Construction of hierarchical pore-network in zeolite catalyst particles using super-resolution single-molecule localization techniques

Mingbin Gao[1], Yuli Liu[1], Mao Ye[1]*, and Zhongmin Liu[1]

1 National Engineering Research Center of Lower Carbon Catalysis Technology, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

**Corresponding author: maoye@dicp.ac.cn*

Highlights

- Application of single molecule fluorescence imaging to catalyst.
- Tacking the diffusion of individual molecules.
- Mapping the hierarchical pore-network of industrial catalysts.
- Unveiling the detailed mechanism of complexed molecular diffusion.

1. Introduction

Understanding the relationship between pore structure network, and molecular diffusion is crucial for improving the performance and lifespan of zeolite catalysts [1]. The pore network within catalyst particle represents the extremely complex and hierarchical characterizations. This implies that the mechanism molecular diffusion in catalyst particles should be described based on local pore structure and network. However, it is still a challenge to construct detailed hierarchical pore-network of catalyst particle. Recent study shows that a super-resolution imaging method, single-molecule fluorescence microscopy, was developed in this study to identify the pore-network structure inside catalyst particles [2]. In addition, by use of single-molecule fluorescence microscopy, the detailed diffusion mechanism of individual molecules can be unveiled in the industrial catalysts.

2. Methods

Single-molecule tracking experiments were performed on HIS-SIM (High Intelligent and Sensitive Structured Illumination Microscopy), provided by Guangzhou CSR Biotech Co. Ltd. Images were acquired using a 100×/1.5 NA oil immersion objective (Olympus). Fluorescence images were recorded as movies using an ORCA-Fusion BT camera. The resulting field of view was 66.56 × 66.56 nm^2 per pixel (1024 × 1024 pixels). The experiment was performed at room temperature (298 K). The probe molecule was diluted to 1.17 µM in DMSO. For the experiment, 100µL of this solution was added to silica-1 particles, and then the system was left to equilibrate for 5 min. The sample was illuminated using a 50nm laser. In 2 h, 3 movies were recorded, totaling 6000 frames, with a time resolution of 26 ms.

Detection of single-molecule events and subsequent track analysis was done using the Localizer plug-in of ImageJ (cite reference). For track analysis, molecules were allowed to blink (i.e. the molecule does not fluoresce intermittently) for consecutive frames. Track classification, analysis, and plotting were done in MATLAB.

3. Results and discussion

This study used single-molecule fluorescence microscopy to investigate microscale self-diffusion of individual probe molecule in hierarchical pores of industrial catalytic cracking catalyst particle. In Figure 1a, the diffusion trajectories of multi-individual molecules are visualized by cross-correlation algorithm and intelligent particle tracking algorithm. Based on the diffusion trajectories (i.e. root-mean-square displacement), the molecular diffusivity can be calculated by Einstein's equation [3]:

$$MSD = 6Dt + b \tag{1}$$

where *MSD* is the root-mean-square displacement, *D* is the diffusivity, *t* is the interval time and *b* is the b is the thermal factor arising from atomic vibrations. As shown in Figure 1b, based on the local MSD, the molecular diffusivity at the local region can be calculated. Due to a mass of diffusion data, we used Thiessen polygon to merge similar value of diffusivity as shown in Figure 1b. It can be found that the distribution of molecular diffusivity within individual catalyst particle is non-uniform due to the nature of hierarchical pore. Based on the distribution of molecular diffusivity, it can be deduced the pore size distribution within catalyst, for instance, the large value in diffusivity represents the large pore size at the local region. We summarized the three types of diffusion trajectories in hierarchical pore. As shown in Figure 1c, in the zeolite pore, most probe molecules show immobile, due to physical adsorption or trapping by micropore of zeolites, while the remaining a portion of molecules diffuse inside the meso- and macro-pores. The molecule at meso- or macro-pores show the large MSD. As above discussion, the developed method can also evaluate and quantify non-uniformity of diffusion performance in complex hierarchical porous materials.

