™ top plate by anodic bonding at 450 °C and 750 V. A mounting unit, shown in the picture in Fig. 3(A), was built to fasten the reactor and connect the reactor outlet to a syringe. The precursor was injected into the microchannel from the syringe until it filled the microchannel volume. After 10 min, the precursor was slowly withdrawn from the microchannel, leaving a thin film of liquid precursor remaining on the inner surface of the microchannel. Multiple infiltrations were performed to increase the film thickness with each infiltration followed by drying on a hotplate at 80 °C. The reactor was then placed in a furnace, dried at 80 °C for 12 h, and calcined at 500 °C for 2 h. The catalyst was reduced at 450 °C by flowing pure H₂ through the heated microchannel reactor for 4 h.

The closed-channel infiltration procedure was easy to carry out as the channel was sealed with the top plate. Fractured cross-section of the microchannel coated with the catalyst layer was examined using a LEO 982 scanning electron microscope with a field emission filament. The thickness of the catalyst layer deposited by two infiltration cycles was about 200 nm as shown in Fig. 4(A). The closed-channel infiltration approach was inefficient, as the withdrawal of the catalyst precursor was required. If the excess precursor was not withdrawn, the precursor would flow towards the inlets and the outlet of the channel due to the thermal expansion of the liquid precursor during the drying step. This flow behavior caused non-uniform distribution of the final catalyst layer along the axial microchannel direction. We observed that some excess amount of the precursor was accumulated at the inlet and outlet locations of the reactor and subsequently solidified into large pieces (~1 mm) instead of forming a coating on the channel wall. Another disadvantage of the closed-channel method was that
the evaporation of the solvent in the catalyst precursor through the small cross-section of the inlets and outlet was slow and therefore increased the time required for drying.

5. Open-channel infiltration

The catalyst precursor was injected into the open-channel from a $\mu$Tip™ (World Precision Instruments) connected to a syringe, which was controlled by a syringe pump. The inner diameter of the tip of $\mu$Tip™ was 10 $\mu$m, and its outer diameter was smaller than the width of the microchannel (Fig. 3(B)). The tip was positioned into the microchannel by moving the reactor on a manually controlled X–Y–Z stage. With this method, we were able to slowly fill a length of the channel with the precursor. The precursor spread along the channel as a result of capillary drawing provided by the wetted channel surface. When the precursor stopped flowing along the channel (typically after filling up 2–3 cm of channel length) and before overflowing onto the top surface, the syringe pump was stopped. Then the reactor was moved laterally, and the precursor was injected into the next section of the channel that was not filled by the previous injection. We note that it was difficult to inject exactly the same volume in every injection, because the injection had to be manually interrupted at some occasions to prevent the precursor overflow.
The catalyst precursor was dried on a hotplate at 80 °C for 20 min. Multiple infiltration-drying cycles could be performed to increase the layer thickness. After multiple cycling, the microchannel reactor was dried at 80 °C for 12 h, and calcined at 500 °C for 2 h in the same furnace. The reactor was then anodically bonded with a Pyrex® top plate at 450 °C and 750 V. The catalyst was then reduced at 450 °C by flowing pure H₂ through the heated microchannel reactor for 4 h.

The fractured cross-section SEM image of the Pt/Al₂O₃ catalyst deposited on the silicon microchannel after one open-channel infiltration cycle is shown in Fig. 4(B). The catalyst layer had a varying thickness in the range of 1–3 μm, with an average thickness of 1.4 μm. The catalyst weights loaded into eight reactors with microchannel dimensions of 5.8 cm × 500 μm × 500 μm (l × d × w) were measured and plotted as a function of infiltration cycles (Fig. 5). The average weight of the Pt/Al₂O₃ catalyst deposited per infiltration cycle was about 0.37 mg/cycle, and the catalyst weight gain increased linearly with respect to the number of infiltration cycles. However, very large variation of ~40% in catalyst loading were measured for the reactors used for the 2, 3, and 4 infiltration cycles (the first three data points in Fig. 5). The major reason for the variations was difficulty in precisely controlling the catalyst precursor volume for each injection, as mentioned earlier.

The catalyst weight deposited per infiltration cycle was also calculated based on the microchannel dimensions and the precursor concentration. The volume of the 5.8 cm × 500 μm × 500 μm channel was 14.5 μL, and about 0.025 mg of the solid catalyst would be formed from every 1 μL of the liquid precursor. Therefore, the catalyst weight deposited per infiltration cycle was calculated to be 0.36 mg, by multiplying the channel volume and the precursor concentration, which was in good agreement with the experimental value (Fig. 5).

