DIFFUSION THROUGH SINGLE POROUS PARTICLES STUDIED IN A MICROFLUIDIC SYSTEM

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ABSTRACT

The understanding of diffusion through porous materials is a crucial aspect for designing superior catalysts. Their performance is often influenced by inter-particle inhomogeneities, which are barely attainable with bulk analytical methods. To overcome this problem, a microfluidic system has been designed and fabricated to perform a mass transfer study at a single-particle level using fluorescence microscopy. This was done by trapping a porous particle and applying a concentration gradient over it. The system allows us to obtain the true value of the diffusion coefficient of a single particle, which is not averaged over many particles and influenced by inter-particle porosity. The diffusion was studied for a Fluid Catalytic Cracking (FCC) and a porous SiO_2 particle, the latter well-known material used as a commercial support material.

KEYWORDS: Effective diffusion, Single-particle, FCC catalyst, SiO_2 particle, epoxy resin, closed valve.

INTRODUCTION

Porous solids find wide application as catalysts or adsorbents since their high surface to volume ratio allows for high capacity and activity. Such materials are composed of complex hierarchical pore networks including macro- (> 50 nm), meso- (50 nm < d_p < 2 nm), and micropores (< 2 nm). Diffusion represents the transport mechanism through these, affecting and controlling the overall rate of the so-called diffusion-limited process [1]. Hence, a fundamental understanding of this phenomenon is essential to describe and, optimize catalytic or adsorption processes, or design superior materials. Several methods are available for investigating intraparticle diffusion in a non-equilibrium state. However, these are bulk analyses and provide only an apparent description, not considering intra- and interparticle heterogeneity [2]. One approach to overcome these limitations is the implementation of microfluidics, which allows the characterization of heterogeneous systems with precise control of micro volumes and small sample sizes. In this work, a microfluidic system has been designed and fabricated to perform a study of the diffusion process at the single-particle level using fluorescence microscopy, to obtain a value for an effective diffusion coefficient. The approach is based on the visualization and study of the diffusion process in an isolated porous particle induced by a concentration gradient in a fluorescent solution.

EXPERIMENTAL

The microfluidic device (Figure **1A**) consists of two layers of clear epoxy resin (EpoFix by Struers) with an elastomeric deformable Viton® membrane (250 µm in thickness) in between. The bottom layer contains an open channel connected to a 45 nL chamber via a porous particle (Figure **1C**), which is put in place during the fabrication process. The top layer includes the channels for the pneumatic control of the valves (Figure **1B**), which are placed to close the small chamber and ensure a fixed volume through the experiment. These three layers are clamped together with 8 screws.

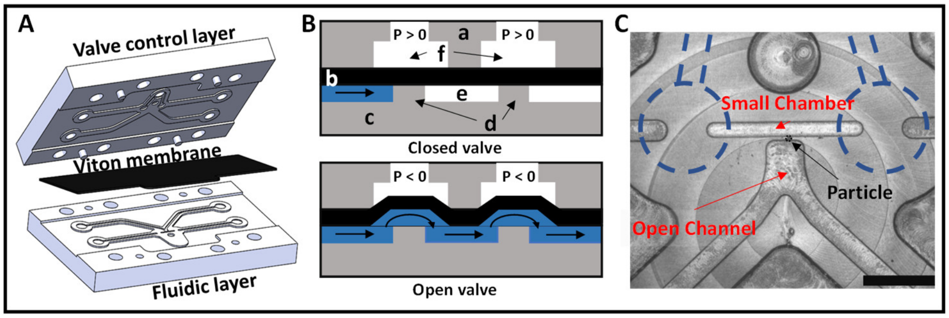

Figure 1: *A) Schematic representation of the microfluidic chip. B) Cross-sectional view of the 3-layer chip to show the valve actuation mechanism: valve control layer (a), Viton membrane (b), fluidic layer (c), obstacles (d), small chamber (e), and displacement chambers (f). C) A silica particle trapped in the flow layer. Scale bar: 1mm.*

The diffusion experiments were carried out using n-heptane as a solvent and Nile Red as a fluorescent molecular probe with a concentration of 50µM. The open channel and the small chamber were first filled up with the solvent and after the particle soaking, the experiment started by filling the open channel with the fluorescent solution. Due to the high volume of the open channel, its concentration change was assumed negligible. Diffusion through the particle caused an increase in the small chamber concentration. This change was measured/followed over time.

