



## Spatially resolved *in situ* FTIR analysis of CO adsorption and reaction on Pt/SiO<sub>2</sub> in a silicon microreactor

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### ABSTRACT

The design, fabrication and testing of a microreactor-FTIR imaging system is shown and used for the first time to demonstrate the ability to obtain *in situ* transmission FTIR analysis of working catalysts with both spatial and temporal resolution. MEMS (MicroElectroMechanical Systems) and microfabrication technologies were used to design and fabricate a microreactor with geometric and optical properties ideal for coupling with a high-throughput transmission FPA-FTIR system. CO adsorption and oxidation on Pt/SiO<sub>2</sub> were used as a model catalyst system. Propagation of adsorbed species down the length of the microreactor was observed and fractional coverages were quantified during pulsed chemisorption experiments. The amount of adsorbed CO was also differentiated at different positions in the microreactor as a function of time during oxidation of the stored surface species.

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### 1. Introduction

Not all catalytic reaction processes are designed to run at steady state. Many require transient and/or cyclical operation and thus reactive surface species are transient in nature. Characterizing the mechanism of such catalytic reactions requires *in situ* transient methods. Additionally, many transient/cyclic catalytic processes are operated using a monolith tube reactor in practice, and thus characterization of their mechanism and performance requires spatially and temporally resolved analytical tools to monitor the catalyst surface and reactive species as a function of position on the catalyst surface and in the reactor channel. The NO<sub>x</sub> storage reduction (NSR) process developed by Toyota [1] for NO<sub>x</sub> removal [2–6] from lean burn diesel engines is an example of such a cyclic process requiring both temporal and spatial resolution for *in situ* catalyst surface analysis.

Spatially Resolved Mass Spectrometry (SpaciMS) [7,8], has been used to study the identity of gas phase species within a monolith reactor during NSR reactions using small capillary probes inserted into the monolith. Such measurements capture only finite points in the reactor and provide no information related to the catalyst

surface or reactive intermediates. No *in situ* analytical or spectroscopic method has previously been demonstrated capable of characterizing the presence and relative abundance of reactive surface intermediates within an operating tube reactor as a function of both time and position along a reaction channel.

High-throughput spectroscopic systems have been reported [9–15], but these are mostly used for analyzing multiple reactors in parallel, not for analyzing different catalyst surface positions during a transient reaction. Our experimental transmission FPA-FTIR system extends the use of the same technology developed by Snively and Lauterbach [9] and previously used for the high-throughput, parallel analysis of catalyst libraries and pellets. Here we demonstrate the use of a silicon fabricated microreactor, coupled with a custom infrared imaging system, to allow observation of the propagation and consumption of adsorbed CO on a Pt/SiO<sub>2</sub> catalyst surface down the length of the microreactor during CO adsorption and oxidation. CO oxidation has been widely studied on Pt supported on a variety of materials [16–18]. This well studied system is used as a basis for characterizing and demonstrating our microreactor-imaging system presented here.

Using silicon as a reactor substrate and microfabrication technologies to process that substrate provides a means for realizing a microreactor with required optical and geometric properties for transmission infrared spectroscopy of working transient catalyst surfaces in microchannels. Silicon and glass microfabricated reactors have previously been used to enable *in situ* Infrared, UV–visible, and Raman spectroscopic analysis of

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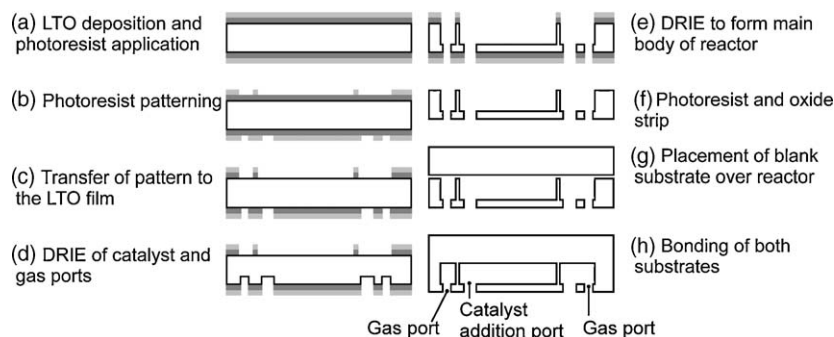


Fig. 1. Microreactor fabrication procedure.

liquids and solids [19–22]; however, without the spatial resolution provided by the FPA system used here.

Microsystem designs developed in a similar fashion as the one presented here would enable the study of catalysts operating in a geometry mimicking monolith channels for automotive and environmental treatment applications. For example, the formation, propagation and disappearance of surface species during NSR storage and reduction in parallel silicon microchannels channels could be observed. Such knowledge would allow researchers to better understand and verify the mechanistic models that have been developed and studied to describe the NSR process [23–29] and used to control diesel engine systems to enable a reduction in vehicular pollution.

