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Flame spray deposition of porous catalysts on surfaces and in microsystems

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Abstract

Flame spray synthesis is investigated as a method for one-step synthesis and deposition of porous catalysts onto surfaces and into microreactors. Using a standard photolithographic lift-off process, catalysts can be deposited on flat surfaces in patterns with submillimeter feature sizes. With shadow masks, porous catalyst layers can be deposited selectively into microchannels. Using Au/TiO_2 as test catalyst and CO oxidation as test reaction, it is found that the apparent activation energy of the deposited catalyst is similar to that normally seen for supported gold catalysts in the literature. The surface area of the deposited material is more than twice as large as when the flame-produced material is collected on a filter at the outlet of the flame reactor unit.

Keywords: Microreactors; Catalysis; Microfabrication

1. Introduction

Microreactors [1] are microfabricated catalytic chemical reactors with at least one linear dimension in the micrometer range. Due to their small size, concentration and temperature gradients can be accurately controlled. The gas flow through the microreactors is laminar and the large surface to volume ratio ensures that heat dissipation is orders of magnitude faster than in conventional reactors. These properties provide precise control of reaction parameters such as temperature, concentrations, and residence time, which is an advantage for both catalyst characterization and optimization of reaction conditions. Microreactors even open a new parameter space for chemical reactions. For example, reaction conditions that would normally result in explosions can be handled in microreactors [2], and dynamic reaction conditions such as rapidly oscillating temperatures or concentrations can be performed [3].

Potential applications of heterogeneous catalysis in microreactors include safe operation with dangerous/explosive gas mixtures and local production of chemicals as, for example, hydrogen for mobile fuel cell technology. Additionally, microreactors are useful tools for rapid screening and testing of catalysts under realistic operating conditions.

Due to their small size, loading of catalysts in microreactors is substantially different from loading of catalysts in traditional macroscopic reactors. Deposition of metals/materials in microsystems is usually done by physical or chemical vapor deposition (PVD/CVD) or electrochemical methods. These methods are typically optimized to give very smooth surfaces with low porosity, and catalysts deposited this way have limited performance. Efficient heterogeneous catalysts have a high porosity and surface area, and production of such catalysts is done in multiple steps including precipitation, filtration, calcination, impregnation, precursor decomposition, etc., that are not directly compatible with microfabrication. As a result, methods have been developed in order to obtain both high surface area catalysts and compatibility with microfabrication. Examples of such

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methods are sol–gel based methods [4–7], wash coating [8], electrophoretic deposition [6], and anodic oxidation of, e.g., aluminum metal layers [6]. These methods have different degrees of complexity and flexibility, but they all include a liquid phase at some stage during the catalyst deposition. Some of the methods provide the possibility of confining the catalyst to a certain area of the microsystem, but the liquid phase makes it difficult to confine the catalyst accurately, especially if different catalysts are to be deposited in the same microreactor.

In this work, a method based on flame spray synthesis is developed as a method for one-step deposition of porous catalysts. Combined with standard masking techniques used in microfabrication, the method is used to deposit microstructured patterns of porous catalyst on a variety of surfaces and in silicon microreactors. With Au/TiO_2 as a model system, the deposition process is characterized with respect to deposition parameters and substrate type. Furthermore, the surface area and the apparent activation energy of the catalyst deposited in the microreactors are measured.

2. Flame spray deposition

Flame spray synthesis of porous nanostructured catalysts is a modification of flame synthesis [9–13]. The working principle of flame spray synthesis is that an oxidizing gas containing an atomized organic solution of organo-metallic precursor compounds is led into a flame zone where the droplets are combusted and the precursors converted into nanometer-sized metal or metal-oxide particles, depending on the metal and the operating conditions. The catalyst is usually collected by passing the particle-containing gas through a filter. If, instead of collecting the particles on a filter, a cold surface is placed in the hot particle-containing gas, the particles will be driven toward the surface due to thermophoresis [14] and diffusion and deposit onto the surface to form a porous layer of catalyst. In the following, this method is denoted flame spray deposition (FSD). Contrary to the traditional microfabrication deposition techniques, it produces a *porous* catalyst layer with high surface area.