RESULTS AND DISCUSSION

The diffusion was studied on a porous silica support and an FCC pristine catalyst particle, both with a diameter of ~ 75µm.

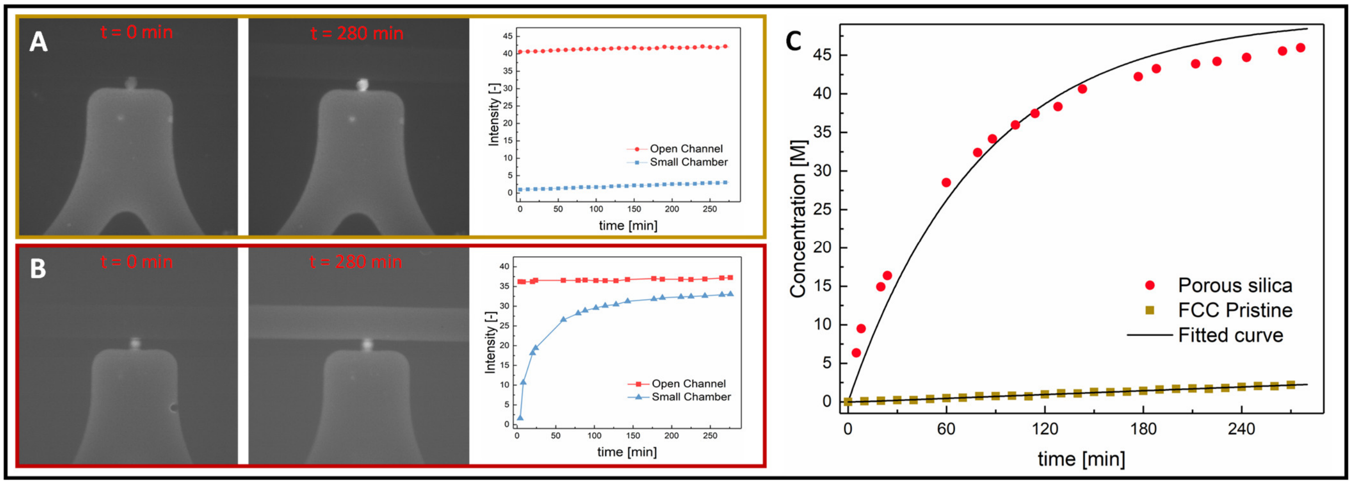

Figure 2: *Fluorescence images and plot of mean fluorescence intensity of the open channel and the small chamber over time for A) FCC pristine particle and B) Silica particle. C) Fitting of the experimental data (small chamber molar concentration obtained via calibration of the fluorescence intensity). The concentration of the open channel was considered fixed (50 µM).*

Our device shows the advantage to visualize and quantify the diffusion process for individual microparticles. For both samples, the experiment was carried out for 5h following the change in fluorescence in the small chamber. The porous silica particle reached equilibrium within almost 5h (Figure **2B**). In contrast, the FCC particle showed only a slight change in the fluorescence of the small chamber (Figure **2A**). This dissimilarity can be ascribed to the lower porosity and pore connectivity of the FCC particle compared to the porous silica one. Moreover, a first fitting of the experimental data (Figure **2C**), allowed us to estimate the effective diffusion constant for both particles. The preliminary resulting value for FCC (3.16E-12 m^2/s) is in line with the literature [3] and is two orders of magnitude lower than the one for porous silica (2.73E-10 m^2/s).

CONCLUSION

The described approach and microfluidic system allowed us to measure the effective diffusion through a single particle. Further experiments are planned for more statistical information. We are also working on the optimization of the mathematical model to describe the diffusion process and obtain the precise value of the diffusion coefficient.

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REFERENCES

[1] K. S. W. Sing, *Pure Appl. Chem.*, vol. 57, pp. 2201–2218, 1985.
[2] J. Kärger *et al. New J. Chem.*, vol. 40, pp. 4027-4048, 2016.
[3] Z. Liu *et al. Energy Fuels*, vol. 24, pp. 2825–2829, 2010.

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