Translated paper

Characterization of mixing performance in a microreactor and its application to the synthesis of porous coordination polymer particles

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ABSTRACT

Here we quantitatively evaluated the mixing performance of a tailor-made microreactor with central-collision type through the iodide/iodate chemical test reaction, and applied the microreactor to the synthesis of zeolitic imidazolate framework-8 (ZIF-8), which is a subclass of porous coordination polymers (PCPs) or metal organic frameworks (MOFs). The chemical test reaction demonstrated excellent mixing performance of the microreactor with a characteristic mixing time shorter than 1 ms, which is approximately 100 times faster than those of a batch reactor and a millimeter-sized Y-shaped mixer. Taking advantage of the rapid and uniform mixing, the microreactor successfully produced ZIF-8 particles with high reproducibility by simply mixing aqueous solutions of zinc nitrate and 2-methylimidazole. The synthesis at room temperature resulted in ZIF-8 particles with chamfered cube shape, while a lower temperature of 5 °C produced raspberry-type spherical particles. We confirmed that prepared ZIF-8 particles have BET surface area of $\sim$1500 m^2/g and exhibit the gate adsorption behavior caused by the structural transition of the ZIF-8 framework.

1. Introduction

Porous coordination polymers (PCPs), also called metal-organic frameworks (MOFs), are a new class of porous materials that are constructed through the self-assembly of metal ions and organic ligands. Because of the regularity and tunability in their pore structures and pore sizes as well as their large surface areas [1], PCPs are promising for a range of applications, including storage, separation, and catalysis [2]. Furthermore, synthesizing submicron- or nano-sized PCP crystals and assembling them as building blocks into ordered structures presents the possibility of fabricating sensors, and electronic and optical devices [3,4].

Zeolitic imidazolate frameworks (ZIFs), which are a type of PCPs, have zeolite-like crystal structures composed of imidazole linkers tetrahedrally coordinated with transition metal ions such as cobalt, copper, and zinc, and exhibit high thermal and chemical stabilities compared with those of other PCPs [5,6]. Moreover, some types of ZIFs show structural flexibility owing to the rotation of the imidazole linkers. ZIF-8 is a typical ZIF composed of Zn ions

and 2-methylimidazole (2-MeIM) linkers that form a sodalite-type crystal structure (Fig. 1a). It exhibits structural flexibility and the accompanying ability to change its pore apertures through rotation of the 2-MeIM linkers (Fig. 1b). This feature leads to unique molecular sieving properties [7] and thereby enables the kinetic separation of hydrocarbons with similar sizes and boiling points [8], such as propane and propylene, which are generally difficult to separate by other means. Because the linker rotation behavior of ZIF-8 depends on its particle size [9], it is important to establish a technique for synthesizing ZIF-8 particles with controlled sizes, aiming at the design of materials with desired separation performances. Furthermore, particle shape control for ZIF-8 is crucial because interactions acting between specific crystal faces direct the self-assembly of ZIF-8 to afford highly oriented structures [10].

ZIF-8 is typically synthesized by solvothermal methods using dimethylformamide and methanol as solvents, yielding large crystals that are several hundred micrometers in size [5,11]. However, the growing interest in the assembly of PCP particles into ordered structures has led to the development of techniques for synthesizing smaller particles with sizes from microns down to nanometers [12], thereby realizing the synthesis of 10 nm-sized ZIF-8 particles [9]. Furthermore, this increased research interest has led to the development of environmentally friendly aqueous synthesis tech-

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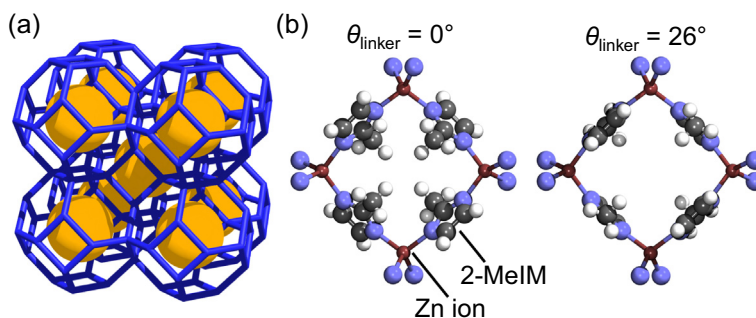
Fig. 1. Representations of (a) the ZIF-8 crystal structure with sodalite topology, and (b) structural configurations of a 4-ring window with linker rotation angles (θ_{linker}) of 0 and 26°.

niques to replace those that rely on organic solvents [13,14]. In these techniques, nanosized ZIF-8 particles were synthesized by mixing high-concentration solutions of Zn ions and 2-MeIM linkers or by prompting deprotonation of 2-MeIM [15] so that a number of small nuclei are formed. However, these techniques employ batch-type reactors, which is problematic because the high concentrations and enhanced deprotonation employed lead to fast reactions. Because mixing and diffusion are rate limiting in fast reactions, the use of a reactor that can achieve instantaneous and homogeneous mixing is desirable for the synthesis of particles with a narrow size distribution. The use of a microreactor is a possible strategy to satisfy the requirements for the synthesis of monodisperse particles. Microreactors have been applied for the synthesis of various types of nanoparticles but rarely for ZIF-8 particles.