The flame spray deposition unit is illustrated in Fig. 1. An air-assisted spray nozzle is fed with an organic solution of metal precursors and spray gas, which produces a spray aerosol of droplets, approximately 10 µm in diameter. The droplets are combusted in the flame, and the evaporated organo-metallic compounds decompose and form nanometer-sized particles in the gas phase. The temperature at this point is above 1500 K. The spray is surrounded by a hydrogen burner that ensures an even and steady combustion.

In the present study, the metal precursor solution consists of 2.9 mM gold-triphenylphosphin-nitrate and 0.70 M Ti–tetraisopropoxide in a 1:4 volumetric mixture of tetrahydrofurane and isooctane. This gives 1 wt% of gold in the final Au/TiO_2 catalyst. The gas flow in the nozzle is air at 12.8 L/min, and the hydrogen burner is supplied with 1.4 L/min of hydrogen. The sample holder (cf. Fig. 2) is positioned a height h above the flame zone and a radial distance r from the center line of the FSD system. The sample holder is water-cooled to prevent the sample from being damaged by the high temperature as well as to enhance the thermophoretic force on the particles and thus the deposition rate. A temperature sensor is mounted on the sample holder, and the water cooling can thus be varied to reach different deposition temperatures. The sample temperature is usually kept close to 50 °C, which is slightly above the dew point of water in the combustion gas.

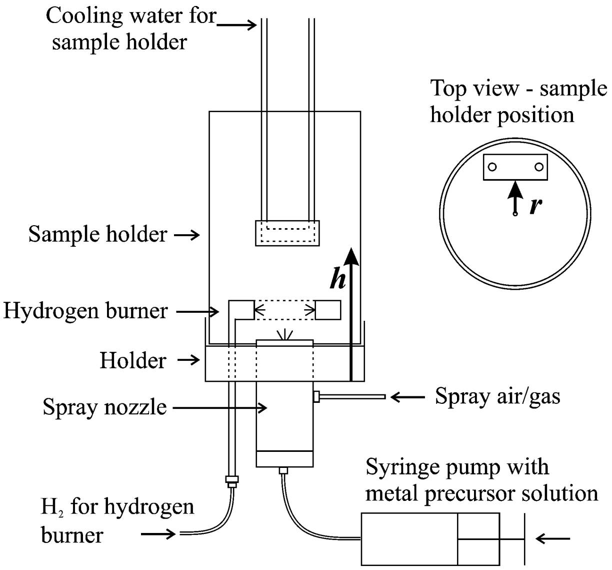

Fig. 1. Experimental setup for flame spray deposition of porous catalyst on substrate surfaces. A metal precursor solution is fed from a syringe pump through a spray nozzle into a combustion zone. The product particles deposit on the substrate positioned on the cooled sample holder. The vertical position of the sample holder is denoted h. The diameter of the flame reactor is 8 cm.

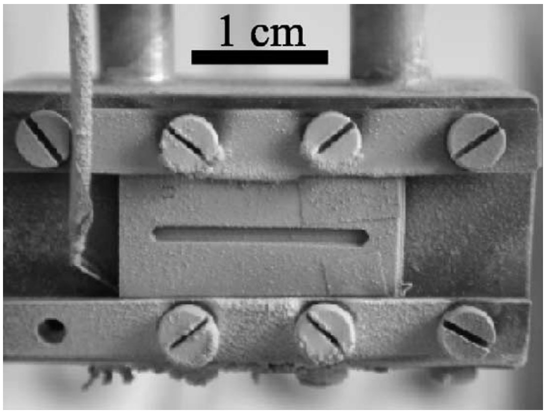

Fig. 2. Photograph of sample holder with a microreactor after deposition of catalyst. The microreactor is covered by a shadow mask enabling deposition only in the reactor channel.