## 2. Experimental

### 2.1. Microreactor fabrication

The dimension of the main reactor channel is a  $10\text{ mm} \times 10\text{ mm}$  square with a depth of  $400\text{ }\mu\text{m}$  to allow sufficient area for *in situ* spectroscopic characterization. The design includes two rows of catalyst retention posts, one near the inlet and one near the outlet, to keep powered catalyst within the reaction channel. Each row contains 334 posts ( $20\text{ }\mu\text{m}$  long by  $20\text{ }\mu\text{m}$  wide and spaced  $10\text{ }\mu\text{m}$ ). Two rectangular ports ( $1\text{ mm} \times 3\text{ mm}$ ) allow catalyst loading into the main channel and two square ports ( $1\text{ mm} \times 1\text{ mm}$ ) allow for gas inlet/outlet.

Fabrication began for the main reactor body with a double-sided polished  $500\text{ }\mu\text{m}$  thick,  $100\text{ mm}$  diameter undoped float-zone (FZ) grown silicon wafer (Silicon Valley Microelectronics), which provides  $>50\%$  transmission of  $25\text{--}250\text{ }\mu\text{m}$  radiation to enable *in situ* FTIR spectroscopic analysis in the microreactor. Standard microelectronics and MEMS processing methods were used for microreactor fabrication [30,31]. 4 reactors are processed on each Si wafer. A  $1.8\text{ }\mu\text{m}$  thick low temperature oxide (LTO) layer was grown at  $410\text{ }^\circ\text{C}$  to serve as a mask for the deep silicon etch (Fig. 1(a)). Photolithography was used to define the main reactor body as well as ports for catalyst loading and gas inlet/outlet (Fig. 1(b)) and the LTO was etched using a 6:1 buffered oxide etch (BOE) solution (Fig. 1(c)). The backside silicon of the reactor body was processed first using a Surface Technology Systems deep reactive ion etcher (STS-DRIE) to etch  $\sim 100\text{ }\mu\text{m}$  (Fig. 1(d)). The topside silicon was then etched  $\sim 400\text{ }\mu\text{m}$ , or until the backside ports were completely etched through to the main body of the reactor (Fig. 1(e)). Photoresist and LTO layers were removed using acetone and BOE, respectively (Fig. 1(f)). Prior to bonding, both the processed reactor wafer and a second double-side polished undoped FZ silicon wafer were cleaned using a piranha bath mixed at room temperature ( $2:1\text{ H}_2\text{SO}_4:\text{H}_2\text{O}_2$  by volume) followed by treatment in a 10 min oxygen plasma at 1.5 Torr and 150 W (Branson barrel etcher). The two substrates were then subjected to

a standard RCA-1 clean [32] for 15 min, rinsed and dried, and contacted by applying pressure to the center of the wafer pair (Fig. 1(g)). The contacted wafer system was annealed at  $\sim 1000\text{ }^\circ\text{C}$  for 90 min in an inert environment to strengthen the bond interface [33] (Fig. 1(h)).

A photograph of the fabricated microreactor is shown in Fig. 2, showing the microreactor channel and ports for gas feeds and catalyst loading. Throughout this paper, all characterizations were carried out at room temperature, although heating elements may be easily integrated into the device either with an external heater mounted within the package [34] or with on-chip resistive heating elements [35,36] to reach relevant temperatures for catalysis studies. Thermal changes in the system should have no adverse effect on the collection of FTIR spectra, even for reactions including NSR for which thermal spikes and transients are expected, as exemplified by spectra collected in transmission at elevated temperatures over pressed self-supporting catalyst disks by Fanson et al. [37].

### 2.2. COMSOL simulations

To capture the nature of gas flows in the silicon microreactor, COMSOL Multiphysics<sup>®</sup> 3.2b was used. The model dimensions drawn into the simulation software are shown in Fig. 3. All boundaries labeled in Fig. 3 were defined with a “no-slip” condition, with the exception of the edges labeled “A” and “B”. Edge “A” was defined with an inflow  $y$ -velocity of  $1.042\text{ m/s}$  and “B” was set with an outflow pressure at atmospheric pressure.

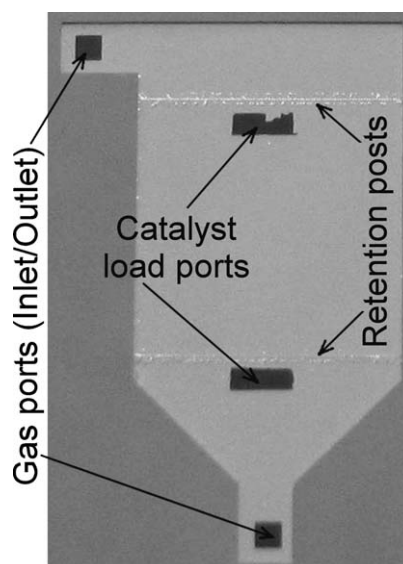


Fig. 2. Photograph of the Si microreactor used in this study.

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