In our previous study, we successfully synthesized submicron-sized ZIF-8 particles using a T-shaped microreactor and demonstrated the higher reproducibility available with the use of this microreactor than that with batch reactions [16]. However, we faced technical challenges in terms of reproducibility under certain experimental conditions, as well as in the precise control of particle size; this may have highlighted the limitations of the T-shaped microreactor for ZIF-8 particle synthesis. Consequently, in the present study, we have employed a central-collision-type microreactor that we reasoned would have the potential to surpass the mixing performance of the T-shaped microreactor. We first quantitatively evaluated the mixing performance of the central-collision-type microreactor. We then applied it to the synthesis of ZIF-8 particles and investigated the effects of the mixing on the size distribution of the resultant ZIF-8 particles. Furthermore, we have examined the effects of concentration and temperature conditions on the size, shape, and adsorption characteristics of the prepared ZIF-8 particles.

2. Experimental section

2.1. Materials

Potassium iodide (KI, 99.998%), potassium iodate (KIO$_3$, 99.5%), boric acid (H$_3$BO$_3$, 99.5%), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, 98%), and 2-MeIM (C$_4$H$_6$N$_2$, 99%) were purchased from Sigma-Aldrich Co., LLC. (USA). Sulfuric acid (H$_2$SO$_4$, 0.1 mol/L), sodium hydroxide (NaOH, 0.1 mol/L), and methanol (MeOH, 99.8%) were purchased from Kishida Chemical Co., Ltd. (Japan). All chemicals and solutions were diluted to the desired concentrations with ultrapure water (18 MΩ cm or above), which was obtained from a Direct-Q3 UV water purification system (Millipore Corp., USA).

2.2. Villermaux-Dushman method

We evaluated the mixing performance through the Villermaux-Dushman (VD) method [17–19], which involves parallel competing neutralization and redox reactions, as follows:

$$H_2BO_3^- + H^+ \rightleftarrows H_3BO_3 \tag{1}$$

$$IO_3^- + 5I^- + 6H^+ \rightleftarrows 3I_2 + 3H_2O \tag{2}$$
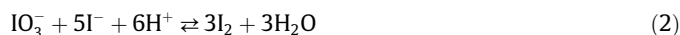
Although the redox reaction of IO$_3^-$ and I$^-$ in Eq. (2) is fast, the neutralization reaction in Eq. (1) is much faster. In the VD method, a sulfuric acid solution that contains fewer protons than that equivalent to the number of borate ions H$_2$BO$_3^-$ is added to a mixed solution of IO$_3^-$, I$^-$, and H$_2$BO$_3^-$. An ideal mixing would not produce I$_2$ because the protons would be consumed only in the neutralization reaction, which proceeds much faster than the redox reaction. In the case of poor mixing, however, the mixed solution is segregated, which leads to local overconcentration of protons relative to H$_2$BO$_3^-$. Protons remaining after the completion of the neutralization reaction are consequently consumed in the redox reaction to produce I$_2$, which quickly reacts with I$^-$ to yield triiodide ions I$_3^-$.

$$I_2 + I^- \rightleftarrows I_3^- \tag{3}$$

The production of I$_3^-$ is thus a measure of the segregation state upon mixing. More quantitatively, the segregation index X_S ($0 \leq X_S \leq 1$) is defined as

$$X_S = \frac{Y}{Y_{ST}} \tag{4}$$

where Y is the ratio of the number of protons consumed in the redox reaction to the total number of protons initially added in the reaction system, and Y_{ST} is the value of Y in the case of infinitely slow mixing. A smaller value of X_S indicates better mixing with less segregation. At the limit of slow mixing, because the proton consumption is proportional to the local concentrations of IO$_3^-$ and H$_2$BO$_3^-$, Y_{ST} is expressed as

$$Y_{ST} = \frac{6[IO_3^-]_0}{6[IO_3^-]_0 + [H_2BO_3^-]_0} \tag{5}$$

where the subscript 0 indicates the concentration of a feed solution, i.e., the initial concentration before mixing, while Y is obtained by the following equation when two solutions with an equal volume are mixed.

$$Y = \frac{2([I_2] + [I_3^-])}{\frac{1}{2}[H^+]_0} \tag{6}$$

The concentration of I$_3^-$, [I$_3^-$], can be obtained by measuring the absorbance A at 353 nm, where I$_3^-$ exhibits its maximum absorbance, and by applying the Lambert-Beer law: