Formation and Characterization of ZIF-8 Supraparticles and Their Packings with Hierarchical Porosity

Satoshi Watanabe*[1], Atsushi Fujiwara[1], Shotaro Hiraide[1], Minoru T. Miyahara[1], and Nicolas Vogel[2]

[1] Dept. of Chem. Eng., Kyoto University, Katsura, Nishikyo, Kyoto, 615-8510, Japan
[2] Institute of Particle Technology, Friedrich-Alexander-University Erlangen-Nürnberg, Haberstr. 9a, 91058 Erlangen, Germany
email for correspondence: nabe@cheme.kyoto-u.ac.jp

Metal–organic frameworks (MOFs) are microporous adsorbents for high-throughput gas separation. Such materials exhibit distinct adsorption characteristics owing to the flexibility of the crystal framework in a nanoparticle, which can be different from its bulk crystal. However, for practical applications, such particles need to be compacted into macroscopic pellets, creating mass-transport limitations. In this work, this problem is addressed by forming materials with structural hierarchy, using a supraparticle-based approach. Spherical supraparticles composed of nanosized MOF particles are fabricated by emulsion templating and they are used as the structural component forming a macroscopic material. Zeolitic imidazolate framework-8 (ZIF-8) particles are used as a model system and the gas-adsorption kinetics of the hierarchical material are compared with conventional pellets without structural hierarchy. We first synthesized ZIF-8 particles with the size of ca. 200 nm, as building units, using a central collision type microreactor [1] and prepared ZIF-8 suspension droplets by mixing an aqueous suspension with an oil phase in a microfluidic device [2], followed by the drying of droplets to form supraparticles. As shown in Fig. 1a, the microfluidic process successfully produced monodisperse supraparticles with a diameter of ca. 40 μm composed of self-assembled nano-sized ZIF-8 particles (Fig. 1b; magnified image of a supraparticle). The calculation of the void fraction of supraparticles based on the ZIF-8 particle concentration, droplet size, and supraparticle size demonstrated that the supraparticles have close-packed structures. Furthermore, it is demonstrated that a pellet packed with supraparticles exhibits a 30 times faster adsorption rate compared to an unstructured ZIF-8 powder pellet. These results underline the importance of controlling structural hierarchy to maximize the performance of existing materials. In the hierarchical MOFs, large macropores between the supraparticles, smaller macropores between individual ZIF-8 primary particles, and micropores inherent to the ZIF-8 framework collude to combine large surface area, defined adsorption sites, and efficient mass transport to enhance performance [3].

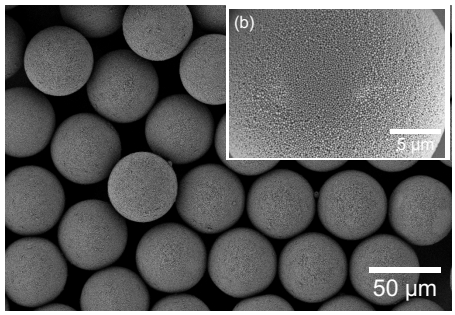

Fig. 1 SEM image of the supraparticles composed of ZIF-8 nanosized particles

References:

1. S. Watanabe, S. Ohsaki, T. Hanafusa, K. Takada, H. Tanaka, K. Mae, M.T. Miyahara, Synthesis of zeolitic imidazolate framework-8 particles of controlled sizes, shapes, and gate adsorption characteristics using a central collision-type microreactor, *Chem. Eng. J.*, 313 (2017) 724-733
2. N. Vogel, S. Utech, G.T. England, T. Shirman, K.R. Phillips, N. Koay, I.B. Burgess, M. Kolle, D.A. Weitz, J. Aizenberg, Color from hierarchy: Diverse optical properties of micron-sized spherical colloidal assemblies, *Proc. Natl. Acad. Sci.*, 112 (2015) 10845-10850
3. A. Fujiwara, J. Wang, S. Hiraide, A. Gotz, M.T. Miyahara, M. Hartmann, B. Apeleo Zubiri, E. Spiecker, N. Vogel, S. Watanabe, Fast Gas-Adsorption Kinetics in Supraparticle-Based MOF Packings with Hierarchical Porosity, *Adv. Mater.*, 35 (2023) e2305980