In comparison to the closed-channel infiltration method, the open-channel infiltration approach was useful in terms of depositing a thicker catalyst layer per infiltration cycle. The drying of the catalyst precursor in the open-channel was faster, and occurred more uniformly than in the closed-channel. SEM observations confirmed that the thickness of catalyst was uniform along the length of the channel, and there was no catalyst build-up as observed at the reactor inlet and outlet locations for the closed-channel infiltration method. Also, the open-channel infiltration method was more useful in depositing the catalyst only on the sections of the microchannel that require the catalyst.

Fig. 4. Fractured cross-section SEM images of the Pt/Al₂O₃ catalyst layer deposited by: (A) closed-channel infiltration on the bottom surface of a microchannel after two infiltration cycles and (B) open-channel infiltration after one infiltration cycle. Note that for the closed-channel method all four microchannel sides were coated.
However, contamination of the top surface of the reactor with spilled over catalyst precursor was found to be a serious issue for the open-channel infiltration method. When the precursor spilled over onto the top surface, it solidified and significantly reduced surface flatness and cleanliness. As anodic bonding requires a direct contact between clean silicon and Pyrex® surfaces, the catalyst contamination on silicon could result in anodic bonding failure as shown in Fig. 6(A). In addition to the contamination issue, the micropipette injection procedure required extreme caution as the μTip™ was fragile and fine, and could be easily broken or clogged by the solidifying precursor. Also, as discussed earlier, controlling the injection volume was another serious problem in terms of predictably loading the microchannel with a desired catalyst amount. In order to address these issues, a modified open-channel infiltration method was developed.

6. Surface-selective infiltration

The key concept behind this improved method is to make the inner surface of the channel to be hydrophilic, while making the top surface of the reactor hydrophobic. As the catalyst precursor is a water-based sol, it therefore selectively wets the inner surface of the channel. The silicon reactors used in this study had a hydrophilic SiO₂ layer, and therefore only the top surface of the reactors had to be made hydrophobic. In this study, we selectively coated the top surface of the reactor with a hydrophobic material, and the inner surface of the channel could remain hydrophilic. Among several hydrophobic materials that we tested, we chose Parafilm® sealing film (American National Can Co.) for subsequent experimental work. A piece of Parafilm® was gently pressed onto the top surface of the silicon reactor. The reactor was heated on a hot plate at 70 °C for 5–10 min, until the film became soft on the silicon surface. After the film was peeled off, a residual layer from the Parafilm® was visible on the top surface of the silicon reactor (Fig. 7(B)). With this procedure, only the top reactor surface could become hydrophobic.

The catalyst precursor with a volume equal to the channel volume (e.g., 14.5 μL precursor for a 5.8 cm × 500 μm × 500 μm channel) was measured using a pipette. When the catalyst precursor was intentionally placed as a large droplet over the microchannel (i.e., the droplet was larger than the microchannel width), the precursor flowed into the channel and the droplet on the top surface shrank and disappeared within a few seconds. As both the mixing zone and the outlet channel were wider than the reaction channel, the capillary effect prevented the catalyst precursor from entering the mixing zone and the outlet channel.

Upon drying of the precursor at 80 °C, the morphology of the hydrophobic layer changed (Fig. 8(B)), but the top surface of the reactor remained hydrophobic. Thus, the hydrophobic layer could be used for multiple infiltration-drying cycles of the catalyst precursor. After multiple infiltration-drying cycles, the hydrophobic layer could be removed during calcination, and the top surface of the reactor became clean and hydrophilic again (Fig. 8(C)).
The average thickness of the catalyst layer deposited per infiltration-drying cycle by the surface-selective infiltration method was similar to that prepared by the original open-channel infiltration. The thickness uniformity was also similar to that observed for the original infiltration method. More importantly, the surface-selective wetting behavior ensured that the catalyst precursor completely flowed into the channel without leaving residues on the top surface. Therefore, the volume of the precursor infiltrated for each cycle was then entirely dictated by the microchannel volume, and consequently could be precisely controlled (i.e., constant catalyst weight loading per each infiltration cycle). Fig. 5 shows the effectiveness of the surface-selective infiltration procedure with comparison to the initial infiltration procedure. The average catalyst loading data measured for four reactors after six multiple infiltration-drying cycles was about 2.3 mg (the last data point in Fig. 5). The variation was only 5% among the four reactor samples in contrast to the 40% variation measured for the initial open-channel infiltration method (the first three data points).

Since there was no surface contamination, the silicon reactor infiltrated with the catalyst layer could be easily bonded with Pyrex™ top plate (Fig. 6(B)). Note that the
reactor shown in Fig. 6(B) has a 100 µm wide channel, which was narrower than the channel shown in Fig. 6(A). Therefore, it would have been more difficult to infiltrate the catalyst precursor with a micropipette without contaminating the top surface if the original method was used. The surface-selective method made the infiltration significantly easier and more precisely controlled while preventing contamination of the reactor top surface for subsequent reactor bonding. The surface-selective infiltration method is expected to be cost-effective, since precise positioning device and micropipettes are not needed to control the precursor injection.