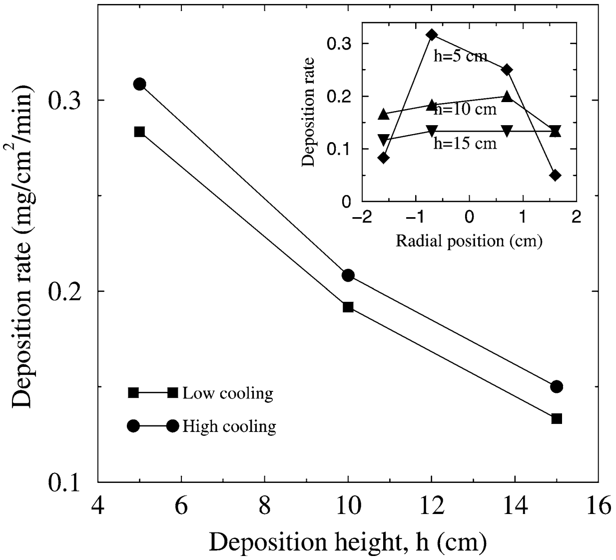

Fig. 3. Catalyst deposition rates, for different sample positions and cooling rates. The deposition rate increases when the sample is placed close to the flame and when a high cooling rate is used. The inset shows the variation of the deposition rate at different positions on the sample holder. The radial position is measured as the distance from the center to the sample position on the sample holder. The deposition is more uniform at higher deposition positions, (h).

3. Characterization of the deposition process

To what extent the FSD method is compatible with microfabrication is investigated in this section. The deposition rate is characterized with respect to sample temperature and position relative to the flame zone. Uniformity of the deposit as well as the adhesion to various substrate types used in microfabrication is investigated, and finally photolithographic patterning of the catalyst is tested.

3.1. Deposition rate

Fig. 3 shows the deposition rates at different sample positions. The overall deposition rate increases by 60% when h is decreased from 15 to 5 cm. The inset in Fig. 3 shows the variation in deposition rate as function of radial distance r to the flame. For small h, i.e., close to the flame zone, there is a strong dependence on the radial distance to the sample. At larger h, this dependence vanishes. Thus, for obtaining a uniform coverage, the height h should not be too small. Further, if the sample is positioned too close to, or in the flame zone, the deposit will contain large quantities of uncombusted material, which is undesirable.

The average temperature difference between the two curves with high and low cooling in Fig. 3 is 13 °C. With this temperature difference, the average deposition rate for the high cooling deposition curve is 10% larger than for the low cooling curve. The deposition rate thus increases with decreasing sample temperature, but below a certain temperature, condensation of water from the gas on the sample limits the minimum temperature during deposition. Above this temperature, typical deposition rates are 0.1–0.6 mg/(cm^2 min), and the layer thickness is between 50 and 150 µm after 20 min of deposition.

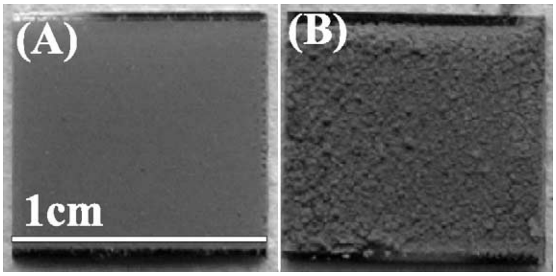

Fig. 4. Photos of two silicon samples covered with porous catalyst. Photos A and B show samples which are covered by a thin and thick layer, respectively. When a very thick layer is deposited, cracks are formed on the surface.

For the samples presented in this work, a height of $h = 6$ cm and a radial position of $r = 0.5$ cm with a sample temperature of 40 °C is used for deposition.

3.2. Adhesion

Adhesion is a key issue for any practical use of the deposits and is therefore tested on a number of surfaces often encountered in microfabrication: Si, Ti, Al, Si_3N_4, H:Si. The first three surfaces are covered with thin native oxide layers, and the H:Si denotes silicon where the native oxide layer has been replaced with a monolayer of hydrogen in a 5% HF solution. This surface reacts slowly with oxygen on a time scale of hours and is expected to form chemical bonds to the initial deposit over time. Good adhesion (deposit difficult to scrape completely off, even with a scalpel) is obtained in all cases except on Si_3N_4. For Si_3N_4 the deposit can be wiped off with a napkin leaving no traces of the deposit. In the following, only silicon substrates are used.

3.3. Morphology

Fig. 4 shows photographs of two pieces of silicon covered with different thicknesses of the porous catalyst. The sample denoted (B) is covered by a thick layer, and the surface shows cracks on length scales between 5 µm and 5 mm. The cracks develop within hours after deposition, and are probably caused by moisture evaporating from the porous material with a corresponding reduction of the volume. The cracks in the thick layer do not by any means ruin the properties of the catalyst, but are merely a result of the time scale of the deposition experiment. The photograph to the left (A) shows a thin, but more uniform catalyst layer.