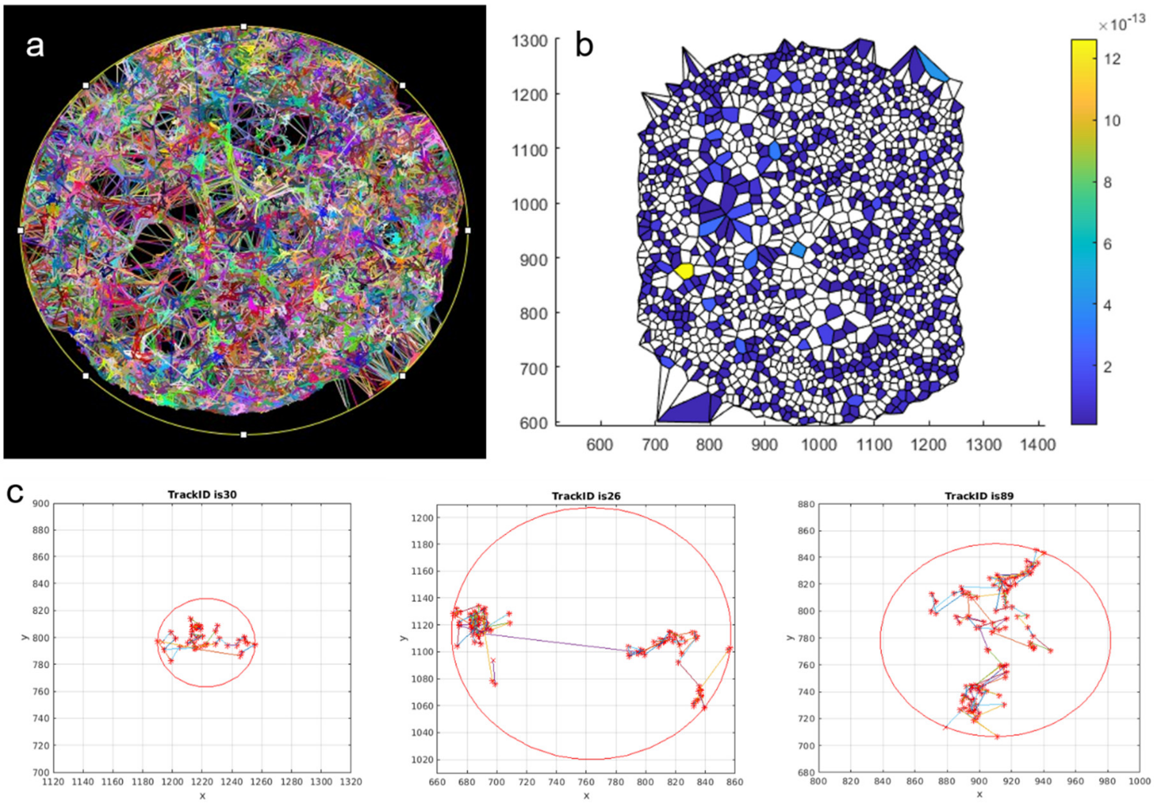

Figure 1. (a) The Trace of single molecule fluorescence image. (b) Voronoi diagram showing localized diffusion coefficients in the middle cross section of the catalyst particle. (c) Types of molecular diffusion.

4. Conclusions

This research provides a new experimental methods and theoretical basis for understanding the diffusion process inside catalyst particles by employing super-resolution single-molecule localization techniques. Understanding the molecular diffusion in hierarchical pore is vital for enhancing the performance of hierarchical porous materials for separation and catalysis.

References

[1] J. Karger, D.M. Ruthven, D.N. Theodorou, Diffusion in Nanoporous Materials, Wiley, 2012

[2] F. C. Hendriks, F. Meirer, A.V. Kubarev, Z. Ristanovic, M.B.J. Roeffaers, E.T.C. Vogt, P.C.A. Bruijnincx, B.M. Weckhuysen, J. Am. Chem. Soc. 139 (2017) 13632-13635

[3] P. Bai, E. Haldoupis, P.J. Dauenhauer, M. Tsapatsis, J.I. Siepmann, ACS Nano 10 (2016) 7612−7618

Keywords

Single-molecule localization techniques; Molecular diffusion; Hierarchical pore; Industrial catalysts.