7. Adhesion issues

Adhesion of the catalyst layer to the microchannel surface is a critical issue, since delamination or detachment of the catalyst can cause plugging and increase pressure drop. During the drying process, the catalyst precursor underwent significant volume shrinkage as the solvent in the precursor evaporated. As the dimensions of the microchannel surface remained the same, residual tensile stresses developed within the catalyst layer in the lateral direction of the layer. Based on our understanding of the fracture mechanics of thin-films, when the layer thickness exceeds a critical value, tensile stress is relieved by cracking and/or delamination [20–23].

From the fracture-surface SEM analysis, it appeared that a catalyst layer thinner than 3 µm usually showed good adhesion and a layer thicker than 3 µm was prone to cracking and delamination (Fig. 9). This value was about an order of magnitude higher than that of dense Al₂O₃ thin-films reported in the literature [16,22]. We suspected that the higher critical thickness could be explained by the strain-tolerant capability of the porous structure [24]. Nevertheless, in order to increase the amount of catalyst in a microchannel reactor, the critical thickness limit of thin-film catalysts must be increased by optimizing the synthesis procedure that leads to less volume shrinkage.

We also observed that the delamination of the catalyst layer usually started from the corners of the microchannel surfaces, as shown in Fig. 4(B) and Fig. 9(B) For a layer on a flat surface, residual stress develops in the direction parallel to the surface, and there is no force directly leading to delamination. However, at corners and free edges, local in-plane tensile stress is created at the interface to pull the layer away from the substrate [25]. The magnitude of this type of interfacial stress is largely determined by the curvature of the corner. The radius of corners must be much larger than the layer thickness to eliminate this type of geometry effect [25]. As seen from Fig. 9, the radius of the corner was about 10 µm, and a ~8 µm thick catalyst layer delaminated from the corner. Similarly, in Fig. 4(B), both the radius of the corner and the catalyst layer thickness were about 5 µm and delamination took place at the corners. Therefore, we expect that designing and fabricating a microchannel with smooth corners will help reduce this delamination problem when a thick catalyst layer is desired.

Fig. 8. Surface evolution of the microchannel reactor during the surface-selective infiltration procedure: (A) after applying the hydrophobic layer; (B) after the catalyst precursor was injected and dried at 80 °C; and (C) after calcining at 500 °C. Note that the rough surface feature observed along the edges of the microchannel were originated from the DRIE etching as fabrication defects.
8. Conclusions

A thin-film Pt/Al₂O₃ catalyst was synthesized by a "one-step" sol–gel synthesis method using hydrogen hexachloroplatinate hydrate and aluminum isopropoxide as precursors in a water-based solvent. The catalyst contained 2–8 nm Pt particles dispersed on amorphous Al₂O₃ support with a specific surface area of 400–450 m²/g and a pore size distribution from 2–8 nm. The catalyst was deposited onto the inner surface of Si microchannel reactors by closed-channel, open-channel, and surface-selective infiltration methods while comparing the merits of these methods. The thickness of the catalyst layer could be varied in the range of 200 nm to 10 μm depending on the infiltration methods and the number of infiltration cycles chosen. However, as delamination occurred preferentially at the sharp corners of the microchannel with thicker layers, the thickness of the catalyst layer that can be practically incorporated into the reactors was limited to ~3 μm.

In comparison to the closed channel method, the open-channel infiltration technique was useful in depositing a thicker catalyst layer per infiltration cycle with faster and uniform drying of the liquid catalyst precursor. On the other hand, the open-channel infiltration which required the use of a micropipette was labor-intensive. More critically, the amount of the catalyst precursor per injection could not be precisely controlled due to spillover of the precursor to the top reactor surface. This problem resulted in inconsistent catalyst weight loading into microchannel reactors. Also, the spillover problem caused contamination of the top surface which resulted in poor sealing of the reactors with a Pyrex cover plate by anodic bonding.

In order to resolve these disadvantages of the open-channel method, a surface-selective infiltration method was formulated. With the top Si surface of the reactors coated with a hydrophobic layer and as the inner microchannel surfaces remained hydrophilic, the catalyst precursor could be selectively infiltrated into the microchannel more controllably without spillover and surface contamination. Due to the precise control of the precursor infiltration volume, catalyst weight loading became more consistent when the same procedure was repeated for four microchannel reactors with the variation of 5%. The surface-selective infiltration procedure provided a clean reactor surface for the subsequent anodic bonding step.

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References


Fig. 9. Effects of the catalyst layer thickness on adhesion: (A) no apparent delamination at 2–3 μm thickness and (B) cracking and delamination originating from the corner at a higher thickness (6–8 μm).