For the Au/TiO_2 catalyst collected by filtering the particle containing gas, the specific surface area measured with the BET method is usually between 100 and 200 m^2/g. The BET area measured on the deposited material is above 350 m^2/g, which corresponds to an average particle size of 4 nm, assuming spherical particles.

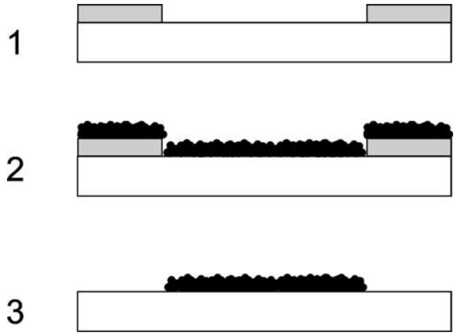

Fig. 5. Schematic representation of the lift-off process for creating well-defined patterns of catalyst deposit: (1) Deposition of photoresist. (2) Deposition of catalyst on entire surface. (3) Removal of catalyst from selected areas by dissolving the photoresist layer.

In the flame reactor, particles grow in size as a result of particle collisions and coalescence of the formed aggregates. At high temperature, the rate of coalescence (or sintering) is high [15]. Consequently, by reducing the residence time at elevated temperature, one can retain a high specific surface area of the product (i.e., small primary particles). With the water-cooled sample holder, the particles are collected close to the flame zone and cooled almost instantaneously to a temperature where coalescence of collided primary particles is effectively frozen. Furthermore, the particles are driven toward the sample by the thermophoretic force, which in combination with a high diffusion coefficient for small particles increases the deposition rate for decreasing particle sizes. This makes the transport of small particles toward the surface more efficient than that of bigger particles. Both effects favor the control of excessive coalescence and the collection of small particles and thus give a high porosity and surface area of the deposited material.

3.4. Patterning of catalyst

Two-dimensional catalyst patterns on flat surfaces are fabricated using a lift-off process as illustrated in Fig. 5:

(1) The substrate surface is spin-coated with a 1.5 µm thick layer of photosensitive polymer (AZ5214E photoresist).
(2) The deposition pattern is defined in the photoresist using standard UV photolithography, whereafter the exposed regions are dissolved in a NaOH solution.
(3) The sample is mounted on the water-cooled sample holder and placed in the hot zone of the spray flame until the desired thickness of catalyst is reached.
(4) The photoresist is dissolved in acetone, whereby the catalyst on the photoresist is removed from the sample.

In a standard microfabrication metal lift-off process, the resist layer is dissolved in acetone in an ultrasonic bath. This treatment is too intense for the porous deposits due to their low mechanical strength, and instead, the sample is gently washed in acetone. Due to the porous nature of the deposit, acetone easily penetrates the deposit and dissolves the photoresist.

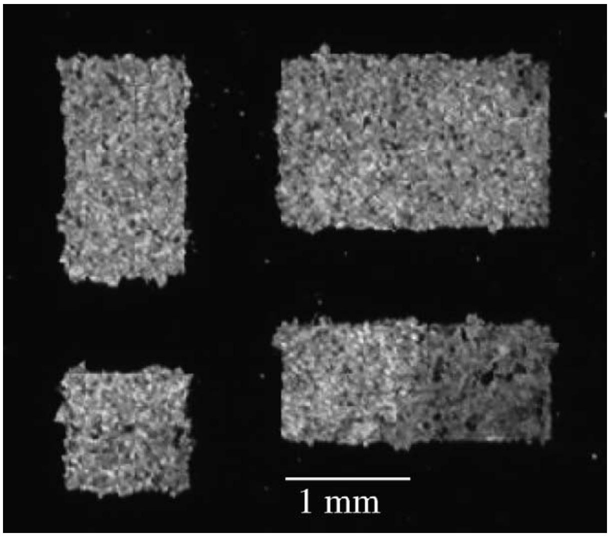

Fig. 6. A photograph of a silicon sample with flame spray deposition of catalyst controlled by the photolithographic lift-off procedure. The sample is prepared by the steps outlined in Fig. 5.

Fig. 6 shows the result of a photolithographic deposition of Au/TiO_2 catalyst on a flat silicon single-crystal surface. The dark area is the silicon surface, and the bright areas are covered with approximately 50 µm deposited catalyst.

