MEMS-Based Microreactor for *in-Situ/Operando* high-Resolution 3D X-Ray Microscopy of Single Catalyst Particles

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Introduction

In the past decades, synchrotron radiation-based X-ray microscopy has become a valuable tool for material chemistry to obtain detailed information on the outer and inner morphology of optically opaque materials, often combined with chemical information. It represents a powerful tool for solid catalyst characterization allowing three-dimensional (3D) (chemical) imaging down to spatial resolution of ten of nanometers enabled by the new generations of focusing lenses and synchrotron sources [1]. Furthermore, the possibility of performing analysis under static or dynamic reaction conditions (temperature and pressure) makes X-ray microscopy ideal for *in-situ* and *operando* studies of heterogeneous catalytic processes.

The main experimental challenge when applying the technique *in-situ* or *operando* is represented by the setup used to position the sample. This setup needs to allow flow (gas liquid), but also the possibility to control and apply high temperatures and pressures, such as experienced under real process conditions. We recently designed and fabricated a new MEMS-based microreactor that can now trap and study an individual catalyst particle of up to ~100 micrometers in size in a free-standing, monolithic silicon nitride capillary while applying high temperatures (≤ 400 °C) and pressures (≤ 30 bar).

Materials and Methods

The microreactor was fabricated in the cleanroom of the MESA+ NanoLab at the University of Twente and is made from a silicon wafer and by using photolithography. The fabrication process is based on the surface channel technology as described in [2]. It results in etched microchannels with 1-µm thick silicon-rich nitride (Si_3N_4) walls, a hydraulic diameter of 100 µm, and back-side fluidic connections (inlet and outlet access holes). Part of the channel is freely suspended outside the substrate allowing optical access (160° over 180°) and equipped with a geometrical trap for catalyst particles, which consists of restrictions along the channel. The temperature is set and controlled by the integration of two meander-shape Platinum-based microheaters (300 x 80 um) present above and below the particle trap (figure **1A**). The microreactor is mounted on a stainless-steel holder for rotation as well as enabling access to the fluidic/electrical connections interfaces, as shown in figure **1B**.

Results and Discussion

The temperature inside the microreactor was validated using temperature-dependent luminescence nanoparticles up to 300°C (stability limit of the nanocrystals) [3] impregnated on a fluid catalytic cracking (FCC) catalyst particle. The microreactor has been tested in the lab for n-hexane cracking over a single FCC catalyst particle at 350°C, used as a model reaction. It was possible to follow the coke formation on the catalyst particle via the fluorescence intensity increase over time using confocal microscopy (CFM) as shown in figure **1C**. Moreover, our microreactor was successfully tested at beamline ID16b, ESRF (Grenoble) using holotomography (see figure **1D**) at 17keV achieving high quality images of the particle inside the capillary (see figure **1E**). Current work is focused on performing in-situ reactions at synchrotron facilities.

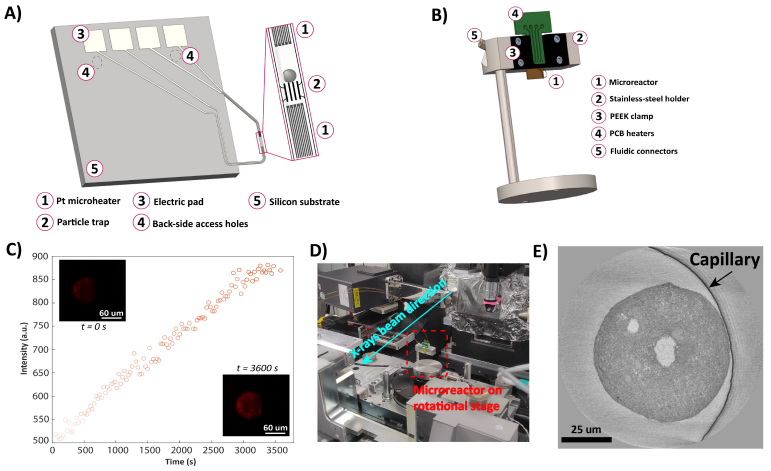

Figure 1. A) 3D rendering of the MEMS-based microreactor (7.3x7.3 mm) and **B)** holder. **C)** Fluorescence intensity plot vs time for the in-situ experiment of n-hexane cracking at 350°C using CFM, the fluorescence is directly related to the coke formed during the catalytic reaction. **D)** Our microreactor tested at beamline ID16b, ESRF. **E)** Single slice reconstructed of an FCC particle measured at 17keV using holotomography.

Significance

We propose a microreactor that can overcome the experimental challenge as mentioned before, enabling X-ray imaging for a wide range of catalytic systems under real operating conditions, thus facilitating the fundamental understanding of heterogeneous catalysts and their design.

References

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