The resolution of the photolithography is about 1 µm, but the resolution of the deposition method is limited by the mechanical properties of the deposited material, when the deposit has to break at the boundaries between the surface with photoresists and the clean surface. The roughness of the pattern edges in Fig. 6 is below 100 µm.

The above results show that the FSD method is applicable for deposition of porous catalyst for use in microsystems. The deposition rate makes it possible to deposit porous layers of hundreds of micrometers within a reasonable time, and depending on the deposition parameters, the deposition is uniform over several centimeters. This is within the range required for microreactors that typically have a lateral size of a few centimeters and channel depths of several hundreds of micrometers. The method is compatible with microfabrication since a standard photolithographic mask is suitable for confining the deposit to certain areas on the surface with a resolution better than 100 µm.

With proper optimization, the method has potential for use in batch fabrication of microreactors, where catalysts are deposited on multiple reactors at the same time in a parallel process.

4. Test in microreactors

To investigate the possibility of depositing catalysts in three-dimensional structures, and to test the catalytic properties of the deposited material, microreactors are fabricated

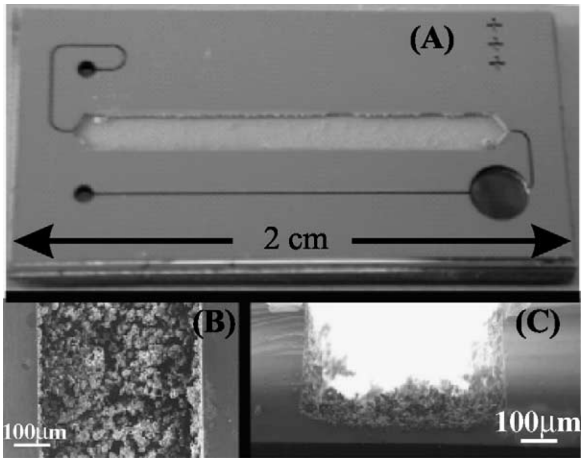

Fig. 7. (A) Photograph of the loaded reactor. SEM image ((B) top view and (C) cross section view) of the catalyst deposit in the reactor channel.

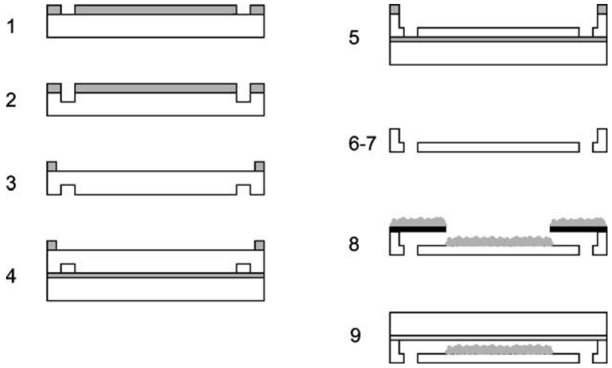

Fig. 8. Fabrication sequence for the microreactors: In Steps 1 through 7 the reactor is etched in silicon using photoresist masks. In 8 the catalyst is deposited and in 9 a Pyrex lid is mounted using adhesive bonding.

and the activity and apparent activation energy of the deposited catalyst with respect to oxidation of CO are measured.

The layout of the microreactors is seen in Fig. 7. The narrow inlet and outlet channels provide diffusional barriers to the reactor volume, but are sufficiently wide to prevent any significant pressure drop. The dimensions of the reactor channel are determined by a required estimated conversion of CO between 1 and 10% at a flow rate of 1 mL/min.

The microreactors are made in silicon using photolithography and deep reactive ion etching (DRIE) [16]. Fig. 8 shows the fabrication sequence: (1) First, the backside of the wafer is covered by a 1.5 µm thick photoresist layer that is subsequently patterned by exposing it with UV light through a mask. The areas of exposed photoresist are removed in a NaOH solution. (2) The in- and outlet holes are then etched to a depth of approximately 50 µm using anisotropic DRIE. After the etch, the photoresist layer is removed using acetone. (3) A layer of 10 µm photoresist is then applied onto the front side of the wafer, and the channel structures are defined in this layer. Before the UV exposure, the channel pattern on the mask is aligned to the in- and outlet holes on the backside of the wafer. (4) Afterward, the wafer is bonded to a handle wafer using photoresist. This is primarily done to achieve a better clamping of the wafer in the DRIE chamber in step 5. (5) The reactor pattern is etched to a depth of approximately 300 µm using DRIE as in step 3, thereby connecting the channels to the in- and outlets. (6) The remaining photoresist and the handle wafer are removed in acetone. (7) The wafer level processing is now finished, and the wafer is sawed into 1 cm by 2 cm chips, each containing one microreactor. (8) The catalyst material is then deposited on each chip through a shadow mask that covers the entire chip except the reactor channel. (9) Finally, a lid is bonded to the chip using epoxy glue.

The nonstandard fabrication steps (8) catalyst deposition and (9) lid bonding are described in detail in the following.

4.1. *Catalyst deposition in microreactors*

Fig. 2 shows the mounting of a microreactor in the flame spray deposition setup. A shadow mask is used to cover everything except the reactor channel during deposition. This is an easy and simple way to confine the catalyst. Only very small amounts of catalyst enter the inlet and outlet channels due to Brownian motion, and after deposition, the surface of the reactor is sufficiently clean for both anodic and adhesive bonding.

Fig. 7 shows a microreactor loaded with Au/TiO_2 porous catalyst using the FSD method and the shadow mask approach described above. A SEM image of the reactor bottom is shown in Fig. 7B. The deposit forms a uniform layer similar to deposits on a flat surface. More interesting is the cross section of the reactor channel shown in Fig. 7C. Clearly, the sidewalls as well as the edge between the bottom and the sidewalls are covered with catalyst. The layer thickness on the sidewalls decreases closer to the top, probably due to a higher temperature during deposition.

4.2. *Adhesive bonding*

To seal the microreactor after deposition, a lid has to be bonded on top. Anodic bonding of Pyrex glass to silicon is a standard way of doing this. However, the high temperature (350–400 °C) needed for anodic bonding may deactivate the Au/TiO_2 catalyst, and instead the reactor is closed by gluing a glass lid onto the reactor structure. Epo-Tek 377 high-temperature epoxy is chosen for the bonding due to the chemical inertness and thermal properties. To ensure good wetting of the glass, the glass lids are etched with a solution of 5% HF for 15 min. Afterward, the lids are spin-coated with the epoxy mixture for 45 s at 2500 rpm. The epoxy is precured at 155 °C for 25 s before the lid is mounted on the microreactor to increase the viscosity and prevent the glue from floating into the channels. The lid is mounted on the microreactor and pressed with a force corresponding to a 1 kg weight to form a hermetic seal. Finally, the epoxy is cured at 150 °C for 1 h.

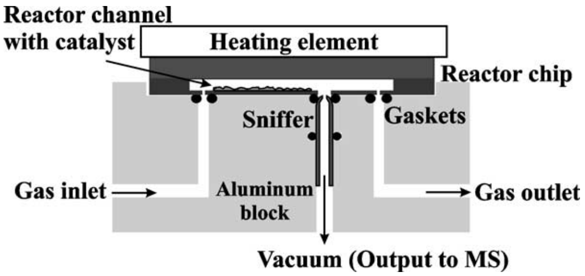

Fig. 9. An outline of the interfacing of the microreactor with the external gas lines and the quartz capillary tube. The capillary tube has a small orifice, which continuously leaks a small sample of the product gas from the reactor outlet directly into the vacuum chamber of the mass spectrometer.

When testing the bonding on microreactors with no catalyst, it is found that the method produces a hermetic seal in more than 50% of the bonding tests. When operated below 175 °C, any outgassing or reaction with the glue is below the detection limit. Above 175 °C, a CO_2 signal increasing exponentially with the temperature is measured. In conclusion, the bonding method is suitable for reactors operating at temperatures up to 175 °C.

4.3. Interfacing

The interfacing between the microreactor and the measurement setup is shown in Fig. 9. The in- and outlet holes in the microreactor are matched with holes in the interface block, which is equipped with Swagelock fittings. Sealing is achieved by placing Viton O-rings between the microreactor and the interface block at the interconnects. The gas flow through the reactor is controlled by mass-flow controllers.

The gas analysis is done with a mass spectrometer and special attention has been given to the interfacing between the microreactor and the mass spectrometer. To minimize the amount of gas sampled to the mass spectrometer, quartz tube orifices [17] are used to reduce the pressure from atmospheric pressure in the microreactor to 10^{-6} Torr in the mass spectrometer. This has the further advantage that the distance between vacuum and the gas stream in the reactor is only about 100 µm, which decreases the response time between changes in the microreactor and the detection in the mass spectrometer to the subsecond range.

4.4. Reactor performance

The test reaction is oxidation of CO to CO_2 with O_2 over a Au/TiO_2 catalyst [18]. Au/TiO_2 is flame spray deposited into a reactor channel with dimensions $15 \times 1.5 \times 0.3\ mm^3$. The mass of the deposited catalyst is too small to be measured directly, but by visual inspection in an optical microscope, a very rough estimate of the amount of catalyst is 10 µg, containing 0.1 µg gold. A gas mixture containing 1% CO and 2% O_2 is led through the reactor at a flow rate of 0.1 mL/min. Fig. 10 shows the concentration of CO and CO_2 as the temperature of the reactor is ramped from room temperature to 150 °C and back to 50 °C during a period of a few minutes. At 150 °C the concentration of CO_2 is 0.55%, which corresponds to a conversion of 55% of the CO in the feed gas. Corresponding decreases in O_2 and CO are observed. Comparing the conversion to the estimated amount of catalyst gives an activity of the order 5 µmol/(s g_{Au}).

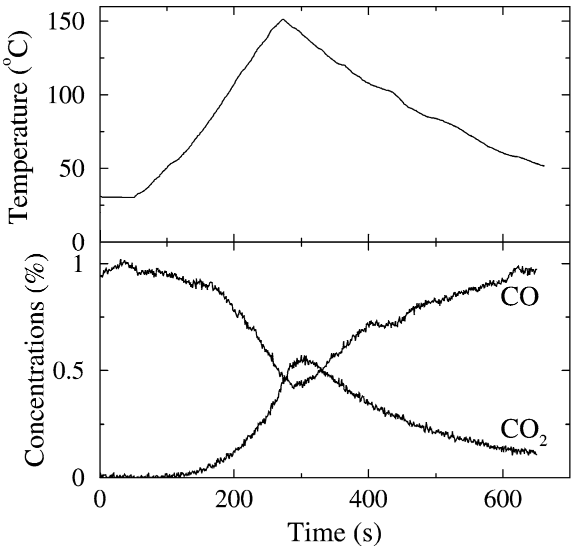

Fig. 10. CO and CO_2 concentrations as a function of time (temperature) during a rapid temperature ramp experiment.

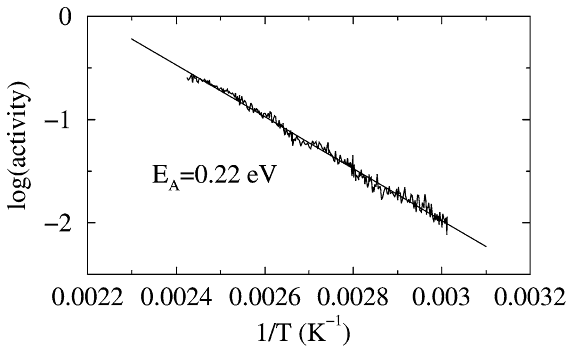

Fig. 11. Arrhenius plot of the activity measurements obtained by ramping the temperature (cf. Fig. 10).

The Arrhenius plot shown in Fig. 11 for the same temperature range gives an apparent activation energy $E_A = 0.22$ eV (21 kJ/mol), which is consistent with values obtained in the literature [19] for the same reaction using standard experimental conditions.

5. Conclusions

Flame spray deposition is a promising, fast, and flexible technique for depositing porous catalyst directly into microsystems. Good adhesion and thus good thermal contact to the reactor walls are achieved for most relevant surfaces.

With the use of photolithography, two-dimensional porous catalyst patterns can be fabricated with a resolution better than 100 µm. Using shadow masks, deposition in three-dimensional structures with deposition on both bottom and sidewalls can be performed. Even deposition of different catalysts in different areas of the same chip is believed to be possible.

The apparent activation energy of the flame spray deposited Au/TiO_2 catalyst is similar to values reported in the literature for oxidation of CO over supported gold catalysts, but the surface area is more than twice the area usually obtained in the flame spray unit using quench cooling and collection of particles on filters.

Interfacing of the mass spectrometer directly into the flow channel of the microreactor reduces response times significantly and makes the microreactors presented a potential technology platform for fast catalyst screening and characterization experiments.

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